POLYMER RETENTION DURING FLOW OF POLYMER SOLUTIONS THROUGH POROUS MEDIA

by
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Imperial College London
Department of Chemical Engineering and Chemical Technology

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DEDICATION

This work is dedicated to my beloved parents for their unconditional love, support, sacrifice...
ABSTRACT

Polymer solution flow and retention through porous media is of interest to many applications in the oil industry such as drilling, water shut-off and enhanced oil recovery. Operators of mature oil and gas fields are faced with the problem of excessive water production (EWP), which can cause a premature abandonment of some oil and gas wells. It has been found that the injection of high molecular weight polymer solutions through the pay zones of the oil and gas wells would induce a sharp decrease of the water production without affecting the oil and gas production. This effect is called disproportionate permeability reduction (DPR) and the polymer solutions inducing such an effect are called relative permeability modifiers (RPM). Hence, the DPR effect has been utilized in the water shut-off or conformance control of oil and gas wells suffering from EWP. In spite of the extensive research of the DPR effect, there is still a lack of agreement on the mechanisms controlling such an effect and relatively high percentage failures are observed during conformance control field applications. Polymer retention in porous media has been attributed to mechanisms such as bridging-adsorption, adsorption-entanglement, and flow-induced adsorption. These mechanisms have been proposed to account for the increase in flow resistance during or after the flow of polymer solutions through porous media. The DPR effect has been attributed to effects induced by this retained polymer such as steric and lubrication effects, wettability change, segregated oil and water pathways, and swelling and shrinking of the adsorbed polymer layer. The aim of this study is to add knowledge on the effect of polymer solution flow on polymer retention in porous media.

In this study, the rheology of high molecular weight polymer solutions was studied using a cone-and-plate setup. Moreover, the characteristics and the effective hydrodynamic thickness of adsorbed polymer layers on glass from these polymer solutions under static conditions were investigated using atomic force microscopy (AFM). Also, quartz crystal microbalance with the dissipation monitoring (QCM-D) was used to investigate the effect of increasing the flow rate of polymer solutions on the adsorbed amount on silica and gold surfaces. Additionally, the mobility reduction and the residual resistance as a result of polymer solution flow through single glass capillaries, 2D and 3D models of porous media were studied. The implementation of the above techniques was used to relate the microscopic effect of the flow of the polymer solutions to the polymer retention in the porous media. The anti-thixotropic behaviour of the polymer solutions, which can be attributed to the shear-induced formation of micron-size transient entanglement networks (TEN), is expected to play a major role in the polymer retention in porous media. These microscopic structures can adsorb on the solid surfaces if the adsorption energy of the polymer/solid system is sufficient. Also, in porous media in which mechanical entrapment is possible, these structures can be entrapped in the small pores and pore throats. Two new mechanisms for polymer retention are proposed in this study: transient-entanglement networks adsorption (TENA) and transient-entanglement networks entrapment (TENE). The TENA is the retention mechanism of the TEN structures in flow systems in which mechanical entrapment is not possible provided that the adsorption energy is sufficient. If mechanical entrapment is possible, then the retention by adsorption and mechanical entrapment are lumped in the TENE mechanism.

The results from this study have given a new insight on the flow and retention of polymer solutions through porous media. Hence, it is believed that the improved understanding will improve the design of high molecular weight polymers in water shut-off applications in oil and gas wells experiencing EWP.
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In the beginning and at the last I am thankful to God who created me the way I am and blessed me with His countless bounties.
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NOMENCLATURE

A  Cross-sectional area, m²
a  Width of the capillary, m
A_H  The Hamaker constant
b  Height of the capillary, m
b_after  Height of the capillary after polymer solution flow, m
b_before  Height of the capillary before polymer solution flow, m
C  Conductance
c  Solution concentration, ppm
c*  Overlap concentration, ppm
c^+  Concentration of the polymer solution below which elongational entanglement does not occur, ppm
c_b  Polymer concentration in the bulk solution, ppm
C_i  (b)  Ion concentration in the bulk (Equation 6.3)
d  Diameter of the packed particles, m, (Equations 2.5 and 2.7).
d  Diameter, m
D  Dissipation (Chapter 7)
D_0  The fundamental dissipation
De  Deborah number
d_p  Hydrodynamic diameter of the pores/capillaries, m, (Equations 2.3 and 2.5),
D_tr  Translational diffusivity in solution (Equations 3.10)
E  Energy
E_lost  Energy dissipated during the oscillation cycle (Equation 7.2)
E_stored  Energy stored in the oscillator (Equation 7.2)
F  Force, N
f  Frequency, Hz
f  Friction factor
f_0  The fundamental frequency, Hz
F_ad  Force of adhesion, N
F_FDL  Electrical double layer force of interaction, N
F_o  Stretching force, N
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>$F_r$</td>
<td>Force acting inward in the <em>radial</em> direction, N</td>
</tr>
<tr>
<td>$F_{VdW}$</td>
<td><em>Van der Waals</em> force of interaction, N</td>
</tr>
<tr>
<td>$G'$</td>
<td>The storage modulus</td>
</tr>
<tr>
<td>$G''$</td>
<td>The loss modulus</td>
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<tr>
<td>$K_{and a}$</td>
<td>Mark-Houwink fitting parameters</td>
</tr>
<tr>
<td>$k$</td>
<td>Absolute permeability (Chapters 2 and 8), m$^2$</td>
</tr>
<tr>
<td>$k$</td>
<td>The Boltzmann constant (Chapters 3, 4, and 6)</td>
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<tr>
<td>$k_{aft}$</td>
<td>Absolute permeability measured <em>after</em> polymer solution flow, m$^2$</td>
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<tr>
<td>$k_{bef}$</td>
<td>Absolute permeability measured <em>before</em> polymer solution flow, m$^2$</td>
</tr>
<tr>
<td>$k_e$</td>
<td>Effective permeability, m$^2$</td>
</tr>
<tr>
<td>$k_o$</td>
<td>Effective permeability to oil, m$^2$</td>
</tr>
<tr>
<td>$k_r$</td>
<td>Relative permeability, dimensionless</td>
</tr>
<tr>
<td>$k_{re}$</td>
<td>Relative permeability to oil, dimensionless</td>
</tr>
<tr>
<td>$k_{rw}$</td>
<td>Relative permeability to water, dimensionless</td>
</tr>
<tr>
<td>$k_s$</td>
<td>Spring constant, N/m</td>
</tr>
<tr>
<td>$k_w$</td>
<td>Effective permeability to water, m$^2$</td>
</tr>
<tr>
<td>$L$</td>
<td>Length, m</td>
</tr>
<tr>
<td>$l$</td>
<td>The average length of the monomer, m, (Equation 3.1)</td>
</tr>
<tr>
<td>$L_c$</td>
<td>Characteristic length scale of the macroscopic flow, m, (Equation 3.10)</td>
</tr>
<tr>
<td>$L_e$</td>
<td>Entry length, m</td>
</tr>
<tr>
<td>$L_{eff}$</td>
<td>Effective length of the capillary, m</td>
</tr>
<tr>
<td>$m$</td>
<td>Slope of the linear plot of $\Delta P$ vs. $Q_w$</td>
</tr>
<tr>
<td>$M_v$</td>
<td>Viscosity-average molecular weight (Equation 3.4)</td>
</tr>
<tr>
<td>$M_W$</td>
<td>Molecular weight, Da</td>
</tr>
<tr>
<td>$N$</td>
<td>Degree of polymerization (Equation 3.1)</td>
</tr>
<tr>
<td>$n$</td>
<td>Overlone number (Chapter 7)</td>
</tr>
<tr>
<td>$N_A$</td>
<td>The Avogadro’s number</td>
</tr>
<tr>
<td>$P_C$</td>
<td>Capillary pressure, Pa</td>
</tr>
<tr>
<td>$P_e$</td>
<td>Peclet number</td>
</tr>
<tr>
<td>$Q$</td>
<td>Fluid flow rate, m$^3$/s</td>
</tr>
<tr>
<td>$q$</td>
<td>The proton charge, C (Equation 6.3)</td>
</tr>
<tr>
<td>$Q_p$</td>
<td>Flow rate of <em>polymer</em> solution, m$^3$/s</td>
</tr>
<tr>
<td>$Q_w$</td>
<td>Flow rate of <em>solvent</em>, m$^3$/s</td>
</tr>
</tbody>
</table>
r  Radian position, m, (Equation 3.9)
R  Radius of a sphere, m
R  Universal gas constant (Equation 3.2)
R₀ The average unperturbed radius of the polymer coil, m (Equation 3.9)
Re  Reynolds number
RF  Flory radius, m
Rg  Radius of gyration, m
Rk  Permeability reduction, dimensionless
Rm  Mobility reduction, dimensionless
S  Extensional component of the strain, s⁻¹
So_r Residual oil saturation, fraction or %
Sw  Water saturation, fraction or %
Sw_i Irreducible water saturation, fraction or %
T  Temperature, °C or K
u  Monomer-surface activation energy
v  Superficial velocity of the fluid (Equation 2.4).
v  Velocity, m/s
v_q  The speed of sound in the quartz crystal (v_q = 3340 m/s)
v_r  Rate of radial migration, m/s, (Equation 3.9)
v_s  Slip velocity, m/s
w_w  Mass fraction of water (Equation 8.4)
X  Distance or separation, m (Chapter 6)
X₀  Point of zero-separation, m
X_∞  Large separation at which the force of interaction is zero, m
X_A  Distance on approach, m
X_A₀  The first point at zero-separation distance on approach, m
X_AJ-I  Jump-in distance on approach, m
X_AR  The distance at which steric-repulsion is observed on approach, m
X_R  Distance on retraction, m
X_RJ-O  Jump-out distance on retraction, m
Z_i  Valency of the ion (Equation 6.3)
ρ_f  Mass density of the fluid, kg/m³, (Equation 2.4)
ΔP  Pressure difference, Pa
\( \Delta P_{\text{after}} \) Pressure difference after polymer solution flow, Pa
\( \Delta P_{\text{before}} \) Pressure difference before polymer solution flow, Pa
\( \Delta P_{\text{polymer}} \) Pressure difference during polymer solution flow, Pa

**Greek Letters**

\[ [\eta]_0 \] Zero shear intrinsic viscosity, \( \text{cm}^3/\text{g} \)
\[ \varepsilon_{cr} \] Critical strain rate value, \( \text{s}^{-1} \)
\[ \varepsilon \] Extensional or elongational strain rate, \( \text{s}^{-1} \)
\[ \varphi_s \] Molar volume of the solvent molecules (Equation 3.2)
\[ \varepsilon \] Monomer-surface sticking energy
\[ \eta_{r0} \] Relative viscosity at zero shear rate
\[ \kappa \] Debye-Huckel parameter (Equation 6.2)
\[ \chi \] Interaction parameter
\[ \gamma_a \] Apparent shear rate, \( \text{s}^{-1} \)
\[ [\eta] \] Intrinsic viscosity, \( \text{cm}^3/\text{g} \)
\[ \varepsilon_c \] Minimum adsorption energy
\[ \alpha \] Intermolecular expansion factor (Equation 3.3)
\[ \Gamma \] Adsorbed amount of the polymer, mg/m\(^2\)
\[ \Gamma^a \] Total amount of the polymer adsorbed on a surface, mg/m\(^2\)
\[ \Gamma^e^x \] Adsorbed amount of the polymer in excess of the concentration in the bulk solution, mg/m\(^2\)
\[ \varepsilon_0 \] Permittivity in free space (Equation 6.3)
\[ \Lambda_P \] Flow resistance, dimensionless
\[ \rho_f \] Mass density of the fluid, kg/m\(^3\)
\[ \varphi_p \] Volume fraction of the polymer molecules (Equation 3.2)
\[ \Pi \] Osmotic pressure
\[ \Gamma_{\text{QCM}} \] Adsorbed amount as can be calculated from the QCM-D measurements, mg/m\(^2\)
\[ \Gamma_{\text{QCM-S}} \] Adsorbed amount as can be calculated from the QCM-D measurements, using the Sauerbrey relation, mg/m\(^2\)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{\text{QCM-V}}$</td>
<td>Adsorbed amount from the QCM-D measurements using the Voigt model, mg/m$^2$</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Thickness of the adsorbed polymer layer, m</td>
</tr>
<tr>
<td>$\delta_{\text{AFM}}$</td>
<td>Hydrodynamic layer thickness of the adsorbed polymer layer as can be interpreted from the AFM measurements, m</td>
</tr>
<tr>
<td>$\delta_{\text{CAP}}$</td>
<td>Effective hydrodynamic thickness of the adsorbed polymer layer as can be calculated from the capillary flow experiments, m</td>
</tr>
<tr>
<td>$\delta_d$</td>
<td>Thickness of the depletion layer, m</td>
</tr>
<tr>
<td>$\delta_l$</td>
<td>Thickness of the adsorbed polymer layer, m</td>
</tr>
<tr>
<td>$\delta_{\text{QCM}}$</td>
<td>Thickness of the adsorbed polymer layer as interpreted from the QCM-D measurements, m</td>
</tr>
<tr>
<td>$\delta_{\text{QCM-S}}$</td>
<td>Thickness of the adsorbed polymer layer as calculated from the QCM-D measurements using the Sauerbrey relation, m</td>
</tr>
<tr>
<td>$\delta_{\text{QCM-V}}$</td>
<td>Thickness of the adsorbed polymer layer from the QCM-D measurements using the Voigt model, m</td>
</tr>
<tr>
<td>$\delta_{\text{rms}}$</td>
<td>Root mean square thickness of the adsorbed polymer layer, m</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Porosity, fraction or %</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Shear rate, s$^{-1}$</td>
</tr>
<tr>
<td>$\gamma_a$</td>
<td>Apparent shear rate, s$^{-1}$</td>
</tr>
<tr>
<td>$\gamma_{\text{cr}}$</td>
<td><em>Critical</em> shear rate above which shear thickening behaviour occurs, s$^{-1}$</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Viscosity of the fluid, mPa.s</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>Viscosity of the polymer solution in the Newtonian regime, mPa.s</td>
</tr>
<tr>
<td>$\eta_{20}$</td>
<td>Viscosity of water at 20°C ($\eta_{20} = 1.002$ mPa.s)</td>
</tr>
<tr>
<td>$\eta_a$</td>
<td>Apparent viscosity, mPa.s</td>
</tr>
<tr>
<td>$\eta_b$</td>
<td>Viscosity of the bulk liquid, mPa.s</td>
</tr>
<tr>
<td>$\eta_{el}$</td>
<td>Elongational viscosity, mPa.s</td>
</tr>
<tr>
<td>$\eta_l$</td>
<td>Shear viscosity of the adsorbed polymer layer, mPa.s</td>
</tr>
<tr>
<td>$\eta_o$</td>
<td>Oil viscosity, mPa.s</td>
</tr>
<tr>
<td>$\eta_p$</td>
<td>Viscosity of the polymer solution, mPa.s</td>
</tr>
<tr>
<td>$\eta_r$</td>
<td>Reduced viscosity (Equation 3.5)</td>
</tr>
<tr>
<td>$\eta_s$</td>
<td>Viscosity of the solvent, mPa.s</td>
</tr>
<tr>
<td>$\eta_T$</td>
<td>Viscosity of water at a certain temperature, mPa.s</td>
</tr>
</tbody>
</table>
\( \eta_w \) Water or solvent viscosity, mPa.s
\( \kappa^{-1} \) Debye length, m
\( \mu_l \) Elastic shear viscosity of the adsorbed polymer layer, mPa.s
\( \theta \) Contact angle (Equation 2.2)
\( \rho_b \) Density of the bulk liquid, kg/m\(^3\)
\( \rho_l \) Density of the adsorbed polymer layer, kg/m\(^3\)
\( \rho_q \) The density of the quartz (\( \rho_q = 2.65 \text{ g cm}^{-3} \))
\( \sigma \) Interfacial tension, N/m
\( \sigma_{\text{Liq Vap}} \) Interfacial tension between the vapour and the liquid, N/m
\( \sigma_{\text{Sol Liq}} \) Interfacial tension between the liquid and the solid, N/m
\( \sigma_{\text{Sol Vap}} \) Interfacial tension between the vapour and the solid, N/m
\( \tau \) Conformational relaxation time, s, (Equation 3.15)
\( \tau_c \) Contraction relaxation time, s
\( \tau_e \) Extension relaxation time, s
\( \tau_r \) Relaxation time, s
\( \tau_R \) Relaxation time of the polymer molecule in a non-dilute solution using the Rouse model, s, (Equation 3.8)
\( \tau_Z \) Relaxation time of the polymer molecule in a dilute solution using the Zimm model, s, (Equation 3.7).
\( \tau_H \) Relaxation time of the macromolecule modelled as a Hookean dumbbell, s, (Equation 3.10)
\( \omega \) Rotational component of the strain
\( \psi_0 \) Surface potential (Equation 6.2)
\( \zeta \) Static dielectric constant of the medium (Equation 6.3)

**Abbreviations**

1D One dimensional
2D Two dimensional
3D Three dimensional
AE Adsorption entanglement
AFM Atomic force microscopy
AG Adsorption-gel
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA</td>
<td>Bridging adsorption</td>
</tr>
<tr>
<td>C→S</td>
<td>Coil-stretch transition</td>
</tr>
<tr>
<td>CPAM</td>
<td>Cationic polyacrylamide</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DPR</td>
<td>Disproportionate permeability reduction</td>
</tr>
<tr>
<td>EHT</td>
<td>Effective hydrodynamic thickness</td>
</tr>
<tr>
<td>EOR</td>
<td>Enhanced oil recovery</td>
</tr>
<tr>
<td>EWP</td>
<td>Excessive water production</td>
</tr>
<tr>
<td>FIA</td>
<td>Flow-induced adsorption</td>
</tr>
<tr>
<td>FTIR-ATR</td>
<td>Fourier transform infrared spectroscopy in attenuated total reflection</td>
</tr>
<tr>
<td>HI</td>
<td>Hydrodynamic interaction</td>
</tr>
<tr>
<td>HPAA</td>
<td>Hydrolyzed polyacrylic acid</td>
</tr>
<tr>
<td>HPAM</td>
<td>Hydrolyzed polyacrylamide</td>
</tr>
<tr>
<td>IR</td>
<td>Infra-red</td>
</tr>
<tr>
<td>LCST</td>
<td>Lower consolute solution temperature</td>
</tr>
<tr>
<td>Liq</td>
<td>Liquid</td>
</tr>
<tr>
<td>OD</td>
<td>Outer diameter</td>
</tr>
<tr>
<td>PAM</td>
<td>Polyacrylamide</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>PEO</td>
<td>Polyethylene oxide</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethylemethacrylate</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PSD</td>
<td>Position sensitive detector</td>
</tr>
<tr>
<td>PV</td>
<td>Pore volume</td>
</tr>
<tr>
<td>QCM-D</td>
<td>Quartz crystal microbalance with the dissipation monitoring</td>
</tr>
<tr>
<td>RPM</td>
<td>Relative permeability modifiers</td>
</tr>
<tr>
<td>SIM</td>
<td>Stress-induced migration</td>
</tr>
<tr>
<td>Sol</td>
<td>Solid</td>
</tr>
<tr>
<td>TEN</td>
<td>Transient entanglement networks</td>
</tr>
<tr>
<td>TENA</td>
<td>Transient entanglement networks <em>adsorption</em></td>
</tr>
<tr>
<td>TENE</td>
<td>Transient entanglement networks <em>entrapment</em></td>
</tr>
<tr>
<td>UCST</td>
<td>Upper consolute solution temperature</td>
</tr>
<tr>
<td>Vap</td>
<td>Vapour</td>
</tr>
</tbody>
</table>
1 INTRODUCTION

1.1 Excessive Water Production (EWP) from Oil-producing Wells

From the drilling of the first oil well in 1860, oil has become one of the most precious commodities around the world. Since then, oil has been the source of around 50% of the world’s energy and the oil industry has grown overwhelmingly attractive to many investors, be it governments or private companies. The final products of oil, from petroleum to plastics are a product of heavily invested petrochemical industries. Nowadays, the oil industry is administrating a significant part of the world economy. Moreover, the interest in securing the oil producing regions triggers political and social problems around the world. As a result, the terms “oil” and “black gold” are frequently used interchangeably.

The production of oil is a result of a long process starting with exploration, passing through the drilling of exploration wells, appraisal wells, and production wells. Due to its origin, oil is usually produced along with water and gas. Hence, this mixture requires the construction of many surface facilities to separate, pump/compress, and transport the separated fluids. Moreover, the separated water should be disposed appropriately so that it does not harm the environment. The exponential growth of technology has been assisting in the decrease in the unit production cost of oil. Moreover, technological advancements in the oil industry have made it possible to produce oil from previously unrecoverable, or uneconomic, reserves.

It is becoming increasingly difficult to discover new reserves of oil all over the world. This is a result of the intensive exploration activities already covering most of the promising regions in the world. Consequently, oil producing companies are implementing new technologies to optimize the production from the presently available reserves. Also, for various reasons, mature oil producing wells can suffer dramatic increase in water production at a certain time, which can lead to the well becoming uneconomic before reserves are depleted. This production problem is called excessive water production (EWP). This thesis seeks to understand the mechanism of a technology implemented for water control and/or shut-off in oil or gas wells suffering from EWP. This technology employs high molecular weight polymer solutions, which has the effect of decreasing the relative permeability to water more than that to oil. Hence, these polymer solutions are called relative permeability modifiers (RPMs) and the effect induced is called the disproportionate permeability reduction
The DPR effect has been implemented in the water shut-off, or conformance control, applications by the injection of high molecular weight polymer solutions or polymer gels through the pay zone without any zonal isolation. This approach has the advantages of low cost, low risk, and low environmental impact (Mennella et al., 1999).

Excessive water production from mature, oil producing wells can shorten the economic life of these wells leading to premature shut down. This is due to the sharp increase in production costs added by the increased amounts of water production. These added costs are due to additional liquid lifting in the well, increase in oil/water separation costs, as well as the increase in the subsequent disposal costs of the separated water. Moreover, EWP is always accompanied by a sharp decrease in the hydrocarbon production due to the increase in the production of water, which has a higher mobility compared to that of oil. Furthermore, water production is frequently a major source of sand production from the oil wells, as well as being corrosive to the production facilities. The EWP problem is more alarming in offshore oil production due to space limitations and the tighter environmental regulations worldwide.

The sources of the EWP vary from poor well completion and stimulation, to reservoir related sources. Hence, these sources can be categorized as mechanical problems and communication problems (Reynolds et al. 2003). Mechanical problems are caused by poor drilling design and the presence of channels and leakages around the well casings. This category of EWP sources can be fixed easily once diagnosed. On the other hand, communication problems are caused by either poor completion designs and/or intrinsic reservoir heterogeneity, and are thus more challenging for remedy. In addition, shale formations, which act as a barrier trapping the hydrocarbons in place, can be fractured leading to water production from upper water formations. Moreover, completions into, or near, the water bearing formation can hasten the process of water conning (vertical wells) as shown in Figure (1.1, a), or cresting (horizontal wells). Also, during the life of the well, the oil-water contact would increase towards the wellbore as shown in Figure (1.1, b). The most common source of EWP in oil reservoirs produced primarily by water-drive recovery and water-flooded reservoirs is channelling through higher permeability zones, and/or fractures, as illustrated by Figure (1.1, c and d). Consequently, many of the lower permeability intervals would remain un-swept, thus leaving behind relatively large quantities of oil that could be produced otherwise. This last problem is a very good candidate for a DPR treatment using polymers/gelled polymers.
1.2 Disproportionate Permeability Reduction (DPR)

If a water producing interval can be identified and isolated for treatment, it can be blocked completely using cement, resins, or strong gels. Most of the time, this isolation cannot be achieved due to the nature of well completion and/or the costs involved. Hence, polymer solutions, or weak polymer gels, are injected through the producing interval to induce the DPR effect (i.e. the decrease in the permeability to water without affecting that of the oil).

Since more and more wells around the world are becoming mature, the EWP problems are becoming increasingly widespread and causing the decline in oil production worldwide. As a result, this has attracted a wider application of polymer solutions and gels in the water control and/or shut-off operations. Such an application has the drawback of low rate of success which is attributed mainly to the lack of understanding of the mechanism by which polymer solutions and gels act as relative permeability modifiers (RPMs). Since the late 1980’s, there has been great attention from researchers to investigate the DPR and several mechanisms have been proposed to account for it. Based on the extensive work performed by different research groups in the area of the DPR, some guidelines and criteria for a successful application of the RPMs have been published (Botermans et al., 2001; Zaitoun et al., 1999;
Mennella et al., 1999). Even with these guidelines to select a suitable candidate for successful DPR application, failure rates are still relatively high. Moreover, there is a lack of consensus about the DPR mechanisms proposed so far. This is mainly due to the complex nature of the problem.

Trying to account for the DPR effect caused by the flow of high molecular weight polymer solutions, several mechanisms have been proposed so far and they can be classified into two main categories:

1. **Bridging-adsorption (filtration) effect** (Zitha et al., 2001; Zaitoun and Chauveteau, 1998; Zitha et al., 1995): This mechanism is a result of polymer molecules bridging and blocking the pore throats after being elongated (stretched) by flow and consequently adsorbed on both sides of the pore walls. Hence, bridging-adsorption is more probable to occur in the low permeability porous media, in which the pore throats are in the same dimensional range as the fully extended macromolecules, i.e less than around 5 µm.

2. **Wall effect** (Elmkies et al., 2002; Zaitoun and Bertin, 1998; Zaitoun et al., 1990; Zaitoun et al., 1988; Zaitoun et al., 1987): This mechanism is based on the formation of an adsorbed polymer layer lining the surfaces of the pores and pore throats making them narrower. The degree of the DPR effect depends mostly on the increase in flow resistance induced by the presence of an adsorbed polymer layer of a certain effective hydrodynamic thickness (EHT). Most of the experimental work has found that the formation of monolayers of adsorbed polymer alone cannot explain the degree of the DPR measured. Hence, the dynamic formation of multilayers of adsorbed polymer in the porous media, as has been previously proposed by Szebo (1972), has recently received greater support (Asghari, 2004; Grattoni et al., 2004; Chauveteau et al., 2002; Al-Sharji et al., 2001; Zitha et al., 1998). These polymer multilayers are formed during the flow of the polymer solutions through the porous media at shear rates above a critical value, $\gamma_{cr}$ (Asghari, 2004; Chauveteau et al., 2002), and/or above a critical polymer concentration (Zitha et al., 1998). Hence, two broadly similar mechanisms have been proposed: flow-induced adsorption, FIA (Asghari, 2004; Chauveteau et al., 2002) and adsorption-entanglement, AE (Grattoni et al., 2004; Al-Sharji et al., 2001).

Both of the above mechanisms (i.e. filtration effect and wall effect) depend on the physical properties of the polymers and the polymer solution such as polymer molecular weight, total charge, flexibility, solvent quality, type of ions and concentration, and solution concentration. Also, they have been found to depend on the flow rate of the polymer solution and the
permeability of the porous media. Strictly speaking, both mechanisms can be valid under certain conditions. For example, the bridging-adsorption mechanism is more probable in low permeability porous media (the size of the pores comparable to the fully stretched polymer molecule), whereas it is not expected to occur in moderate to high permeability porous media. On the other hand, the wall effect due to the adsorbed polymer layer can induce the DPR effect in all porous media provided that adsorption is possible (i.e. sufficient adsorption energy). There are four possible reasons for the DPR induced by the presence of adsorbed polymer layers (i.e. the wall effect):

1. **Steric and lubrication effects** (Zaitoun et al., 1988) by which the adsorbed polymer layer adds resistance to water flow and simultaneously lubricating the flow of oil.

2. **Wettability change** (Elmkies et al., 2001) by which the hydrophilic nature of the porous media is enhanced by the adsorption of aqueous polymers.

3. **Segregated oil and water pathways** (Nilsson et al., 1998; Liang and Seright, 1997; Liang et al., 1995): According to this hypothesis, water and oil flow through different paths primarily due to the wettability and to some extent the pore size distribution. In hydrophilic (water-wet) porous media, the decrease in the flow dimensions by the presence of the adsorbed polymer layers would create higher flow resistance to water, since it is flowing on the liquid-solid interface of the smaller pores and the narrower pore throats (as discussed in Chapter 2, Section 2.2). On the other hand, oil, which is flowing through the middle of the larger pores and pore throats, would not be largely affected.

4. **Polymer layer swelling and shrinking** (Mennella et al., 1999; Mennella et al., 1998): According to this mechanism the adsorbed polymer layers swells (hydrates) in contact with water and shrinks (dehydrates) in contact with the oil phase. Recently, this mechanism has received agreement among some researchers (Denys, 2003; Singleton et al., 2002).

### 1.3 Scope of the Present Study

The objective of this work is to add knowledge on the effect of polymer solution flow on polymer retention in porous media. In spite of the great deal of research available in the area of polymer solution rheology and polymer retention in porous media, the field is still poorly understood. Several retention mechanisms of high molecular weight polymers in porous media have been proposed, which indicates a lack of consensus among researchers regarding the mechanism of polymer retention. This is due to the complex nature of the flow and
retention of polymer solutions in porous media. Consequently, failure rates in the implementation of high molecular weight polymer solutions as relative permeability modifiers in the oil wells suffering from excessive water production are relatively high. In the present study, the emphasis is on what is happening physically during the flow of polymer solutions through porous media. Moreover, the interplay between the microscopic events in the bulk of the flowing polymer solutions and polymer retention will be presented. The implication of such an understanding on the implementation of high molecular weight polymer solutions for water control (i.e. the DPR effect) in the oil/gas producing wells will be dealt with.

1.4 Thesis Outline

The study of polymer retention in porous media is complex in nature and involves the understanding of several factors that might affect such retention such as the rheology of the high molecular weight polymer solutions and the adsorption of polymers on solid surfaces. Before the presentation of the results of this study, the chapters from 2 to 4 introduce the reader to polymer retention mechanisms in porous media, rheology of the high molecular weight polymer solutions, and the adsorption of polymer at the liquid/solid interface.

Chapter 2 will briefly present the mechanisms of polymer retention in porous media as a result of the flow of polymer solutions through these media. It will start with introducing the reader to some basic terminologies frequently used in the oil industry.

Chapter 3 will deal with the flow of Newtonian and non-Newtonian liquids through porous media. It will start with the migration of polymer molecules as a result of flow through Couette and Poiseuille flow systems. This will lead to a discussion of the formation of polymer-depleted layers and thus the slip effect. Also, flow of polymer solutions in simple systems will be discussed. Moreover, elongational flow of polymer solutions will be introduced and discussed in the context of the flow through porous media.

Chapter 4 will deal with polymer adsorption under equilibrium and non-equilibrium conditions. The retention of polymer solutions by adsorption in porous media will be reviewed.

Chapter 5 will present of the rheological studies of the polymer solutions used in this study. Special attention will be paid to the anti-thixotropic behaviour of these polymer solutions. Chapter 6 will present the AFM measurements conducted in the present study. These measurements will help in the characterization of the adsorption of these polymers.
from aqueous solutions on glass surfaces. They will provide information about the adsorption energy and thickness of the adsorbed polymer monolayers. Chapter 7 will give the results obtained using a quartz crystal microbalance with dissipation monitoring (QCM-D) in order to study the effect of flow on polymer adsorption using some of the polymer solutions used in Chapters 5 and 6. It will give a quantitative study of the effect of increasing the flow rate of the polymer solution on the adsorbed amount and the effective hydrodynamic thickness (EHT) of the polymer layer on silica and gold surfaces. Chapter 8 will present the results of flow of the polymer solutions through single glass capillaries, 2D and 3D models. Two new mechanisms will be proposed for the polymer solution retention in porous media as a result of the collective understanding from the different techniques used in this study (i.e. rheology, AFM, QCM-D, and the flow through the single capillaries, 2D and 3D models).

Finally, Chapter 9 will present the conclusions drawn from this study. Also, the results from some previous studies of the polymer flow and retention in porous media will be discussed in light of the new retention mechanisms proposed in this study. Finally, some recommendations for further studies that can be conducted in future to enhance the understanding of the polymer retention in porous media from the prospective of the new mechanisms proposed in the present study.
2 POLYMER RETENTION IN POROUS MEDIA

2.1 Porous Media

The term porous media refers to any solid matrix with pores (voids) distributed within such a matrix. These pores can be interconnected or isolated throughout the bulk matrix. From such a definition, one can realize the wide existence of porous media and their role in our daily life. Items like cloths, coffee beans, bricks, wood, and paper are just samples of numerous porous media around us; even our body can be considered as a porous medium. Our skin, lungs, bones are porous by nature and it is this nature that enables them to function for the sake of our survival. Overall, porous media and the flow through them govern our life. The flow through rocks is the focus of this study, thus fluid flow through rocks is introduced below.

A given amount of consolidated, inorganic grains formed by geological processes over a certain geological history is called a rock. Generally, rocks do not consist of grains having identical composition, and homogeneous grain sizes. On the contrary, rocks consist of different degrees of randomly distributed grains with different sizes and chemical and physical properties. Hence, a very complex network of voids (pores) can exit between these grains. The proportion of the total pore size with respect to the bulk volume of the rock is called the porosity ($\phi$). The porosity can be original and/or induced. The original porosity is a result of the nature of initial grains in the deposition. On the other hand, the induced porosity could be a result of subsequent geological processes such as fracture development (shale and limestone), and vugs or solution cavities (limestone). Furthermore, porosity can be effective, or total, depending on whether the pores are interconnected or not. Logically, fluids can flow only through the interconnected pores. As a result, another term indicating the ability of the rock to transmit fluid is known as the permeability ($k$), frequently referred to as the absolute permeability.

This chapter gives an introduction to the flow through rocks (i.e. porous media). This will be discussed in the context of oil producing rocks (i.e. oil reservoirs). First, the flow regimes encountered during the flow of the Newtonian fluids through porous media will be briefly presented. Also, the permeability according to Darcy’s law will be addressed. Moreover, some models for the flow through rocks will be described, the chapter concludes with a description of the retention mechanisms of polymers in porous media.
### 2.2 Permeability and Newtonian Flow through Porous Media

A Newtonian fluid is any fluid which has a constant viscosity (\( \eta \)), independent of the induced shear rate (or shear stress) under isothermal conditions. Under steady state and isothermal conditions, the permeability (\( k \)) of a regular piece of rock with a cross-sectional area (\( A \)) and length (\( L \)) can be calculated using Darcy equation:

\[
Q = -kA \frac{\Delta P}{\eta L}
\]  

(2.1)

The permeability depends on interdependent parameters of the rock such as the porosity (\( \phi \)), grain sizes and polydispersity, and packing structure. For slowly flowing, viscous Newtonian fluid, volumetric flow rate (\( Q \)) has a linear relationship with pressure drop (\( \Delta P \)).

In oil bearing formations, water and hydrocarbons (oil and/or gas) coexist in the same pores with different fractions. The fraction of the pore volume occupied by either fluid in percentage terms is the fluid's saturation. This coexistence of two or more fluids in the same porous structure gives rise to terms like wettability, capillary pressure (\( P_C \)), and relative permeability (\( k_r \)).

**Wettability** is the degree of affinity of a liquid to adsorb on a solid surface. This depends on the chemical composition of both the solid and the adsorbed liquids. The wettability of a certain solid surface can be determined by measuring the angle between the liquid and the solid surface through the liquid phase, as illustrated in Figure (2.1). Hence, this angle is called the contact angle (\( \theta \)). The liquid is wetting if the contact angle is less than 90°. On the other hand, it is non-wetting if the contact angle is higher than 90°. The contact angle and hence the wettability is related to the interfacial tensions (\( \sigma \)) between vapour (\( \text{Vap} \)), liquid (\( \text{Liq} \)), and solid (\( \text{Sol} \)) by the Young’s equation (Goodwin, 2005):

\[
\cos \theta = \frac{\sigma_{\text{SolVap}} - \sigma_{\text{SolLiq}}}{\sigma_{\text{LiqVap}}}
\]  

See Figure (2.1)  

(2.2)

Generally speaking, sandstone formations are hydrophilic (water-wet) due to the negatively charged silica surfaces. On the other hand, limestone formations being dominantly positive charged are hydrophobic (oil-wet). The discussion throughout this thesis is about solid surfaces and porous media where water is the wetting phase and oil and/or gas are the non-wetting phases (i.e. hydrophilic surfaces) unless mentioned otherwise.
Figure (2.1): Wettability and contact angles; (a) hydrophilic (water-wet) surface on which a water droplet spreads forming a contact angle ($\theta$) less than 90°, and (b) hydrophobic (oil-wet) surface on which a water droplet forms a contact angle ($\theta$) greater than 90°.

The pressure required to displace the wetting fluid out of a pore throat in a porous medium (a rock) is known as the capillary pressure ($P_C$) [www.wikipedia.org]:

$$P_C = P_{\text{non-wetting phase}} - P_{\text{wetting phase}} = \frac{2\sigma_{\text{Sol-Liq}} \cos \theta}{r} \quad (2.3)$$

where $r$ is the radius of the capillary/pore. In the oil industry, water-wet formations require less energy (pressure) to displace the valuable oil phase because the contact angle in Equation (2.3) would be less than 90° (i.e. $P_C$ is positive and $P_{\text{oil}} > P_{\text{water}}$). Also, it can be deduced from Equation (2.3) that higher capillary pressure is required as the pore throat size gets smaller. As a result of the capillary pressure, it is impossible to displace 100% of any fluid out of a hydrocarbon formation. The fraction of the wetting phase (i.e. water) saturation which cannot be displaced by any means is called irreducible water saturation ($S_{iw}$). On the other hand, the remaining non-extracted fraction of the non-wetting phase (i.e. oil and/or gas) is referred to as the residual (oil) saturation ($S_{or}$).

Figure (2.2): Schematic of oil-water distribution in water-wet rocks
The distribution of water and oil in porous media (rocks) depends mainly on the wettability. In the case of a water-wet rock as shown in Figure (2.2), the wetting phase (i.e. water) flows on the solid surfaces, whereas oil flows in the middle of the pores and pore throats separated from the rock surfaces by water films. Also, water preferentially occupies the smaller pores whereas oil occupies the larger ones due to the capillary pressure effect. This is because in water-wet rocks, the contact angle is less than 90° and hence the capillary pressure is positive. Also, the capillary pressure tends to infinity as the pore radius tends to zero as can be deduced from Equation (2.3).

![Relative permeability curves for both water and oil (k_{rw} and k_{ro}). The wettability of the rock can be interpreted from the water saturation at the intersection point (S_x): if S_x > 50% then the rock is water-wet, and if S_x < 50% then the rock is oil-wet.](image)

**Relative permeability** is a very important parameter in petroleum engineering. It is a shared property of both fluids and rocks. The relative permeabilities to water and oil (k_{rw} and k_{ro}) are the ratios of the effective permeability (k_{w} and k_{o}) of one liquid phase (i.e. water or oil) to the absolute permeability (k) of the rock. Hence, the relative permeability has a value between zero and one. The relative permeability curves to both oil and water are commonly plotted with respect to the water saturation (S_w). These curves are very instructive and information of oil-bearing formation can be interpreted from them, such as the wetting phase,
the residual oil saturation ($S_{or}$) and irreducible water saturation ($S_{wi}$) as illustrated in Figure (2.3). The equations of the different types of permeability are summarized in Table (2.1).

Table (2.1): Summary of different types of permeability of porous media

<table>
<thead>
<tr>
<th>Effective permeability</th>
<th>$k_w$ (to water)</th>
<th>$k_w = \frac{Q_w \times \eta_w \times L}{A \times \Delta P}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_o$ (to oil)</td>
<td>$k_o = \frac{Q_o \times \eta_o \times L}{A \times \Delta P}$</td>
<td></td>
</tr>
<tr>
<td>Relative permeability</td>
<td>$k_{rw}$</td>
<td>$k_{rw} = \frac{k_w}{k}$</td>
</tr>
<tr>
<td>$k_{ro}$</td>
<td>$k_{ro} = \frac{k_o}{k}$</td>
<td></td>
</tr>
</tbody>
</table>

Figure (2.4): A cross-sectional representation of the different capillary models. The white area represents the capillary (Denys, 2003).

2.3 Models of Porous Media

Since science needs to be based on reproducible and repeatable results in order to draw validated conclusions out of any scientific work, scientists have frequently avoided the complexity of natural rocks by using some models of complex systems. These models range from very simple to more complex. Nowadays, capillaries are the simplest models of porous media (Sorbie, 1991). The flow through the pores is represented by the flow through a bundle of capillaries placed in parallel. Moreover, the simplest capillary model is the capillary bundle model with identical, straight tubes as illustrated in Figure (2.4, a). These tubes have the same length and diameter. Complexities are added by having different diameters of the parallel tubes [Figure (2.4, b)], varying the diameter along the tubes (sinusoidal) [Figure (2.4,
c)], and adding tortuous path along the tube [Figure (2.4, d)] (Denys, 2003). These models can be called one dimensional (1D) models as the flow is only in one dimension except the tortuous path model, which is a two dimensional (2D) model.

2D models of porous media have been used to represent the flow in two dimensions. The pores represented by the capillaries above are interconnected to form a flow path made up of pores and pore throats around and in between the grains. Such models can be designed now using computer models which are etched onto glass to form the desired flow network. Hence, control over the sizes and distribution of the grains, pores, and pore throats can be achieved. The advantage of the 2D models is that through such idealized and transparent representation of a porous media, visualization of the flow is possible using available microscopes. A section in a 2D model is shown in Figure (2.5).

Packs of granular materials of different chemical composition and texture are three dimensional (3D) representations of porous media. The properties of the packs can be carefully designed to have a porous medium of different permeabilities, and different degrees of heterogeneities controlled mainly by the sizes of the granules, and their size distribution, respectively.

![Figure (2.5): A 2D micromodel for porous media (Al-Sharji et al., 2001)](image)

### 2.4 Flow Regimes through Porous Media

Analogous to fluid mechanics through pipes, dimensionless quantities such as Reynolds number (Re) and friction factor (f) are encountered in the literature of the flow through
porous media. Reynolds number (Re) is the ratio between the inertial and viscous forces and defined by the following equation (Denys, 2003):

\[
Re = \frac{\rho_f v d_p}{\eta}
\]  

(2.4)

where \(d_p\) is the hydraulic diameter of the pores or capillaries.

For packed beds, it can be also defined as (Denys, 2003):

\[
Re = \frac{\rho_f v d}{\eta (1 - \phi)}
\]  

(2.5)

where \(d\) is the particle size, and \(\phi\) is the porosity.

The flow resistance \(\Lambda_p\) can be obtained using the following equation (Denys, 2003):

\[
\Lambda_p = \frac{\Delta P}{L} \frac{d_p^2}{\eta v}
\]  

(2.6)

Furthermore, for the packed beds, it can be also defined as (Denys, 2003):

\[
\Lambda_p = \frac{\Delta P}{L} \frac{\phi^3 d^2}{\eta v (1 - \phi)^2}
\]  

(2.7)

The Darcy equation (i.e Equation 2.1) is valid under creeping flow conditions where \(Re \leq 1\). Table (2.2) below summarizes the flow regimes through porous media as addressed by Dybbs et al. (1984).

**Table (2.2): Flow regimes encountered during the flow of Newtonian fluids through porous media.**

<table>
<thead>
<tr>
<th>Reynolds Number</th>
<th>Flow Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Re \approx 1)</td>
<td>Development of a boundary layer.</td>
</tr>
</tbody>
</table>
| \(Re \approx 10\) to \(Re \approx 150\) | • The boundary layer becomes more pronounced.  
• The relationship between the pressure drop and flow rate is not linear.  
• This regime is called “inertial regime”. |
| \(Re \approx 250\) to \(Re \approx 300\) | • Development of vortices. |
| Above \(Re \approx 300\) | • Highly chaotic and unsteady flow.  
• Resemble “turbulent flow”. |
2.5 Polymer Retention in Porous Media

The residual resistance induced by the flow of polymer solutions through porous media is due to a retained fraction of the injected polymer. This retained polymer reduces the effective hydrodynamic diameters of the pores and the pore throats. Also, blockage of small pores and pore throats is possible especially in low permeability porous media. Consequently, the flow of any fluid subsequent to polymer flow is restricted by smaller passages as well as part of the pore volume (PV) becoming inaccessible. There are three basic retention mechanisms during the flow of polymer solutions through porous media (Sorbie, 1991). These mechanisms are:

1. **Polymer adsorption:** Retention of polymer through the formation of an adsorbed polymer layer at the solid-liquid interface is inevitable for adsorbing surfaces as shown in Figure (2.6). Since adsorption of polymers on solid surfaces is crucial in the present study, it will be discussed in a separate chapter (Chapter 4).

![Mechanical entrapped polymer in narrow pore throats](image)

![Flow paths through the porous medium](image)

![Hydrodynamically-trapped polymer in stagnant zones](image)

*Figure (2.6): Schematic diagram of polymer retention mechanisms in porous media (Sorbie, 1991).*

2. **Mechanical entrapment:** This happens when large polymer molecules and/or aggregates become stuck while flowing through very narrow pore throats as shown in Figure (2.6). This is synonymous to the filtration effect by which the larger molecules are trapped on the face of the inlet (Szebo, 1975). Due to the presence of very narrow pore throats, inaccessible pore volume exists during the flow of polymer solution through the porous medium (Deminguez and Willhite, 1977) as a result of this filtration effect. It has been
found that increasing the polymer solution concentration and flow rate would increase the amount of the mechanically retained polymer (Deminguez and Willhite, 1977; Szebo, 1975). Generally, the mechanical entrapment is irreversible due to its nature of entrapment and increases the residual resistance to solvent flow by decreasing the permeability of the porous medium due to the increase of the inaccessible pore volume. Using low adsorbing porous media (i.e. Teflon pack), Deminguez and Willhite (1977) have concluded that resistance factors are two to three times lower than that if the adsorption was stronger (i.e. higher adsorption energy) for similar porous media. Generally, residual mechanical retention is the main polymer retention mechanism in porous media especially that of intermediate and low permeability. Cohen and Christ (1986) concluded that the contribution of the adsorptive retention of the polymer used in their system accounted for 35.2%, leaving the rest 64.8% for the mechanical and hydrodynamic retention. Consequently, the mechanical entrapment is crucial in the study of polymer retention in porous media.

3. **Hydrodynamic retention:** This occurs when the polymer molecules are dragged by flow into the stagnant zones as illustrated in Figure (2.6). It has been stated by Sorbie (1991) that this particular mechanism is the least well defined and understood retention mechanism. Hence, this mechanism is discussed below in more detail.

The last two mechanisms (i.e. mechanical and hydrodynamic retention) are associated with the flow of polymer solutions through porous media only. They exist in porous media of intermediate to low permeabilities. The hydrodynamic retention mechanism is synonymous with the shear-induced migration of polymer molecules into stagnant cavities. Such migration was studied by Metzner et al. (1979) using the configuration shown in Figure (2.7 a). They studied the flow of high molecular weight polyacrylamide solutions of concentrations in the range (0.05-0.2 wt%) under shear rates from 1400 to 1600 s⁻¹. The concentration of the solution within the cavities (c₂) (i.e. stagnation zones) has been found 5-30% higher than concentration of the bulk flowing solution (c₁). Geller (1979) used a similar idea to measure the effect of flow on the migration of polymer molecules towards stagnant zones provided in the inner cylinder of a Couette system as shown in Figure (2.7 b). He used the same polyacrylamide used in the study of Metzner et al. (1979), with polymer solution concentration of 250 ppm. The polyacrylamide solution was sheared from 20 to 60 s⁻¹. The concentration in the cavity was found 2-12% higher than the bulk solution in the gap. On the other hand, Rangle-Nafaile (1981) found that the concentration in the stagnant cell in the
outer cylinder was the same as the bulk solution between the cylinders. It should be noted that Rangle-Nafaile (1981) used 2 wt% concentration of the same polyacrylamide solution used in the above two studies (Metzner et al., 1979; Geller, 1979) with a shear rate range between 11 and 850 s\(^{-1}\). One might conclude from the study of Rangle-Nafaile (1981) that polymer molecules do not migrate towards the outer cylinder as compared to evident polymer migration towards the inner cylinder as has been concluded from the study of Geller (1979). However, for the same polymer/solvent system they used; the polymer concentration was very high in the study of Rangle-Nafaile (1981), which can be the reason for the polymer migration being hindered. Also, it has been found that polymer molecules, in a curvilinear flow, migrates in the radial direction \textit{inward}, as will be discussed in the next chapter (Chapter 3, Section 3.2). Hence, it can be concluded that the hydrodynamic entrapment of polymers, as a result of polymer solution flow through porous media, can be more comprehended in light of the shear-induced migration of the polymer molecules towards the stagnant zones.

\begin{center}
\textbf{Figure (2.7):} Schematic representation of (a) Poiseuille flow past cavity and (b) Couette flow past cavity (Agarwal et al., 1994).
\end{center}
Hydrodynamic retention of polymer in porous media has been found to depend on polymer solution flow rate. In their core experiments using HPAM, Chauveteau and Kohler (1974) found that the outlet polymer concentration decreased when they stepped up the flow rate of the polymer solution from 3 m/day to 10.3 m/day through silica sand packs as shown in Figure (2.8). Lowering the flow rate back to 3 m/day resulted in a maximum in the effluent concentration, which was higher than the input concentration. This has been attributed to the liberation of the previously retained polymer at higher flow and hence, the hydrodynamic retention is reversible. This hydrodynamic retention of polymer in porous media was later concluded by Deminguez and Willhite (1977). Prior to these two studies (i.e. Deminguez and Willhite, 1977; and Chauveteau and Kohler, 1974), Maerker (1973) found that polymers can be retained by the hydrodynamic forces as the result of experimental flow studies through porous sandstone cores using polyacrylamide and xanthan solutions. Furthermore, flowing dilute polystyrene (0.053 wt%, $M_W = 1.75 \times 10^4$ to $2.0 \times 10^7$ Da) solutions through packed chromatographic column, Aurbert and Tirrell (1980) have reported that polymer retention increased with shear rate as well as polymer molecular weight. Since a non-adsorbing porous medium was used (column was treated with silane), then the retention mechanism was probably hydrodynamic.

Figure (2.8): Hydrodynamic polymer retention as a result of stepping up the flow rate of the polymer solution (Chauveteau and Kohler, 1974).
2.6 Summary

The flow of water and oil through rocks is very complex and affected by rock properties such as surface chemistry, grain sizes and distribution, wettability, porosity, and permeability. Since the flow through actual rocks is very complex, models of porous media can be used of various types (1D, 2D, and 3D) in the scientific studies. The degree of complexity of these models can be controlled in order to eliminate some effects and hence studies of the flow through porous media can be achieved in a systematic and scientific manner. Also, these models can enable visualization of the flowing system and hence more understanding of the different flow effects can be achieved.

A fraction of polymer is retained in porous media during and after the flow of polymer solutions through these media. Polymer retention by adsorption and mechanical entrapment is irreversible and can induce a residual resistance to the flow of fluids after the flow of polymer solutions. On the other hand, the hydrodynamic polymer retention occurs during polymer solution flow as a result of polymer molecules migrating towards the stagnant zones of the system. Hence, this retention mechanism is enhanced by higher polymer molecular weight and the increase in the flow rate of the polymer solution. Also, migration of the polymer molecules is hindered by the increase in the polymer solution concentration. The hydrodynamic retention is generally reversible and the polymer molecules in the stagnant zones of the porous medium can flow back to the main stream whenever the flow rate of the polymer solution is decreased or stopped.
3 RHEOLOGY OF POLYMER SOLUTIONS

3.1 Conformation of a Polymer Molecule in Solution

A polymer molecule can be thought of as a series of connected segments (i.e. monomers). These polymers can exist naturally such as proteins and polysaccharides, or can by synthetic such as polystyrene (PS), polyethylene oxide (PEO) and polyacrylamide (PAM). Polymers may be synthesized in several shapes including simple linear chains, branched chains, and star-like molecules. In this chapter, the focus is on the simple linear polymer molecules. Linear polymers can be synthesized to be made either of one type of monomer (i.e. homopolymers) or with more than one monomer (i.e. copolymers). In this study, the focus is on linear homopolymers unless stated otherwise.

In solution, the real polymer molecule under excluded volume condition can be thought of existing as a coil with its dimensions defined by the radius of gyration ($R_g$). In the case of a $\theta$-solvent, there are no interactions (attractive, repulsive, or excluded volume) between the macromolecule segments. Hence, a $\theta$-solvent can be regarded as “ideal” for the polymer at a certain temperature, concentration, and composition of the polymer-solvent system. The polymer coil in solution is porous with solvent molecules filling the pores, which comprises the major volume of the coil (Israelachvili, 1991). Theoretically, the ideal picture of the polymer molecule in solution is a fully flexible (i.e. no bond constraints) chain undergoing a ‘random walk’ motion where no solvent constraints are present. For a macromolecule in solution, the radius of gyration ($R_g$) in a $\theta$-solvent can be defined as (Israelachvili, 1991):

$$R_g = \frac{l\sqrt{N}}{\sqrt{6}}$$  \hspace{1cm} (3.1)

where,

$N$ : degree of polymerization, $N = \frac{\text{Polymer} \ M_w}{\text{Monomer} \ M_w}$, and

$l$ : the average length of the monomer.

The quality of a certain solvent depends on the solvent-solvent interaction, the polymer-solvent interaction, and the polymer-polymer interaction. The solubility of the polymer is determined by the strength of the polymer-solvent interaction in comparison to the other two interactions. Hence, the solvent for a certain polymer can be classified as poor,
theta (θ), and good based on the famous interaction parameter (χ), which is defined according to Flory-Huggins theory. According to this theory, the osmotic pressure (Π) of the dilute polymer solution can be defined by the following equation (Goodwin, 2005):

\[
Π = \frac{RT}{V_s} \left[ \phi_p + \left( \frac{1}{2} - \chi \right) \phi_p^2 + \ldots \right]
\]  

(3.2)

\[
\Pi = \frac{RT}{V_s} \left[ \phi_p + \left( \frac{1}{2} - \chi \right) \phi_p^2 + \ldots \right]
\]

The conformation and size of the macromolecule in solution depends on the type of solvent as shown in Figure (3.1). The quality of the solvent is based on the values of the interaction parameter (χ):

\[\chi < 0.5: \text{the solvent is good and the coil would swell with further decrease of } \chi \text{ below 0.5},\]

\[\chi = 0.5: \text{the solvent is ideal (i.e. } \theta \text{-solvent)},\]

\[\chi > 0.5: \text{the solvent is poor with decreasing solubility as } \chi \text{ increases further above 0.5}.\]

Departure from the ideal case (θ-solvent) can be expressed in terms of an intermolecular expansion factor (α), which is multiplied by the radius of gyration (R_g) in order to account for the effect of solvent quality. The product is called Flory radius (R_F). Hence, 

\[R_F = aR_g \approx l^{1/2},\]  

(Israelachvili, 1991)

(3.3)

The value of the expansion factor (α) depends on the quality of the solvent:

i) \[α = 1, \text{ implies a } \theta \text{-solvent},\]

ii) \[α > 1, \text{ swelling of the polymer coil in a good solvent},\]

iii) \[α < 1, \text{ compaction of the polymer coil in a poor solvent}.\]

The solubility of a polymer in a certain solvent depends on temperature. At a certain concentration (c), a single phase solution is formed between two temperature boundaries.
Crossing such boundaries can result in the polymer coming out of solution (i.e. two-phase system). The upper boundary is called the lower consolute solution temperature (LCST), while the lower boundary is called the upper consolute solution temperature (UCST) as schematically illustrated in Figure (3.2). A polymer solution can be classified into dilute, semi-dilute, and concentrated solutions depending on the concentration (c). These classifications are indicated in Figure (3.2), which shows a typical phase diagram of a polymer solution. The boundary between dilute and semi-dilute solutions is denoted by an overlapping concentration (c*). Normally such an overlapping concentration (c*) is defined by Mark-Houwink equation:

\[ c^* \approx \frac{1}{[\eta]} = \frac{1}{KM_v^a} \]  

(3.4)

where, K and a are Mark-Houwink fitting parameters.

![Figure (3.2): Polymer solution phase diagram (reproduced from Goodwin 2005)]

Monomers of a polymer molecule are constrained by the presence of the neighbouring ones and are influenced by the attractive Van der Waals forces. If there is no counter effect (i.e. to the attractive Van der Waals forces) by the solvent molecules, the polymer chain would collapse into a tight ball excluding all the solvent. Several other effects and interactions can exist in a polymer system (e.g. Coulomb repulsion, hydrophilic and hydrophobic, etc.). If the polymer molecules do not have any total charge, they are neutral (non-ionic); otherwise they are called polyelectrolytes (i.e. cationic, anionic, or amphoteric).
Polyelectrolytes in solution are affected by the presence of ions, which can screen the charge. On the other hand, neutral polymers are much more weakly affected by the presence of ions. The behaviour and conformation of the polymer molecules in solution influences the response of the polymer solution to an externally applied flow field (i.e. rheology of polymer solutions).

Before considering the study of the rheology of polymer solutions through different media, there are three main properties of a polymer solution that should be comprehended and quantified if possible: intrinsic viscosity \([\eta]\), radius of gyration \((R_g)\), and relaxation time \((\tau_r)\). The intrinsic viscosity is the limit of the reduced viscosity \((\eta_r)\) as the solution concentration of polymer tends to zero (Sorbie, 1991) as shown by the following equation:

\[
[\eta] = \lim_{c \to 0} \frac{\eta_p - \eta_s}{c \eta_s} = \lim_{c \to 0} \eta_r
\]

where \(\eta_p\) and \(\eta_s\) are the viscosities of the polymer solution and the solvent, respectively.

The intrinsic viscosity is a fundamental property of a polymer solution since it is independent of concentration. It can be related to the molecular weight of the polymer solution by the Mark-Houwink equation (Equation 3.4) with the related parameters for the polymer-solvent system in question. For flexible polymers, the radius of gyration \((R_g)\) can be obtained from the Flory-Fox equation (Omari et al., 1989):

\[
R_g^3 = \frac{[\eta]_0 M_w}{\Phi}
\]

where the constant \(\Phi = 3.66 \times 10^{24}\).

The relaxation time \((\tau_r)\) of the polymer molecules depends on solvent viscosity, polymer molecular weight, intrinsic viscosity of the polymer solution, and temperature. For strictly dilute polymer solutions, it can be obtained using the Zimm model (Chauveteau et al., 1984):

\[
\tau_z = \frac{6}{\pi \eta_s [\eta]_0} \frac{M_w}{RT} \text{ where } [\eta]_0 \text{ is the zero shear intrinsic viscosity.}
\]

For strictly non-dilute polymer solutions, the Rouse model by which intermolecular interaction is taken into account can be used to calculate the relaxation time \((\tau_r)\) using the following equation (Chauveteau et al., 1984):

\[
\tau_R = \frac{6}{\pi \eta_s} \frac{\eta_{R0} - 1}{c RT} \frac{M_w}{RT} \text{ where } \eta_{R0} \text{ is the relative viscosity at zero shear rate.}
\]
3.2 Migration of Polymer Molecules under Flow

The flow of homogeneous polymer solutions can develop position-dependent concentration gradients. This was found to be due to the molecular migration of polymer molecules with respect to the bulk flow (Agarwal et al., 1994). Molecular migration can be defined as the situation in which the centre of mass of a solute molecule (e.g. polymer molecule) does not move with the local solvent velocity at the position of the centre of mass (Aubert and Tirrell, 1980). The discussion below is based on reviews by Larson (1992) and Agarwal et al. (1994) as well as other experimental and theoretical works. Here the focus is on the stress-induced migration (SIM) of macromolecules in three systems: Couette flow, Poiseuille flow, and flow through porous media.

![Figure (3.3): The circular shearing flow stretches the coiled polymer molecule, causing a component $F_r$ of the stretching tension $F_o$ (acting clockwise) to act radially inwards. This produces an inward radial pressure and the molecules migrate towards the centre (Dill, 1979).](image)

In order to conserve their entropy, polymer molecules tend to migrate downstream the stress field (i.e. from high stress regions towards regions of low stress). Consequently, macromolecules migrate in the radial direction inward in curvilinear flow (e.g. concentric cylinders, or cone-and-plate flow). Another intuitive way to put such an effect is that the macromolecule in solution can shorten its distorted length if its centre migrates inward as
shown in Figure (3.3). This migration of polymer molecules induces concentration fluctuation in the radial direction (i.e. demixing effect). Taking advantage of such a demixing effect, a fractionation method of mixtures of high molecular weight DNA molecules has been proposed by Dill and Zimm (1979). The velocity of migration in the radial direction \(v_r\) was estimated by Dill (1979) using the following relation:

\[
v_r \approx \frac{\eta_s \nu^2}{r k T} R_0^5
\]

(3.9)

From the above equation, it can be deduced that the migration velocity is enhanced by the increase of the molecular weight of the polymer (i.e. increase in \(R_0\)). As a result, time can be optimized at which only the desired range of polymer molecular weight can be fractionated out of the solution, which was the principle applied by Dill and Zimm (1979) in their fractionation method. Such cross stream migration of macromolecules in curvilinear flow regimes has been predicted by the theoretical work of Aubert and Tirrell (1980). Moreover, they have concluded that for appreciable polymer migration to occur, polymer molecular weight must be higher than \(10^6\) Da. Hence, polymer migration is significant only during the flow of high molecular weight polymer solutions. Also, they have emphasized the great significance of the concave-side-directed migration. Such migration can be of great importance to the flow of polymer solutions through porous media due to the nature of flow through porous media, which involves the flow through constrictions between spherical grains, as well as predominately curvilinear flow regime even with non-spherical grains. Theoretical work based on a two-fluid model has been used to predict the migration phenomenon in a cone-and-plate system for dilute polymer solutions. This model predicts flow-enhanced fluctuations for entangled (i.e. semi-dilute and concentrated) solutions (Larson, 1992).

The same argument of the preference of the polymer molecules to conserve their entropy has been proposed to account for the migration of polymer molecules away from the walls in the Poiseuille flow (e.g. capillary flow). Consequently, this migration may create a polymer-depleted layer near the walls where the concentration is less than the bulk. The theoretical work conducted by Bhave et al. (1991) has predicted the presence of a polymer depleted layer during rectilinear flow. Bhave et al. (1991) have concluded that the importance of migration and its effect on stress scale with the ratio:

\[
\frac{De}{Pe} = \frac{\tau_{\mu} D_u}{L^2}
\]

(3.10)
where, $Pe$ is the Peclet number ($Pe = \frac{\gamma R_e^2}{d}$)  \hspace{1cm} (3.11)

Typically, the length scale for diffusion was found to be small and the importance of macromolecular migration is confined to very small-scale systems, such as narrow pores and channels. This is caused by a very high stress gradient present in the flow through such geometries. Moreover, the analysis of Bhave et al. (1991) suggests that slip associated with migration, which will be discussed in the next section (Section 3.3), is not important in the measurement of rheological properties. The existence of a polymer-depleted layer during capillary flow has been validated experimentally by several studies (e.g. Ausserre et al., 1991; Muller-Mohrnessen et al., 1990; Cohen and Metzner, 1986).

The formation of polymer-depleted layers at the liquid-solid interface suggests that macromolecules ought to migrate across the stream lines towards the centre of the channel. Such a cross flow argument has not been supported by some theoretical studies (e.g. Aubert and Tirrell, 1980). The conclusion of the work of Aubert and Tirrell (1980) was that migration of polymer molecules is along the flow streams. Recently, migration along the stream lines rather than cross flow has been also supported by the theoretical work of Bhave et al. (1991). Bhave et al. (1991) have found that no cross flow can be predicted solely from a non-homogeneous velocity field. On the other hand, cross flow has been predicted in rectilinear flow, if the hydrodynamic interaction (HI) is incorporated in the model (Usta et al., 2006). Usta et al. (2006) investigated theoretically the lateral migration of a confined polymer under pressure and uniform shear flows. They have concluded that the migration of macromolecules is driven by a combination of shear and hydrodynamic interactions with the wall. Their investigation suggests that polymer molecules migrate toward the centreline when the hydrodynamic interactions are included. Moreover, at sufficiently narrow channels (width/$R_g < 5$), they have concluded that the macromolecules migrate toward the wall, which is in contradiction to the vast majority of experimental evidence.

3.3 Slip in Capillary Flow of Polymer Solutions

It is conventional in the calculations involved in fluid mechanics and during polymer flow on a solid-liquid boundary to assume homogeneous and “no-slip” boundary conditions. The existence of polymer-depleted layers mentioned above, is the cause of the so called “slip” effect. Slip velocity ($v_s$) is a non-zero velocity adjacent to the solid wall in the region of the polymer-depleted layer, where the velocity increases from zero to $v_s$ within the thickness of
the depleted layer ($\delta_d$). The relationship between the slip velocity ($v_s$) and the velocity ($v$) of the bulk fluid is (Agarwal et al., 1994):

$$\frac{v_s}{v} = 1 - \frac{\text{vol. flow rate without migration}}{\text{vol. flow rate with migration}}$$  \hspace{1cm} (3.12)

Kozicki et al. (1970) investigated the flow of aqueous hydroxyethyl cellulose solutions through capillary tubes of different diameters. They have concluded a critical capillary diameter below which only slip occurred. Also, they have concluded a critical shear stress above which only slip was dominant. These conclusions have been supported by the study of Cohen and Metzner (1982, 1985) who observed diameter dependent flow curves using 0.5% aqueous high molecular weight polyacrylamide solutions. They have also concluded that slip is enhanced by the decrease in capillary diameter (Cohen and Metzner, 1985). A similar conclusion has been drawn by Muller-Mohnssen et al. (1987) using a similar polymer/solvent system.

The thickness of the polymer-depleted layer ($\delta_d$) has been found to be in the order of the radius of gyration ($R_g$) of the polymer molecules in solution. This depleted layer can provide a lubrication effect for the flow, which is enhanced by decreasing the capillary diameter (Kozicki et al., 1987; Cohen and Metzner, 1985 and 1986; Ouibrahim, 1978). Consequently, the macroscopic effect of slip is a reduction in the apparent viscosity of polymer solutions measured through capillaries. This has been observed experimentally in the study of Cohen and Metzner (1986).

The thickness of the polymer-depleted layer ($\delta_d$) has been found to decrease with polymer solution concentration and flow rate. Tirrell and Malone (1977) calculated theoretically the capillary length-diameter (L/D) ratio required for the development of the slip effect (i.e. polymer-depleted layer), and found it in the order of 5000. Contrary to some experimental results, Tirrell and Malone (1977) found that the inhomogeneity of polymer concentration (due to the polymer-depleted layer) in the radial direction increases with flow rate, as well as polymer molecular weight. This argument was supported by the theoretical work of Janssen (1980), who predicted the formation of the depleted layer once a critical shear rate is exceeded. The influence of polymer solution concentration on slip was experimentally investigated by Cohen and Metzner (1985), who have attributed the apparent decrease in the slip velocity with the increase in polymer solution concentration to an entanglement effect (i.e. formation of thick adsorbed polymer layer). Similar results were obtained during the flow of dilute polymer solutions (5-200 ppm) through glass capillaries.
A transition from slip (i.e. positive wall velocity) to adsorption (i.e. negative wall velocity) was observed with the increase in the concentration of the polymer solution. Also, the effective hydrodynamic thickness (EHT) of the adsorbed polymer layer was found to be enhanced by the increase in polymer molecular weight, concentration of the polymer solution, and shear stress during the flow of the polymer solution. The plateau of the EHTs (0.25 to 0.75 µm) was obtained mainly at polymer concentrations higher than 100 ppm.

Since porous media can be modelled as a bundle of capillaries, Omari et al. (1989) investigated the slip effect during the flow of high molecular weight, non-ionic and anionic polyacrylamide solutions through small diameter packed membranes. The concentration of the polymer solutions covered a wide range, from dilute to semi-dilute. They have concluded that slip has been the cause of the decrease of the measured viscosity. The thickness ($\delta_d$) of the polymer-depleted layer was calculated to be in the order of the radius of gyration ($R_g$) of the polymer molecules in the polymer/solvent system. This thickness was found to be a function of the polymer molecular weight, solvent ionic strength, and polymer solution concentration. Moreover, the $\delta_d$ has been observed to decrease rapidly with polymer concentration in the semi-dilute regime.

### 3.4 Rheology of Polymer Solutions under Simple Shear

It is well known that in isothermal, turbulent-free flow of Newtonian fluids, the viscosity is constant at all shear rates. On the other hand, non-Newtonian fluids have shear-dependent viscosities. They are categorized as shear thinning, and shear thickening (dilatant) fluids. Polymer solutions fall under the category of non-Newtonian fluids, and exhibit very interesting flow behaviour with shear rate.

At sufficiently high concentrations, polymer solutions are classified as viscoelastic. At very low shear rates, the flow regime resembles Newtonian flow. The viscosity of the polymer solutions in this range of shear rate is constant and can be denoted by ($\eta_0$). At the end of the Newtonian regime, the viscosity of the polymer solution starts to decrease with shear rate. In this range, the polymer solution exhibits a shear thinning behaviour where the flow can be modelled by a power law. For some types of polymers (high molecular weight, flexible polymers) and above a critical shear rate ($\gamma_{cr}$), the viscosity of the solution starts to increase and exhibits a shear thickening behaviour.
Some polymer solutions experience a rheological phenomenon called thixotropy. Thixotropy is a result of deforming the orientation of the macromolecules of the polymer in the direction of flow as a result of increasing the shear rate (Schramm, 2001). The effect of this deformation can be recovered only after leaving the polymer solution for a certain period at quiescent state (i.e. relaxation time). It is as if the polymer solution has a memory for the history of flow it has experienced and this ‘memory’ needs a certain time at static conditions in order to be fully or partly ‘erased’. This is very important for both industrial and research purposes since reproduction of certain results can be obtained if the polymer solution has had a certain time in quiescent state, assuming that the polymer molecules have not been degraded.

The shear thinning behaviour of the polymer solutions is a result of the decrease in the intra- and inter- macromolecular interactions during flow. This is due to the shear-induced alignment of polymer chains in the direction of flow. The subsequent shear thickening behaviour after a critical shear rate is agreed upon many researchers as a result of reversible, gel-like polymer aggregates (Briscoe et al., 1999), concentration fluctuation (Moldenaers et al., 1993), coil-stretch transition (Georgelos and Torkelson, 1988), and various macromolecular associations (Hu et al., 1995; Dupuis et al., 1994; Kishbaugh and McHugh, 1993a,b). Both mechanical and optical experimental techniques have been conducted to investigate the formation of such gel-like structures (Migler et al., 1996, Hu et al., 1995; Kishbaugh and McHugh, 1993 a,b; Moldenaers et al., 1993). Irreversible, flow-induced phase separation may occur at even higher shear rates (Migler et al., 1996; Barham and Keller, 1989).

The shear thickening behaviour of polymer solutions passes through two main steps (Briscoe et al., 1999). The first step is the opening up of the coiled polymer chain. The second step is the formation of new associations and entanglements. The first step is enhanced by the increase of the solvent viscosity and the increase in the relaxation time of the longest polymer molecules (i.e. the increase in the polymer molecular weight and polymer solution concentration). Consequently, higher flow rates (or shear rates) can enhance the probability of collisions and hence the formation of the polymer entanglements.

Using a capillary viscometer, Vrahopoulou and McHugh (1987) investigated the shear thickening phenomena of several dilute, high molecular weight polymers [polyethylene/xylene (6, 16, and 29 million Da), polypropylene/tetralin (30 million Da), and PEO/ethanol (0.9 and 4 million Da.)]. The first two polymer solutions exhibited a shear thinning behaviour followed by a shear thickening behaviour at a critical shear rate. The
apparent viscosity increased to a plateau before decreasing again. On the other hand, the PEO solutions showed predominant shear thinning behaviour. The authors discarded several possible mechanisms to account for the shear thickening behaviour, like the adsorption-entanglement (AE) mechanism previously proposed by Hikmet et al. (1985). On the other hand, they have attributed the shear thickening behaviour to transient entanglement networks (TEN) in solution formed during flow. The second shear thinning region is where such entanglements would be destroyed by the higher shear stress values.

Kishbaugh and MucHugh (1993a) conducted simultaneous measurements of the optical and rheological responses using three different, high molecular weight (2-17 million Da) polystyrene solutions in a Couette system. The concentrations investigated covered the dilute and semi-dilute regimes of the polymer solutions. The rheo-optical measurements were conducted using dichroism and birefringence. The dichroism response was found to be more sensitive to polymer network structures. On the other hand, birefringence was not sensitive to such structures and was most likely governed by the chains or entanglements remaining in the completely dissolved state. The maxima of the dichroism response coincided with the minima in viscosity demonstrating that the shear-thickening was caused by large polymer structures, which were formed during flow above a critical shear rate. The kinetics governing the formation of such structures was found to be instantaneous and reversible. For a given molecular weight, a concentration window exists above or below which, only shear-thinning can be observed. Below the lower value of this concentration window, the solution is so dilute that entanglements are insufficient in number to form significant sizes of structures which were responsible for shear-thickening behaviour. On the other hand, above the upper value of the concentration window, the density of the entanglements in the quiescent state is so high that most of the chains form a complete network which shears apart upon the start of flow. Hence, only shear thinning behaviour prevails in this case. Furthermore, Kishbaugh and MucHugh (1993b) conducted light scattering calculations in order to correlate between such calculations and the shear thickening behaviour of the PS solutions. Their calculations have suggested that the shear-thickening can be attributed to the production and growth of micron-size (2.5 to 5 microns), optically isotropic polymer structures during flow. Even for predominantly shear-thinning behaviour, sub-micron size entangled polymer chains exist that can grow to form the micron-size structures responsible for the shear thickening behaviour at the higher shear rates.

Hu et al. (1995) investigated the shear thickening behaviour of HPAM solutions as a function of polymer solution concentration, solvent composition (glycerol/water ratio),
temperature and prior shear history. Rheological and rheo-optical techniques were used to generate a new insight on the source of the shear thickening behaviour. For semi-dilute solutions and below a critical shear rate, initial overshoot upon start-up of shear was followed by a levelling off to a plateau of the shear stress. For shear rates above the critical value, a second slow growth in stress followed the initial overshoot. Hu et al. (1995) have concluded that there were network associations in the polymer solution in quiescent conditions. The initial overshoot in stress was a manifestation of the energy dissipated in the disruption of the pre-existent associations. The shear thickening at shear rates above the critical shear has been attributed to shear-enhanced coagulation to produce sufficient inter-chain bonding to re-establish non-equilibrium structures in the solution. Hence, the mere chain stretching as a mechanism for the shear thickening behaviour has been ruled out.

3.5 Elongational Flow and Coil-Stretch Transition

In simple shear flow (such as Poiseuille flow through a capillary or in Couette flow) the extensional (S) and rotational (ω) components of the strain are equal. In such a case, full extension and/or alignment of the polymer molecules cannot be achieved. Flexible chains under the influence of such a flow field (i.e. simple shear flow) can be slightly deformed. However, the coiled conformation of the polymer molecules in solution can be opened up and partly extended at relatively high shear rates, which can result in a shear thickening behaviour of the polymer solution as discussed above. Full chain extension of the polymer molecules can be achieved by subjecting the polymer chains to “persistently extensional” flow (Keller and Odell, 1985). Such extensional flow still contains the rotational component (ω) but the extensional component must be dominant (i.e. |S| >> |ω|). On the other hand, pure extensional flow can be achieved in which there is no rotational component (i.e. ω = 0). If uniaxial extension along the Cartesian axis (x) occurs, the velocity in such a case is:

\[ v = \varepsilon (x, -\frac{1}{2}y, -\frac{1}{2}z) \]  \hspace{1cm} (3.13)

where \( \varepsilon \) is the extensional or elongational strain rate. The viscosity associated with such a flow system is different from the simple shear viscosity (\( \eta \)). The elongational viscosity (\( \eta_{el} \)) has been found to be three times the simple shear viscosity (\( \eta_{el} = 3\eta \)) in uniaxial elongation (Boger, 1987). The non-zero stress components in elongational flow are \( \tau_{xx}, \tau_{yy}, \) and \( \tau_{zz} \).
The relationship between normal stress difference and elongational rate is as follows (Sorbie, 1991):

\[(\tau_{xx} - \tau_{zz}) = \eta_{el} \varepsilon \]  

(3.14)

For flexible chains in polymer solutions (e.g. PEO, PS, and PAM), the elongational viscosity \((\eta_{el})\) is a function of the elongational strain rate \(\varepsilon\) and time. According to the theoretical work of de Gennes (1974), high molecular weight, flexible molecules should undergo a coil-stretch (C–S) transition in the elongational flow fields when \(\tau_z \cdot \varepsilon > 1\) where \(\tau_z\) is the longest relaxation time of the coil towards a stretched chain. The coil-stretch transition is sudden and has been attributed by de Gennes (1974) to the change of the draining characteristics of the coiled molecules as they become stretched out. Hence, the C–S transition is accompanied by a dramatic increase in the frictional contact between the stretched molecules and the solvent (i.e. dramatic increase in viscosity). Moreover, de Gennes (1974) has predicted hysteresis between the extension and contraction due to the change in the respective relaxation times. The contraction relaxation time \((\tau_c)\) was found experimentally to be about 30 times longer than the extension relaxation time \((\tau_e)\) (Keller and Odell, 1985). This has been attributed to the hindrance of contraction due to the frictional contact of the solvent with the fully extended chain (de Gennes, 1974). Also, saturation of the stretched chains exists above which the increase in strain can result in a chain rupture, which has been predicted by de Gennes (1974) and has been proven experimentally by Keller and Odell (1985). Hence, extensional flow has always led to polymer degradation. The rupture of macromolecules is anticipated in the mid-point of the fully stretched chain as has been demonstrated by the study of Keller and Odell (1985). Since the response of the flexible polymer chains is different from the less flexible ones (e.g. xanthan gum), Keller and Odell (1985) utilized the use of polyelectrolytes (e.g. HPAM) in order to study the effect of flexibility on the elongational flow. This is due to the control of the flexibility of such polymers by the addition of salt. Such an effect was utilized in the pure extensional flow experiments conducted by Odell et al. (1988) using HPAA in excess salt solutions.

Most of the studies conducted to observe and investigate the coil-stretch (C–S) mechanism of polymer solutions used an opposed jet device. Keller and Odell with other co-workers undertook extensive studies using this device to study and visualize such a transition using high molecular weight PEO solutions (e.g. Keller et al., 1987; Keller and Odell, 1985). This apparatus consists of two narrow jets opposing each other and immersed in the polymer
solution as shown in Figure (3.4). The elongational flow can be created by simultaneously sucking the polymer solution into the opposed jets. The stretched macromolecules in the centre point (i.e. stagnation point) between the jets can be visualized using flow-induced birefringence measurements. A laser light in combination with two polarizers placed perpendicular to each other can make the laser reflected from the aligned macromolecules after being stretched.

Figure (3.4): a) A schematic view of the jets and the flow-field created between them. The stagnation point is marked by a cross; b) The birefringent line between the jets for a 0.1% solution of atactic polystyrene observed with monochromatic light and crossed polarizers at 45° to the jet axis (Keller and Odell, 1985).

The theoretical work of de Gennes (1974) has been validated experimentally by various experimental works performed under pure extensional flow. Flexible polymer chains (e.g. PAM and PEO) have been found to respond to an increase in elongational strain rate through a sudden extension from an almost random coil state to practically full extension at a critical strain rate value \( \dot{\varepsilon}_{cr} \) (Keller and Odell, 1985). The resistance to such extension by the chain is the conformational relaxation time (\( \tau \)). The coil-stretch (C\( \leftrightarrow \)S) transition has been found to occur during pure extensional flow at a critical Deborah number (De = 1) [i.e. critical strain rate \( \dot{\varepsilon}_{cr} \)](Sorbie, 1991; Keller and Odell, 1985) where:

\[
De = \dot{\varepsilon} \tau
\]  

(3.15)

Stretching the macromolecules under the elongational flow signals the onset of macromolecular associations, geometric entanglements in particular (Keller and Odell, 1985). The thickening behaviour under pure elongational flow has been attributed to the formation of polymer entanglement networks (Keller et al., 1987). The concentration below which such
elongational entanglements cannot be formed is denoted as \( c^+ \). This entanglement concentration \( (c^+) \) has been found to be an order of magnitude less than the overlap concentration \( (c^*) \) at quiescent conditions (Muller et al., 1988; Keller at al., 1987).

Since concentration fluctuation is induced mainly by the elongational flow, many studies have been conducted to investigate the pure extensional flow of polymer solutions (e.g. Smitten et al, 2001; van Egmond and Fuller, 1993; Menasveta and Hoagland, 1992; Chow et al., 1988; Keller et al., 1987; Keller and Odell, 1985). Even for extremely dilute polymer solutions, the elongational flow was found to induce a profound impact on concentration fluctuation (Smitten et al, 2001; Ferguson, 1990; Keller and Odell, 1985).

### 3.6 Elongational Flow through Porous Media

Based on their theoretical analysis of viscoelastic effects in non-Newtonian flows through porous media, Gupta and Sridhar (1985) concluded that the stress from the stretched polymer molecules depends *not* only upon the Deborah number, but also on the ratio of the maximum to the minimum diameter of a tube with periodically varying diameter (i.e. a sinusoidal channel). Their analysis has been based on modelling the flow of polymer solutions through the sinusoidal channel. If the ratio of the maximum to the minimum diameter is *not* too large, shear thickening was not predicted, irrespective of the value of the Deborah number. On the other hand, Kulicke and Hass (1984) found that the shear thickening behaviour as a result of aqueous polyethylene glycol (PEG) solution flow through porous media occurs at a critical Deborah number of 0.5. The same critical value had been obtained by Durst et al. (1982) for the flow of HPAM solutions through a porous medium.

Chin et al. (1989) conducted a flow birefringence study of dilute polystyrene (PS) solutions (\( M_W = 20 \text{ million Da} \)) through periodically converging/diverging channels. Such a flow channel has been constructed to model the flow through porous media. It has been concluded that the onset of periodic birefringence was observed only after chains have experienced several cycles of stress at a point deep into the channel. This indicates that the flexible polymer chains have a memory on time scales much more than the relaxed flexible coil.

Saez et al. (1994) have investigated the flow of high molecular weight polystyrene solutions through porous media. They have concluded that the coil-stretch (C→S) transition of the isolated molecules in solution cannot be the only mechanism responsible for the extensional thickening. They have attributed the great increase in the elongational viscosity
beyond a critical strain mainly to the formation of transient entanglement networks (TEN). The entanglement concentration ($c^+$) was found to be an order of magnitude less than the overlap concentration ($c^*$) at quiescent conditions. Similar results and conclusions had been reported above (in Section 3.5) for the same polymer solutions using birefringence of pure extensional flow (Muller et al., 1988). Torres et al. (2002) have investigated the effect of adding ethanol to aqueous PEO solutions on the extensional thickening of such solutions during the flow through porous media. The addition of ethanol caused two main effects. First, it increased the relaxation time of disentanglement of the transient networks. Second, the poor ethanol solvent enhanced the coil-coil interactions. The overall effect was lowering the onset strain rate for the extensional thickening. The entanglement concentration ($c^+$) during the flow through porous media has been found to be very low (1.25 ppm).

Kauser et al. (1999) have investigated the flow of polyethylene oxide (PEO) and hydrolyzed polyacrylamide (HPAA) solutions and their mixtures through porous media. In deionized (DI) water, PEO behaves as a flexible coil whereas HPAA behaves as a semi-flexible chain due to its extended conformation in solution. Hence, the shear thickening of PEO was critical with Reynolds number (Re) whereas HPAA exhibited a more gradual thickening behaviour with the increase in Reynolds number. Addition of excess salt was found to enhance the coil conformation of HPAA molecules. Consequently, the HPAA solution behaved in a flexible manner like the PEO solution and the thickening behaviour of the HPAA in salt solutions was critical with the Reynolds number (sharp increase in flow resistance with the Reynolds number). In all cases, the shear thickening behaviour has not been attributed only to the individual coil-stretch mechanism, which has been previously concluded by the study of Kulicke and Hass (1984). However, the shear thickening behaviour during the flow of high molecular weight polymer solutions in porous media has been mainly attributed to the formation of transient entanglement networks (TEN) between the stretched chains. Such TEN structures at high Reynolds numbers (Re) can modify the flow field in pores and pore throats. Since there is a saturation point of the extending the polymer chains, the shear thickening behaviour can level off at higher values of Reynolds number. Consequently, mechanical degradation of the polymer solutions flowing through porous media can occur at relatively high flow rates (i.e. shear rates) due to the rupture of the polymer molecules.
3.7 Summary

Slip occurs during the flow of polymer solutions through narrow capillaries as a result of macromolecular migration away from the liquid-solid interface at the walls of the capillary towards the flow centreline. This results in the formation of polymer-depleted layer of a thickness ($\delta_0$), which is in the order of the radius of gyration ($R_g$) of the polymer coil in solution. The thickness of the polymer-depleted layer depends on the polymer solution concentration and flow rate and a slip-adsorption transition can occur at critical values. Migration of polymer molecules occurs towards the concave side of a Couette flow system and may well be the source of polymer retention-enhancement during the flow of polymer solutions through porous media around the spherical-shaped grains.

In simple flow regimes (Couette and Poiseuille), the transition of the flow curves from a shear thinning behaviour to a shear thickening behaviour is agreed upon by most researchers to be the result of the formation of shear-induced transient entanglement networks (TEN) in the bulk solution. This occurs above a critical shear rate ($\gamma_{cr}$) that can induce extension of the macromolecules. Hence, the entanglement between such stretched chains can form polymer networks of different sizes and strength. The size of the TEN structures has been measured using in-situ light scattering and they were found to grow to several micrometers. Such a transition (i.e. from shear thinning to shear thickening) is reversible if the stress is relieved and the solution is allowed to rest for a certain period (i.e. relaxation time) given that the polymer molecules have not been mechanically degraded at the high shear rates. Moreover and at sufficiently high shear rates, irreversible stress-induced phase separation can occur.

Coil-Stretch (C$\rightarrow$S) transition of polymer molecules occurs at a critical shear rate ($\gamma_{cr}$), which is the inverse of the relaxation time of the macromolecules. This has been visualized in pure extensional flow systems (e.g. opposed-jet) using birefringence. Shear thickening behaviour under pure extensional flow has been attributed to the formation of transient entanglement networks (TEN), which might be formed even at very low polymer concentrations. A critical entanglement concentration ($c^+$) has been determined to be an order of magnitude lower than the overlap concentration ($c^*$). These results were found to be also valid for the elongation-dominant flow through porous media. The shear thickening during the flow of high molecular weight polymer solutions through porous media has been attributed mainly to the transient entanglement networks (TEN) formed in the bulk solution and not merely to the extension of the individual macromolecules.
4 POLYMER ADSORPTION AT THE SOLID/LIQUID INTERFACE

4.1 Adsorption of Polymers from Solution

Polymer adsorption is the process by which the polymer molecules diffuse from the bulk of the solution towards the solid/liquid interface and attach to it. Once attached to the surface, polymer molecules undergo a subsequent conformational rearrangement, which is a process called spreading. Polymer molecules change their coiled shapes in the bulk solution to find the set of conformations at the interface to minimize their free energy (Fleer et al., 1993).

Polymer adsorption can be categorized as chemisorption and physisorption depending on the type of interaction between the monomers of the polymer molecule and the solid surface. Chemisorption involves the formation of covalent bonds between some reactive segments on the polymer molecules and some groups on the solid surface (O’Shaughnessy et al., 2003b). Hence, a large monomer-surface activation energy ($u$) is involved in the chemisorption ($u \gg kT$) as well as a large sticking energy ($\varepsilon \gg kT$). As a result, chemisorption is a slow process and strictly irreversible due to the large energy barrier for desorption as can be shown in Figure (4.1 b). On the other hand, physisorption is a result of weaker forces such as Van der Waals forces (dipole-dipole, dipole-induced dipole, fluctuating dipole-induced dipole, which is also known as London or dispersion forces) and/or electrostatic interactions (Pashley et al., 2004). Also, hydrogen bonding can be formed between some groups of the polymer (e.g. amide or carboxyl groups in the case of polyacrylamide) and some groups on the solid surface (e.g. Oxygen, hydroxyls, or silanols) (Luckham et al., 1999). In physisorption, the monomer-surface activation energy ($u$) is very small as illustrated in Figure (4.1 a). As a result, monomers in physisorption stick once in contact with the surface with sticking energy ($\varepsilon$) in the order of $kT$. For large polymer molecules (i.e. high molecular weight), the sum of these sticking energies is large enough to make the relaxation of the adsorbing molecules very slow and hence hindering desorption considerably (i.e. irreversible adsorption). A recent review on the irreversibility of physisorption from high molecular weight polymers has been conducted by O’Shaughnessy and Vavylonis (2005). The discussion in this study will be about physisorption and hence the word adsorption will refer to physisorption, unless stated otherwise.
Figure (4.1): The two types of polymer adsorption: physisorption and chemisorption (reproduced from O’Shaughnessy and Vavylonis, 2005). In the case of physisorption (a), the energy barrier ($u$) is very small and the sticking energy ($\varepsilon$) is in the range of $kT$. In the case of chemisorption (b), both the energy barrier ($u$) and the sticking energy ($\varepsilon$) are very high (i.e. far higher than $kT$).

The monomer-surface sticking energy ($\varepsilon$) of a polymer molecules should compete against the loss in entropy of the macromolecule caused by adsorption. Hence, minimum adsorption energy ($\varepsilon_c$) should exist for the polymer molecule to adsorb on the solid surface (Cohen-Stuart et al., 1986). In the case of a fresh solid surface in solvent, the adsorption of a long polymer chain (molecule) is only allowed by the liberation of the previously adsorbed solvent molecules. Hence, the limitation of adsorption sites on the solid surface accompanied with the interaction between the polymer segments and the solvent molecules forces the adsorbed polymer molecule to attain a certain conformation at the liquid/solid interface. In other words, the thermodynamic balance between the entropy and the enthalpy of the adsorbed polymer molecule determines the conformation of the adsorbed macromolecule (Luckham et al., 1999). This conformation should enable the polymer molecule to attain a situation of minimum free energy (Fleer et al., 1993; Cohen-Stuart et al., 1986).

4.1.1 Adsorption Equilibrium

Nowadays, the adsorbed polymer macromolecule is agreed to conform as shown in Figure (4.2), when equilibrium is achieved (Fleer et al, 1993). The adsorbed macromolecule is pictured to consist of trains, loops, and two long tails (Fleer et al, 1993). Trains are the attached segments of the macromolecule and this is the bound fraction of the macromolecule.
Hence, they act as anchors to the whole macromolecule on the solid surface. In between the trains, loops extend towards the solution away from the solid surface. Tails are the extending parts at both ends of the adsorbed polymer molecule. They are believed to be the longest part of the adsorbed polymer molecule. Their contribution to the effective hydrodynamic thickness (EHT) of the adsorbed polymer layer is widely accepted as being the dominant factor (Yoram Cohen, 1988; Takahashi et al., 1980). It should be stressed that the adsorbed polymer does not have a fixed configuration; rather different segments of the polymer chain are in constant motion changing from attached train segments to unattached loop or tail segments.

![Figure (4.2): A qualitative model for a polymer macromolecule adsorbed on a solid surface](image)

The thickness adsorbed polymer layer depends greatly on the measurement technique used. Some techniques such as ellipsometry give greater indication to the contribution of the loops and their extension into solution while others such as atomic force microscopy (AFM) indicate the effect of tails. Moreover, hydrodynamic methods are thought to detect the most extended polymer tails. These methods include dynamic light scattering and the increase in flow resistance of solvent flow through capillaries and porous media after polymer solution flow. Generally, the root mean square thickness of the adsorbed polymer layer ($\delta_{\text{rms}}$), measured by techniques such as ellipsometry is lower than the effective hydrodynamic thickness (EHT) (Fleer et al, 1993) as illustrated in Figure (4.2). In the present study, the EHT of the adsorbed polymer layer is of the main interest but the $\delta_{\text{rms}}$ can be frequently used since the $\delta_{\text{rms}}$ can give information about the adsorbed polymer layer thickness similar to those given by the EHT. Generally, for a monolayer, the EHT can reach up to 5-7 times the

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radius of gyration \( (R_g) \) especially with higher molecular weight polymers. This was predicted theoretically by Cohen-Stuart et al. (1984) as well as obtained experimentally (e.g. Braithwaite and Luckham, 1997).

An adsorption isotherm is the plot of the adsorbed amount \( (\Gamma) \) in mass of adsorbed polymer per either mass or area of adsorbent with respect to the polymer concentration in the bulk solution \( (c^b) \) at a constant temperature. The adsorbed amount \( (\Gamma) \) can be expressed in two ways (Fleer et al, 1993): (i) the amount of polymer in the interfacial region in excess of \( c^b \) denoted by \( \Gamma^{ex} \) or (ii) the total amount in contact with the surface denoted by \( \Gamma^a \). In the present study, the second expression will be used and will be denoted by \( (\Gamma) \) with the unit of mg/m\(^2\) or mg/g. Figure (4.3) shows a typical curve of polymer adsorption isotherms (i.e. \( \Gamma \) versus \( c^b \)). Polymer adsorption is classified as a high affinity adsorption isotherms with a pseudo plateau of the curve reached at low concentrations. In the case of adsorption from a quiescent polymer solution, the effective hydrodynamic layer thickness (EHT) increases with the adsorbed amount. Furthermore, thicker adsorbed layers (i.e. longer tails) are formed using higher molecular weight polymers. This has been observed both theoretically and experimentally (Fleer et al, 1993). Moreover, the length of the tails is higher for higher polymer concentrations at a constant adsorption energy, polymer molecular weight, and quality of solvent.

![Figure (4.3): A typical polymer adsorption isotherm.](image)

### 4.1.2 Adsorbed Polymer Layers in Non-equilibrium Situations (Adsorption Kinetics)

Adsorption kinetics of the polymer solutions can be represented by the adsorbed amount with time elapsed since contact has been established. A typical curve of the adsorption kinetics
\( \Gamma(t) \) is represented in Figure (4.4). It can be observed that the adsorbed amount increases linearly from zero to about 90% coverage, at which a transition to quasi-steady state is reached. In this linear range:

\[
\frac{d\Gamma}{dt} = k \cdot c^b
\]  

(4.1)

\[\text{Figure (4.4): Adsorption kinetics of poly(ethylene oxide) from aqueous solution onto silica (Cohen-Stuart and Fleer, 1996).}\]

In the initial linear range, adsorption is driven primarily by the diffusion of the macromolecules to the surface and subsequently attaching to it (Cohen-Stuart and Fleer, 1996). After “sticking” to the surface, the adsorbed macromolecules undergo a conformational change to lower their energy on the surface (i.e. relaxation process). The first macromolecules tend to adsorb initially in a flat configuration to a fresh, solid surface due to the existence of plenty space. Longer loops and tails are formed during the subsequent relaxation process. Moreover, the late comers have limited “sticking” sites and hence adsorb and form longer loops and trains. Hence, as the adsorbed amount of the polymer increases, the polymer chain forms longer loops and tails. The contribution of tails to the adsorbed amount is small but they largely determine the effective hydrodynamic thickness (EHT) of the adsorbed layer. Consequently, a small change in the adsorbed amount with respect to time would be accompanied by a substantial change in the EHT. Desorption experiments conducted by some investigators made use of such a feature to monitor any possible desorption during the wash out process (Cohen-Stuart and Fleer, 1996). It should be emphasized that the actual steady state (i.e. equilibrium) cannot be reached in polymer
adsorption due to the presence of exchange kinetics between the adsorbed layer and the polymer in solution and/or perturbation of any state of equilibrium by a flow field (Cohen-Stuart and Fleer, 1996).

The adsorbed amount can take up to one day to reach the steady state value as was observed by Takahashi et al. (1980) when they investigated polystyrene (PS) adsorption from a cyclohexane solution on a chrome plate using an ellipsometer. On the other hand, it has been found that it can take minutes to reach 80% of the equilibrium value of the adsorbed layer thickness (i.e. the root-mean square thickness, $\delta_{\text{rms}}$) but can take 2-3 hours to reach the steady state value (Takahashi et al., 1980). This was shorter than the time needed for the steady state thickness of polyethylene oxide (PEO) adsorption through porous filters, which can take up to one week depending on the solution concentration in the dilute regime (Kawaguchi et al., 1988). These obvious contradictory results can be attributed to the difference between the two methods used (i.e. the ellipsometry and the hydrodynamic method). It can be concluded that the thickness of the loops measured by the ellipsometer in the study of Takahashi et al. (1980) reached a steady state value within 2-3 hours. However, the thickness of the tails measured by the hydrodynamic method in the study of Kawaguchi et al. (1988) can take very long time (up to one week) to reach a steady state value. Hence, it can be concluded that the tails grow longer during the relaxation process mainly in expense of the segments of the trains with little effect to the loops. On the other hand, adsorption of concentrated PEO solution on an oxidized silicon wafer reached the steady state value of layer thickness in about one minute (Dijt et al., 1992). The measurements of Dijt et al. (1992) were conducted during the flow of the polymer solutions, which might have an effect on the adsorption kinetics (i.e. promoted adsorption and hindered relaxation). The increase in the thickness of the adsorbed polymer layer with time is attributed mainly to the relaxation of the adsorbed chains (Mubarekyan and Santore, 2001a). Hence, this layer relaxation can take longer time (up to several days) for the higher molecular weight polymers (Mubarekyan and Santore, 2001b) due to the high concentration in the layer as well as the adsorbed macromolecules being hindered by attachments. During such a relaxation process, entanglements can be formed within the adsorbed layer which can dramatically increase layer relaxation time (Granick, 2002; Mubarekyan and Santore, 2001a)

For a polydisperse, homogeneous polymer solution in contact with a solid surface, lower molecular weight chains adsorb first due to their high diffusion coefficient. Subsequently, the longer chains (i.e. higher molecular weight chains) would displace the
short ones due to their preferential adsorption although this may be a slow process. The
displacement occurs during both the *attachment* and the subsequent *spreading* process.
Moreover, *trapping* of the early adsorbing macromolecules can occur due to the longer
relaxation time of the large macromolecules, which adsorb in later stages (Cohen-Stuart,
1998). However, the short polymer chains can displace the long ones *only* if they have higher
adsorption energy (i.e. a displacer polymer). Exchange between the macromolecules in the
bulk solution and the adsorbed ones have been studied both theoretically and experimentally
using several experimental techniques (Cohen-Stuart and Fleer, 1996). Such a subject has
been reviewed by Fleer et al. (1993) and more recently by O'Shaughnessy and Vavylonis
(2005). Since the non-equilibrium situation during the flow of polymer solutions and the
subsequent wash out by solvent is of interest in the present study, it is introduced below.

### 4.1.3 Effect of Flow on Polymer Adsorption

The conformation of the macromolecules in solution might affect the adsorption of such
macromolecules on a solid surface. This depends on the polymer type, molecular weight,
solvent quality, and the deformation of this conformation by a flow field. The effect of the
flow of polymer solutions on polymer adsorption at the liquid-solid interface of the flo
system has been extensively investigated. This is due to the importance of polymer flow in
applications such as viscometry, chromatography, and enhanced oil recovery.

Comparing the flow through hydrophobic and hydrophilic stainless steel capillaries,
Cohen and Metzner (1982) obtained thick (up to 1.5 µm) adsorbed polymer layers. They used
concentrated solutions of high molecular weight polyacrylamide and polystyrene. The
thickness of the adsorbed layer was found to increase using narrower capillaries. On the other
hand, it decreased with the increase in the shear stress. Cohen and Metzner (1982) have
attributed the formation of such thick layers to the entanglement between the flowing and the
adsorbed macromolecules. Three years later, Barham and several co-workers have proposed
a mechanism called adsorption-entanglement (AE) by which very thick polymer layers (i.e.
several micrometers) are formed during the flow of concentrated, high molecular weight
polymer solutions in Couette and Poiseuille flow systems (Hikmet et al., 1985). They used a
visualization technique to confirm the AE mechanism. Effects of the chemical and physical
nature of the adsorbing surface (Narh et al., 1986), and solution concentration and solvent
power (Barham et al., 1986) were investigated. Moreover, the rates of layer formation and
decay after the cessation of flow was studied (Barham, 1986).
The formation of the AE polymer layers was initially proposed by Hand and Williams (1973). They have attributed the drag reduction behaviour induced by the addition of dilute solutions of high molecular weight polymers to the formation of thick AE layers at the liquid/solid boundaries. They used the flow of polymer solutions through capillaries and an infra-red (IR) cell to visualize such formation. It should be noted here that IR technique is indicating the adsorbed amount rather than the hydrodynamic layer thickness. The increase of the adsorbed amount under an elongational flow is not necessarily an indication of thicker adsorbed polymer layers (Besio et al., 1988). Also, Zwijnenburg and Pennings (1973, 1975, and 1976) have postulated the AE as a result of their observations from successful experiments aimed at growing polyethylene fibres nucleated by polymer seed crystals. The AE is the process by which a monolayer of adsorbed polymer grows by a subsequent hook (entanglement) of the flowing polymer coils. Hence, the thickness of the base adsorbed layer would be progressively increased by the entanglement process. They used both Poiseuille flow (Zwijnenburg and Pennings, 1975) and Couette flow (Zwijnenburg and Pennings, 1976) systems in their experiments.

Szebo (1972) has concluded build-up of polymer multilayers when the pressure was maintained constant during the flow of aqueous, high molecular weight polyacrylamide (PAM) solutions through Millipore paper filters and sand porous media. At constant pressure, flow of the polymer solution was found to decrease continuously without reaching a steady-state. The steady-state was reached only when constant flow rates experiments were conducted. This has been attributed to the build-up of shear stress at constant flow rates to an extent that it tears up the outer parts of the polymer multilayers. It was found that the multilayer build-up depends on polymer solution concentration, flow rate, and counternion concentration. In 1975, Szebo attributed part of the polymer concentration and flow rate dependent retention to the mechanical entrapment of the polymer in narrow pores and pore throats. This was later supported by the work of Thomas (1976) who conducted flow measurements of high molecular weigh polyacrylamide solutions through a glass-capillary bundle. He observed a decrease in the polymer solution flow rate with time at a constant pressure especially in the case of a capillary diameter of 2 µm. The EHT of the adsorbed polymer layers measured in his study were found to be three to four times the average radius of gyration of the polymer molecules in the solution, which indicated a possible formation of multilayers and/or a filtration effect in the case of the low diameter capillaries. It should be noted here that Thomas (1976) interpreted the EHT by comparing the flow of solvent before
an after the polymer solution flow, which might have caused some polymer desorption during the wash out stage.

Al-Sharji et al. (2001) have attributed the increase in the mobility reduction ($R_m$) of the polymer solution during the flow of high molecular weight cationic polyacrylamide (CPAM) through 2D porous models to the AE mechanism. The residual adsorbed layers have been found to be very thick and were visualized using a video camera through a microscope. Moreover, Grattoni et al. (2004) measured AE layers up to 6 µm in thickness during the flow of 1 wt% high molecular weight PAM solutions through rectangular glass capillaries. Also, they measured thicknesses of the residual adsorbed polymer layers of about 10 times the layer formed under quiescent conditions using both capillary flow and atomic force microscopy (AFM).

A similar mechanism to that of the AE called flow-induced adsorption (FIA) has been proposed to account for the increase in mobility reduction ($R_m$) and permeability reduction ($R_k$) with the increase of polymer solution flow rate through porous media (silicon carbide, SiC packs) (Asghari, 2004; Chauveteau et al., 2002; Zitha et al., 1998). The only difference between the FIA and the AE has been given by Zitha et al. (1998), which is that in the FIA, adsorption can occur individually and/or collectively from the bulk solution. However, the FIA in the study of Chauveteau et al. (2002) was described as being equivalent to the AE. Moreover, the FIA layers were observed to increase dramatically after a critical shear rate (Asghari, 2004; Chauveteau et al., 2002), which was found to depend on the polymer type (Asghari, 2004), and concentration (Zitha et al., 1998).

After investigating the flow of high molecular weight polymer solutions through packed beds, Kozicki et al. (1967) have concluded the formation of adsorption-gel (AG) polymer layers. The EHT of the AG layers was found to be substantial and can reach up to 6 µm. Similar effect was obtained during the flow of polymer solutions through capillary tubes of different diameters (Kozicki et al., 1970). Values of the EHT of the AG layers ranging from 4 to 180 µm have been interpreted using different polymer concentrations and capillary diameters. They found that there was a critical capillary diameter below which the shear thickening effect of the polymer solution did not occur due to the transition towards slip. This critical capillary diameter was found to be independent of the polymer concentration in the range investigated. Moreover, the transition from AG formation to the slip effect at the wall occurred above a critical shear stress. Also, the EHT of the AG layers was found to be
inversely proportional to the shear stress applied. Furthermore, the EHT was higher for higher concentrations using capillaries of the same diameter.

In 1988, Kozicki et al. conducted more work on polymer adsorption during the flow through packed beds. They interpreted that very dilute polymer solutions (0-100 ppm) can form AG layers of EHT as high as seven times the calculated macromolecular diameter (i.e. 2\( R_g \)). Similar results have been obtained during the flow of dilute polymer solutions (5-200 ppm) through glass capillaries (Kozicki et al., 1993). Transition from slip (i.e. positive wall velocity) to adsorption (i.e. negative wall velocity) with the increase in polymer solution concentration has been observed. The measured EHT of the adsorbed polymer layer was enhanced by the increase in the polymer molecular weight, polymer solution concentration, and shear stress. The plateau of the EHT (0.25 to 0.75 \( \mu m \)) was obtained mainly at concentrations higher than 100 ppm.

As a result of pure extensional flow using an opposed jet setup, an extraordinary firmness of the adsorption of fully extended polyelectrolytes along polar surfaces has been observed by Keller and Odell (1985). Such adsorption was observed to be irremovable due to its high adsorption energy. The effect of the elongational flow on the adsorption has been investigated by Besio et al. (1988) using dilute solutions of high molecular weight polystyrene in cyclohexane. They conducted measurements of the adsorbed amount and the thickness of the adsorbed layer under static conditions as well as under elongational flow. The elongational flow was conducted by directing a jet of solutions perpendicular to a chrome mirror in order to produce an elongational velocity field at the stagnation point on the surface. For the higher molecular weight (20\( \times 10^6 \) Da) polystyrene, the adsorbed layer was measured to be an order of magnitude thinner than a layer adsorbed under static conditions as well as the polymer concentration in the layer under the elongational flow being 3.4 times higher. During the desorption stage (i.e. wash off by solvent), polymer desorption was not observed at the stagnation point. On the other hand, when the mirror was dried, a centre of the adsorbed polymer was observed followed by a polymer-free annular ring where shear forces had desorbed and/or prohibited the adsorption of the polymer. Away from the annular ring, a region of the adsorbed polymer was seen. For the un-deformed molecules under the rates investigated (\( M_W = 1.8\times10^6 \) Da), the thickness of the adsorbed polymer layer was about 0.6 that under quiescent conditions. McGlinn et al. (1988) have observed an increase in the adsorbed amount of different molecular weights; polymethylmethacrylate (PMMA) solutions of dilute concentrations in \( \text{CCl}_4 \) using Fourier transform infrared spectroscopy in attenuated
total reflection (FTIR-ATR). This occurred at very small shear rates (3 s\(^{-1}\)) which is much less than the elongational strain rate. Hence, McGlinn et al. (1988) have attributed this increase in the adsorbed amount to the reorientation of the polymer chains with respect to the surface, hence promoting the adsorption of such chains. It was anticipated that the adsorption of such reoriented polymer chains would have a lower energy barrier, which is caused primarily by the loss of the entropy (i.e. some loss of entropy already caused by the reorientation process). Hence, it is anticipated that very high adsorption energy is associated with the elongational flow (Besio et al., 1988; Keller and Odell, 1985). This may be true provided that the shear stress at the solid-liquid interface does not exceed a critical value above which desorption and/or adsorption prohibition can occur (Besio et al., 1988).

The elongational experiments of Besio et al. (1988) contradicts the results of Lee and Fuller (1985) who have concluded “flow-inhibited adsorption” from their experiments flowing polymer solutions over an adsorbing substrate. At steady-state, Lee and Fuller (1985) observed that the coverage and the final surface concentration decreased with shear rate. However, the thickness of the adsorbed layer was not affected by the elongational rates up to 1000 s\(^{-1}\). The adsorption of high molecular weight polystyrene in both good and \(\theta\)-solvents flowing through a simple channel and from an impinging jet (i.e. elongational flow) was conducted by Chin and Hoagland (1991). Under the \(\theta\)-solvent, little influence was observed between the two flow environments, whereas in the good solvent, a greater impact was noticed. In the good solvent, a decrease in the adsorbed amount with the shear rate was concluded (0 to 800 s\(^{-1}\)). On the other hand, the adsorption was found to be enhanced by the elongational flow at the stagnation point. The adsorbed amount increased with the elongational rate up to around 19000 s\(^{-1}\) at which it starts to decrease. In both cases, desorption occurred during the wash off stage. This apparent contradiction regarding the effect of the flow system (simple shear vs. elongational shear) may be attributed to the migration of macromolecules away from the surface in the case of the channel flow as has been discussed in Chapter 3 (Section 3.2).

### 4.1.4 Polymer Desorption and Residual Polymer Layer

It has been stated above that the adsorption of high molecular weight polymer solutions is generally irreversible. Usually, polymers cannot be readily desorbed by solvent wash off. Hence, the adsorbed polymer layers are extremely long-lived (i.e. metastable state) (Cohen-Stuart and Fleer, 1996). Cohen-Stuart and Fleer (1996) predicted that it can take time in the order of years to achieve 10% desorption. This time is longer for longer chains due to the
longer relaxation time, thus greatly hindering the transport of material away from the surface. However, Dijt et al. (1992) monitored desorption of relatively low molecular weight PEO (7×10^3 to 56×10^3 Da) adsorbing from water onto glass capillaries by using streaming potential measurements. They have concluded that desorption occurred during the solvent wash off stage.

The residual adsorbed polymer layer is the layer remaining after the wash off by the solvent flow. Since the disproportionate permeability reduction (DPR) effect depends presumably on the thickness of such layers (as has been discussed in Chapter 1, Section 1.2), a summary of the results from previous studies on the effect of solvent flow rate through simple channels and porous media on such adsorbed polymer layers is given below.

Over the last thirty years, studies have been conducted to investigate the response of pre-absorbed layers to flow of the solvent over such layers. The methods of study range from using solvent flow through filters (Bagassi et al., 1989; Gramain and Myrad, 1981), capillaries (Churaev et al., 1995; Cohen, 1988; Thomas, 1976), ellipsometry (Lee and Fuller, 1984), FTIR-ATR (Soga and Granick, 1998) and comparing the flow of polymer solutions through adsorbing and non-adsorbing capillaries (Cohen and Metzner, 1982) and silica sand beds (Cohen and Christ, 1986). In general, increasing solvent shear rate decreases the EHT of the adsorbed polymer layer. Such an effect of the solvent flow on a pre-adsorbed polymer layer has been investigated using FTIR-ATR by Soga and Granick (1998). They have concluded that the layer thinning with shear is a result of the layer being compressed and flattened by shear of the solvent. Also, they did not notice a significant desorption of the adsorbed polymer even at very high shear rates.

An exception to the thinning of adsorbed polymer layers by solvent flow is the work of Gramain and Myrad (1981), in which reversible, shear thickening behaviour of the adsorbed layer was observed. The EHT caused by such an effect increased by a factor of 3-6 reaching 1.5 µm in some cases. This has been attributed to the reversible, coil-stretch transition of the coiled loops caused by the elongational flow. This thickening behaviour of the residual polymer layer had been also found by Szebo (1972) after a critical value. This elongational flow has been justified by the presence of inhomogeneties in the adsorbed polymer layer. Later, Bagassi et al. (1989) have demonstrated that the presence of irregularities on the solid surfaces is a requirement for the shear thickening behaviour of the adsorbed polymer layer. This is necessary to produce an elongational component of the velocity perpendicular to the surface. Hence, for saturated (i.e. fully covered), smooth
surfaces, layer shear thinning would be always exhibited by solvent on the pre-adsorbed layer. Several models have been proposed to account for the thinning behaviour of the hydrodynamic thickness of the adsorbed polymer layers with solvent shear rate (e.g. Parnas and Cohen, 1991; Lee and Fuller, 1984).

4.2 Summary

Adsorption (physisorption) of polymer molecules occurs once the polymer solution comes into contact with an adsorbing, solid surface. At equilibrium, the adsorbed amount and layer thickness is a function of the adsorption energy, polymer type and molecular weight, solvent quality and ion concentration, and polymer solution concentration. Generally, the effective hydrodynamic layer thickness (EHT) is proportional to the adsorbed amount for the same polymer type, molecular weight, and polymer solution concentration. Moreover, adsorption of polymer molecules is generally irreversible due to the many sticking sites of the same macromolecule on the surface. This makes it hard for the macromolecule to desorb due to the high increase in the relaxation time of the macromolecule in the adsorbed layer. Such irreversibility is enhanced by the increase in the polymer molecular weight.

The effective hydrodynamic thickness (EHT) of adsorbed polymer monolayers can be up to 5 times the radius of gyration ($R_g$) of the polymer molecules in solution. On the other hand, micron-scale thicknesses of the adsorbed polymer layers were measured during the flow of polymer solutions through several media, which can indicate a build up of polymer multilayers. This has been attributed to several mechanisms such as adsorption-entanglement (AE), adsorption-gel (AG), and flow-induced adsorption (FIA), which are probably different names for the same microscopic phenomenon. Moreover, studies exist that obtained rate-dependent residual polymer layers as a result of these mechanisms. It should be noted that most of the studies that obtained multilayers of adsorbed polymers were conducted by the flow of polymer solutions through porous media. Also, thickening of the thickness of the adsorbed polymer layer with the shear rate of the solvent has been attributed to the presence of elongational velocity factor perpendicular to the surface. Generally, this occurs during the flow through porous media.
5 AN EXPERIMENTAL STUDY OF THE RHEOLOGY OF AQUEOUS HIGH MOLECULAR WEIGHT POLYMER SOLUTIONS

5.1 Introduction

Flow of polymer solutions can produce effects such as flow-induced haziness or cloudiness, precipitation of gel-like particles, solid fibre formation in a flowing solution, and flow-induced or flow-influenced crystallization (Larson, 1992). Hence, the rheological studies of the polymer solutions are vital in explaining many observations of these solutions when subjected to flow. There has been also an interest in the study of the microscopic mechanisms that can originate any specific rheological response (Larson, 1992). For example, the antithixotropic behaviour of some polymer solutions has been attributed to the formation of various gel-like structures (as discussed in Chapter 3, Section 3.4). Since this study is interested in the flow of high molecular weight polymer solutions through porous media, the effects of elongational flow, which occurs at high shear rates in simple flow systems (Couette, and Cone and Plate), are of a particular interest.

Table (5.1): Some properties of the polymers used in this study

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_W (10^6 \text{ Da})$</th>
<th>Charge Density (%)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAM</td>
<td>18</td>
<td>&lt; 0.1</td>
<td>PolySciences</td>
</tr>
<tr>
<td>CPAM</td>
<td>6</td>
<td>10</td>
<td>SNF Floerger</td>
</tr>
<tr>
<td>PEO</td>
<td>4</td>
<td>0</td>
<td>Aldrich</td>
</tr>
</tbody>
</table>

5.2 Experimental Section

5.2.1 Polymer Solutions

Three polymers were used in this study: polyacrylamide (PAM), cationic polyacrylamide (CPAM), and polyethylene oxide (PEO). Some information of these polymers such as molecular weight, density of charge and supplier are listed in Table (5.1). The PAM is essentially a non-ionic, very high molecular weight, linear polymer made of acrylamide
monomers, which has a chemical structure shown in Figure (5.1 a). In practice, there is usually a finite but small degree of hydrolysis of the amide group into acrylic acid (Denys, 2003). This polymer was supplied by Polysciences as solid granules with a quoted molecular weight of 18 million Daltons. The CPAM is a linear, high molecular weight random copolymer of acrylamide and (N,N,N-trimethyl)-aminoethyl chloride acrylate with a structure shown in Figure (5.1 b). The charge density of this cationic polymer is 10%. This polymer was produced by SNF Floerger in a solid granular state with a molecular weight of 6 million Daltons. The PEO was supplied from Aldrich as a powder with a molecular weight of 4 million Daltons. The chemical structure of the ethylene oxide monomer is shown in Figure (5.1 c). The molecular weight distribution of these polymers is not known but it is likely that they have a broad molecular weight distribution.

![Chemical structures of monomers](image)

(a) Acrylamide
(b) (N,N,N-trimethyl)aminoethyl chloride acrylate.
(c) Ethylene Oxide

*Figure (5.1): Structure of the monomers composing the CPAM (monomers a and b), the PAM (monomer a) and the PEO (monomer c).*

There are two solvents used to prepare the polymer solutions in this study:

1. De-ionized (DI) water.
2. 0.34 M Sodium Chloride (NaCl).

Traces (100 ppm) of Sodium Azide (NaN₃) were added to the solvents, especially with the PAM and the CPAM to act as a stabilizer against bacterial degradation. The solvents were
filtered through 0.22 µm Millipore filters to remove any particulate impurities prior to use for the preparation of the polymer solutions and in the flow experiments.

5.2.2 Preparation of the Polymer Solutions

The procedure followed in the preparation of the polymer solutions is critical and has been proven to be vital in the interpretation of the experimental results (Sorbie, 1991). Hence, the procedure followed in the preparation of the polymer solutions used in the experiments of this study is described in detail below.

Once the desired weights of both the polymer and the solvent were ready, the solvent was put in a beaker and stirred vigorously using a magnetic stirrer. After that, the polymer granules or powder was sprinkled on the shoulder of the well-developed vortex caused by the stirrer. This procedure, if performed properly, would ensure full separation between the polymer particles and hence prohibits the otherwise possible conglomeration of the polymer inside the solution. Once the entire amount of the polymer granules or powder had been added to the solvent, the solution was magnetically stirred under milder conditions. The solution was then stirred for about 24 hours in order to allow enough time for dissolution to occur and hence the formation of a homogeneous polymer solution. The polymer solutions were kept at room temperature in a dark place. No polymer solution was used more than 30 days after preparation, since these solutions can undergo chemical degradation with time.

The polymer solutions used in this study were visually clear without any visible cloudiness which might indicate incomplete dissolution. Hence, the polymer solutions were not filtered to conduct the rheology experiments in the present study. It is worth noting that the filtration of similar high molecular weight polymer solutions was not conducted in most of the rheological studies using high molecular weight polymer solutions (e.g. Tapadia and Wang, 2004; Buitenhuis and Springer, 2003; Briscoe et al., 1998; Migler et al., 1996; Dupuis et al., 1994; Magda et al 1993; Kishbaugh and McHugh, 1993 ). Also, the use of diluted solutions from the non-filtered solutions in the AFM measurements in the present study (as discussed in Chapter 6) did not result in any measurement anomalies, which would suggest the presence of microgels and/or impurities. However, the presence of polymer aggregates in these non-filtered solutions cannot be completely excluded.

Prior to the use of the polymer solutions in any flow experiment (QCM-D cells, single glass capillaries, 2D model, and 3D models), the solutions were filtered through a series of Millipore filters (8 µm, and 3 µm). This removes any dust particles from the polymer solution
as well as any polymer microgel particles which may be present, which can be misleading in the interpretation of the results. The flow rate of the polymer solution during the filtration process was adjusted to 6 cm³/min. This filtration procedure has been advised by Chauveteau and Kohler (1980) in order to remove any polymer microgel from xanthan solutions but can be applied for other polymer solutions such as those used in this study (Sorbie, 1991). Since these polymer solutions were relatively viscous and with very high molecular weight, the 1.2 µm filter advised by the study of Chauveteau and Kohler (1980) was not used in order to avoid any possible mechanical degradation due to the small pore sizes of this filter. This mechanical degradation is speculated from the rheological study of one of the polymer solutions used in this study (CPAM) as discussed below and has been reported by Keller and Odell (1985).

5.2.3 Procedure

Flow and viscosity-time curves were obtained using a Paar Physcia (US100) rheometer with a cone-and-plate configuration (MK 24; 75mm cone,1°) with a gap set at 0.05 mm. The rheology of the polymer solutions was studied to give a possible explanation of the results of the flow of these solutions through single capillaries, 2D and 3D models, which are presented in Chapter 8. The flow and viscosity-times curves were obtained at a temperature of 20 °C, which is the temperature at which the QCM-D measurements were conducted, as well as being the average room temperature of the other flow experiments (single glass capillaries, 2D model, and 3D model).

Each polymer solution sample was allowed to rest for 10 minutes prior to the start of the rheological measurement (i.e. start of cone rotation) in order to allow a fixed time for the polymer solution to attain an equilibrium state after the possible deformation of the polymer structure in the solution which can be caused by simply pouring the solution on the plate of the setup. This procedure resulted in reproducible behaviour and trends of the flow and time curves in this rheological study. Each polymer solution sample was sheared in two steps to obtain the following flow curves:

1. **UP-ramp curve**, which was obtained starting from a minimum shear rate of 0.1 s⁻¹ to a maximum shear rate of 2500 s⁻¹ in 10 minutes, and
2. **DOWN-ramp curve**, which was obtained from the maximum shear rate (i.e. 2500 s⁻¹) to the minimum shear rate (i.e. 0.1 s⁻¹) in 10 minutes without allowing a resting time after
the UP-ramp curve (i.e. there was no stoppage time between the UP- and DOWN- ramp curves).

The hysteresis between these two curves (UP-ramp and DOWN-ramp curves) for a particular polymer solution was used to identify the possible thixotropic (or anti-thixotropic) behaviour. Thixotropy exhibited by the polymer solution is a result of deformation induced to the macromolecules as a result of increasing the shear rate (Schramm G., 2001). If the DOWN-ramp curve is below the UP-ramp curve, then the polymer solution exhibits thixotropic behaviour, whilst if the DOWN-ramp curve is above than the UP-ramp curve, then anti-thixotropic (rheopectic) behaviour occurs.

The viscosity (\(\eta\)) was measured as a function of time (t) at a constant shear rate in order to obtain the viscosity-time curves. The polymer solution samples were subjected to a constant shear rate for a certain time. Fresh samples were used for each shear rate run and the samples were allowed to rest for 10 minutes before the start of shear. The aim of these measurements was to observe the viscosity behaviour at a given shear rate. The viscosity-time curves in this study will prove to be helpful in showing some rheological responses that would not be seen otherwise using solely the flow curves. These curves are presented in relative viscosity versus time plots. Hence, before the presentation and discussion of the results (Section 5.3.2), three parameters have to be defined:

1. **Initial viscosity**, \((\eta_{\text{ini}})\): is the viscosity obtained after 2 seconds of flow of the polymer solution at a constant shear rate. The viscosity obtained after 1 second was found to be very high which is likely to be a start-up effect of the rheometer.

2. **Relative viscosity** \((\eta_R)\): is the viscosity at a certain time (t) divided the initial viscosity \((\eta_{\text{ini}})\). This parameter will help in showing the behaviour of the viscosity at a certain shear rate irrespective of any viscosity values.

3. \(\eta_{\text{MAX}}\): is the maximum viscosity obtained during the constant shear rate of a certain polymer solution.

### 5.2.4 Characteristics of the Polymer Solutions

Table (5.2) lists some characteristics of the polymer solutions used in this study. It should be noted that in this study, the main purpose was to categorize the concentration regime of the polymer solutions used in the flow experiments (i.e. to determine whether the polymer solution was in the dilute, or semi-dilute regime). Hence, the results from other studies have
been used to obtain more detailed information concerning the polymer solutions. Unfortunately, it was not possible to obtain any information concerning the CPAM in water because (to the knowledge of the writer) no previous studies have been performed using this solution. However, the characteristics of the CPAM in 0.34 M NaCl were obtained from the book of Denys (2003) for almost the same polymer system (i.e. CPAM of $M_W= 6$ million Da. (10%) dissolved in 0.34 M NaCl). Since the polymer chains are more extended in the absence of electrolytes, then the overlap concentration ($c^*$) which is the boundary between dilute and semi-dilute solutions of the CPAM in water solution would be expected to be less than that of the CPAM in 0.34 M NaCl solution.

Table (5.2): Some Characteristics of the polymer solutions.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>$[\eta]$ \text{ cm}^3/\text{g}</th>
<th>$R_g$ \text{ (nm)}</th>
<th>$c^*$ \text{ ppm}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPAM</td>
<td>Water</td>
<td>1750</td>
<td>140</td>
<td>560</td>
</tr>
<tr>
<td></td>
<td>0.34 M NaCl</td>
<td>1750</td>
<td>140</td>
<td>560</td>
</tr>
<tr>
<td>PAM</td>
<td>Water</td>
<td>3470</td>
<td>257</td>
<td>290</td>
</tr>
<tr>
<td>PEO</td>
<td>Water</td>
<td>152</td>
<td>152</td>
<td>450</td>
</tr>
</tbody>
</table>

The intrinsic viscosity $[\eta]$ in cm$^3$/g of the PAM solution was obtained using the following equation (Omari et al., 1989):

$$[\eta] = 2 \times 10^{-3} M_W^{0.86}$$  \hspace{1cm} (5.1)

The overlap concentration ($c^*$) can be determined by setting $[\eta] c^*=1$. The radius of gyration ($R_g$) of the PAM solution was obtained using the Flory-Fox equation (Omari et al., 1989):

$$R_g^3 = \frac{[\eta]}{\Phi} M_W$$ \hspace{1cm} (5.2)

where the constant $\Phi = 3.66 \times 10^{24}$.

Moreover, the following relation was used to obtain the radius of gyration ($R_g$) for the PEO in water solution (Dasgupta et al., 2002):

$$R_g = 2.15 M_W^{0.583} \text{ (nm)}$$ \hspace{1cm} (5.3)

The overlap concentration ($c^*$) for this polymer solution (i.e. PEO in water) was calculated assuming that the polymer chains are confined to a spherical domain of a radius equals to the radius of gyration ($R_g$). Also, since the polymer coils are contiguous to each other at $c^*$, the
overlap concentration ($c^*$) was calculated using the following equation (Dasgupta et al., 2002):

$$c^* = \frac{M_w}{(4/3) N_A \pi R_k^3}$$

where $N_A$ is the Avogadro’s number.

Figure (5.2): Flow curves of different polymer solutions. UP-ramp and DOWN-ramp curves are shown for every polymer solution to show the possible thixotropic (or anti-thixotropic) behaviour. All measurements were conducted at a temperature of 20°C.
5.3 Results and Discussion

5.3.1 Flow Curves

The flow curves (i.e. viscosity vs. shear rate) of four polymer solutions (1000 ppm PAM in water, 1000 ppm CPAM in water, 1000 ppm CPAM in 0.34 M NaCl, and 10000 ppm PEO in water) are shown in Figure (5.2). These polymer solutions were used at the same concentrations for the flow through models of porous media (i.e. single capillaries, 2D and 3D models), which are discussed in Chapter 8. The results from this rheological study will prove to be important in understanding the microscopic origins of multilayer formation of some polymer solutions used in the flow through these models.

From the UP-ramp curve shown in Figure (5.2), the 1000 ppm CPAM in water solution showed a shear thinning behaviour until a critical shear rate of about 700 s\(^{-1}\). At this shear rate (i.e. 700 s\(^{-1}\)), shear thickening behaviour dominated, reaching a plateau at a shear rate of 2000 1/s, which persisted to the maximum shear rate of 2500 s\(^{-1}\). The DOWN-ramp curve can be observed to be above the UP-ramp curve for the shear rates above 1 s\(^{-1}\), which is an indication of anti-thixotropic behaviour of the 1000 ppm CPAM in water solution.

Among other possible explanations, the shear thickening and anti-thixotropic behaviour of the 1000 ppm CPAM in water solution could be due to the shear-induced dissolution of any polymer aggregates already present in the solution. This may be occurring since the polymer solutions used in the rheological study were not filtered and hence the presence of such aggregates cannot be excluded. Progressive hydration of these aggregates can occur at a critical shear rate and hence apparent shear thickening behaviour can be observed above such a shear rate because of the increase in the viscosity of the solution. This can reach a steady state value and higher viscosity values would be measured during the DOWN-curve measurements, which could give rise to the anti-thixotropic behaviour. Such an explanation is possible but several studies have obtained such a shear thickening behaviour from the flow curves of non-filtered, high molecular weight polymer solutions above a critical shear rate (Briscoe et al., 1999; Migler et al, 1996, Hu et al., 1995; Kishbaugh and McHugh, 1993 a,b; Moldenaers et al., 1993; Vrahopoulou and McHugh, 1987). Hence, the shear thickening behaviour in this study might have been a real effect and the shear-induced dissolution of aggregates in the polymer solution being possible, can be ruled out based on the responses of the viscosity-time measurements in Sections 5.3.2 and 5.3.3. The antithixotropic behaviour from the time curves was observed for only some polymer solutions, while others showed a thinning behaviour with time. Also, the antithixotropic
behaviour was found to be reversible as discussed in Section 5.3.3, while the shear-induced dissolution of aggregates is totally irreversible in nature.

There is a consensus among scientists that the shear thickening and anti-thixotropic behaviour are attributed to the formation of large gel-like structures at sufficiently high shear rates as discussed in Chapter 3 (Section 3.4). These structures are reversible in nature and have been called with different names such as gel-like aggregate formations (Briscoe et al., 1999; Dupius et al., 1994), concentration fluctuation (Moldenaers et al., 1993; Larson, 1992), and transient entanglement networks (Buitenhuis and Springer, 2003; Buitenhuis and Ponitsch, 2003; Torres et al., 2002; Kauser et al., 1999; Saez et al., 1994). It was found that even in the shear thinning range, the gel-like structures can exist but in a sub-micron size (Kishbaugh and MucHugh, 1993b). These sub-micron particles can grow in size as the shear rate increases to micron-size particles up to 5 \( \mu \)m (Kishbaugh and MucHugh, 1993b). This was measured assuming that these particles were isotropic. On the other hand, Kalashnikov and Tsiklauri (1996) viewed such gel-like structures formed during elongational flow as fibrils, which extended forming a network inside the solution. These fibrils were visualized using the method of drying and consequently viewed using a microscope. The formation of reversible, micron-size structures during the flow of the polymer solutions can further grow in size inducing a liquid-liquid phase separation (Le Meins and Tassin, 2001; Migler et al., 1996; Larson, 1992; Barham and Keller, 1990). Such a liquid-liquid phase separation has been found to be reversible in very long time scales (i.e. much longer than the relaxation time of a single polymer chain in solution) (Larson, 1992). In this study, the term “transient entanglement networks” (TEN) will be used to indicate these gel-like structures. The CPAM chains in the water solution have an expanded conformation due to the repulsion between the charged monomers in the chain. Hence, at sufficiently high shear rates, transient entanglement networks (TEN) can be formed between these expanded chains by the hydrodynamic forces. The area between the UP- and DOWN- ramp curves might be an indication of the size and persistence of these structures (i.e. larger area indicates larger and more persistent aggregates).

It was found that this area and hence the sizes of the TEN structures increased with the increase of the polymer solution concentration of the CPAM in water as can be observed in Figure (5.3). For the 100 ppm CPAM in water, thixotropic behaviour was observed. The concentration of this solution is very low and hence the TEN structures might not have been formed by the shear rates covered in this rheological study (i.e. from 0.1 to 2500 \( \text{s}^{-1} \)).
However, this should not eliminate the possibility of TEN structures being formed in such a dilute solution but with sizes not large enough to be detectable. The increase in the concentration is likely to increase the degree of chain entanglements probabilities promoted by the increase in the shear rate. Hence, larger and more persistent TEN were formed using higher concentrations of the CPAM in water solution. It should be reminded here that the UP-ramp and DOWN-ramp curves were obtained over 10 minutes as described above. The time over which the polymer solution is subjected to a certain shear rate proved to be a parameter that should be taken into account whenever the anti-thixotropic behaviour is observed. This is discussed further below in the context of the time dependence of viscosity.

Figure (5.3): Flow curves of different concentrations of the CPAM in water solution. UP-ramp and DOWN-ramp curves are shown for every polymer solution to show the possible thixotropic (anti-thixotropic) behaviour. All measurements were conducted at a temperature of 20°C.
For the other polymer solutions shown in Figure (5.2), a dominant shear thinning behaviour was observed with a slight shear thickening of some solutions (the 1000 ppm CPAM in 0.34 M NaCl and the 1000 ppm PAM in water). This slight shear thickening behaviour of the 1000 ppm CPAM in 0.34 M NaCl solution was observed above 1600 s\(^{-1}\) from the UP-ramp curve of this solution. However, the DOWN-ramp curve of the 1000 ppm CPAM in 0.34 M NaCl did not show any detectable hysteresis with the UP-ramp curve above 1 s\(^{-1}\).

In the case of the 10000 ppm PEO in water solution, the Newtonian behaviour dominated for the shear rates up to 1 s\(^{-1}\), as shown from the UP-ramp curve in Figure (5.2). Above 1 s\(^{-1}\), the polymer solution exhibited a dominant shear thinning behaviour to the maximum shear rate of 2500 s\(^{-1}\). This dominance of the shear thinning behaviour for the PEO solutions in water has been also observed by Vrahopoulos and McHugh (1987). The DOWN-ramp curve of the 10000 ppm PEO in water solution showed no hysteresis at all in the shear rates down to 1 s\(^{-1}\).

For the 1000 ppm PAM in water solution, the UP-ramp curve in Figure (5.2) shows a strong shear thinning behaviour starting at 0.1 s\(^{-1}\) until the maximum shear rate of 2500 s\(^{-1}\). A shear thickening behaviour and a slight anti-thixotropic behaviour can be detected above 1000 s\(^{-1}\) as a slight hysteresis between the UP- and DOWN-ramp curves. The degree of the shear thinning behaviour (i.e. the difference between the maximum and the minimum viscosity in the shear rate range) is the highest in the case of the 1000 ppm PAM in water solution as can be observed from Figure (5.2). This might be due to the very high molecular weight of this polymer, as compared to the other polymers (CPAM and PEO), coupled with the coiled conformation when in the quiescent state. With an increase in the shear rate, the coiled conformation can be elongated and aligned in the direction of flow. Hence, the shear thinning behaviour would take place at lower shear rates and the large coils can be elongated further with the increase in the shear rate. The absence or the slight anti-thixotropic behaviour observed for the three polymer solutions; the 1000 ppm CPAM in 0.34 M NaCl, the 1000 ppm PAM in water, and the 10000 ppm PEO in water; does not imply the absence of the TEN structures in these solutions at the given range of shear rate. These structures might have been formed but in sizes that were not large enough to counteract the high viscosity of these solutions especially in the case of the PAM and the PEO in water solutions. It has been found that the shear thickening behaviour cannot be observed above a certain concentration of the polymer solutions (Dupuis et al, 1994).
Figure (5.4): (a) Viscosity-time curves of the 1000 ppm CPAM in water solution at different shear rates using the cone-and-plate setup. (b) The curves are plotted in semi-log plots in order to show the behaviour more clearly especially at the initial stage. The measurements were conducted at $T = 20^\circ C$. 
5.3.2 Time Dependence of the Viscosity

The viscosity-time dependence of the 1000 ppm CPAM in water solution is shown in Figure (5.4 a) at different shear rates. Figure (5.4 b) shows the same curves but with the time plotted in a log scale to enable the reader to observe the events which occur at the beginning of the experiment, particularly in the first 10 seconds. The curves show an interesting behaviour where the viscosity increases with time until a critical time is reached, after which the viscosity decreases depending on the applied shear rate. At a low shear rate (i.e. 50 s⁻¹), the viscosity increased to a plateau value of 1.2 times the initial viscosity (ηᵢ) (i.e. ηᵢ of 1.2) in the time limit of the experiment (30 minutes). There was no indication of any subsequent increase/decrease in the viscosity with time at such a low shear rate. On the other hand, at the shear rate of 500 s⁻¹, one can identify four regions with different behaviour. Initially, a relatively fast increase in viscosity can be observed in the first 30 seconds. This is followed by a more gradual increase in viscosity with time followed by a more dramatic increase before reaching a plateau value. The relative viscosity stabilized at about 2.2 at this plateau region. This plateau region is followed by a decrease in the viscosity with time. At the shear rate of 1000 s⁻¹, the viscosity-time curve exhibited an initial overshoot followed by an increase of the relative viscosity (ηᵢ) to a plateau region of about 2.4. This is followed by a decrease in the viscosity reaching a semi-plateau region. Similar behaviour can be observed at the shear rate of 1500 s⁻¹, but the maximum value of the viscosity (ηᵢ_MAX) is lower than that obtained at the shear rate of 1000 s⁻¹. The behaviour of the viscosity at higher shear rates (i.e. 2500 and 5000 s⁻¹) exhibited the same initial overshoot followed by a monotonic decrease of the viscosity to a plateau region of viscosity, lower than the initial viscosity at the respective shear rates (i.e. ηᵢ of 0.75 and 0.58 at 2500 and 5000 s⁻¹, respectively). It can be observed that higher shear rates are inducing faster kinetics in the case of the shear rates at which a maximum viscosity is reached (neglecting the initial overshoot) (i.e. shear rate ≤ 1500 s⁻¹).

This increase of the viscosity with time at a constant shear rate (or shear stress) has been observed for various high molecular weight polymer solutions (Tapadia and Wang, 2004; Buitenhuis and Springer, 2003; Buitenhuis and Ponitsch, 2003; Briscoe et al., 1999; Migler et al., 1996; Magda et al, 1993; Larson, 1992; Barham and Keller, 1990). In these studies, the increase in viscosity with time at a constant shear rate was attributed to the formation of shear-induced aggregates, which are called transient entanglement networks in the present study. Hence, the origin of the above behaviour of the viscosity of the 1000 ppm CPAM in water solution with time can be also explained in the context of the transient
entanglement networks (TEN), which possibly caused the anti-thixotropic behaviour in the flow curve of the same polymer solution discussed above. However, hydration of polymer aggregates present in the polymer solution with time of shear at the higher shear rates (up to 1500 1/s) cannot be completely excluded at this point as another possible explanation of the shear thickening (anti-thixotropic) behaviour shown by the viscosity-time curves of the 1000 ppm CPAM in water.

Buitenhuis and Ponitsch (2003) have proposed a model explaining the time-dependent viscosity which was qualitatively similar to the model proposed by Briscoe et al. (1999), which has been explained in Chapter 3 (Section 3.4). This model divides the viscosity behaviour with time in three main regions starting with a slight increase of the viscosity with time followed by a more dramatic increase. This dramatic increase in the viscosity is followed by a plateau region, which in turn is followed by the decrease in the viscosity reaching a plateau region. This model can be used to explain the behaviour of the viscosity in the case of the 1000 ppm CPAM in water solution in this study. Buitenhuis and Ponitsch (2003) have explained the shear thickening of the viscosity behaviour with time by the formation of transient entanglement networks (TEN). For high molecular weight polymer solutions, the elongation of the polymer chain under the action of the applied shear stress (shear rate) can induce the formation of TEN. Two main steps can contribute to the occurrence of the shear thickening behaviour (Briscoe et al., 1999). The first step is the opening up of the coiled polymer chain. The second step is the formation of new associations and entanglements (i.e. transient networks). The first step is enhanced by the increase of the solvent viscosity and the increase in the relaxation time of the longest polymer molecules (i.e. the increase in molecular weight and concentration). The shear rate has to be of sufficient magnitude to force the formation of polymer entanglements as a result of hydrodynamically-driven collisions between the extended macromolecules.

For the semi-dilute CPAM in water solution, due to the positively-charged monomers in the chain and the absence of the screening electrolytes, the polymer chain is relatively extended with possible coils in between the charged monomers. Interchain entanglements are present in the polymer solution even in the quiescent state. These entanglements can be further enhanced with even low shear rates. This is the reason behind the increase in viscosity with time at relatively low shear rate (i.e. 50 s⁻¹). At the higher shear rate of 500 s⁻¹, the initial fast kinetics might be due to the sudden extension of the coiled parts of the polymer
chains. At even higher shear rates (i.e. ≥ 1000 s⁻¹), this was a cause of the initial overshoot due to such elastic effects. This type of behaviour has been obtained previously by Larson, 1992; Magda et al., 1993; Hu et al., 1995; and Migler et al., 1996. This initial overshoot was followed by a second overshoot in the cases of the shear rates 1000 and 1500 s⁻¹, which might be due to the consequent formation of the TEN structures. At the shear rates where the chains were being stretched (i.e. shear rates ≥ 500 s⁻¹), transient entanglement networks can be formed due to the hydrodynamic forces which can promote the inter-chain collisions. Hence, faster kinetics of the formation of the TEN can be observed at the higher shear rates, as long as the shear stress at such shear rates does not grow in magnitude, causing mechanical degradation of the individual chains and the destruction of any formed TEN. The growth of the TEN structures is accompanied by an increase in the shear stress. The increase of the shear stress with the increase of the TEN sizes is the cause of the subsequent decrease in the viscosity after reaching a maximum value (i.e. for the shear rates ≤ 1500 s⁻¹). The stress at the
maximum viscosity value could have been sufficient to induce mechanical degradation of the previously formed TEN structures. Above the shear rate of 1500 s\(^{-1}\), the shear stress might have been already sufficiently high to destroy the TEN as well as mechanically degrading the individual chains. This resulted in the monotonic decrease of the viscosity after the initial overshoot. The requirement of sufficient shear rate to promote the formation of the TEN is counteracted by the increase in the related shear stress. Hence, an optimum shear rate and/or time of shear are required for the formation of large TEN structures. Moreover, the increase in the concentration of the polymer solution increases the formation kinetics of the TEN as well as increasing their maximum sizes (i.e. maximum relative viscosity). This is shown in Figure (5.5) using four different concentrations of the CPAM in water at a constant shear rate of 1500 s\(^{-1}\). It can be observed that there is no indication of any major increase in viscosity with time in the case of the very dilute polymer solution (i.e. 100 ppm).

![Figure (5.6): The viscosity-time curves of the 1000 ppm CPAM in 0.34 M NaCl solution at three different shear rates using the cone-and-plate setup. The measurements were conducted at T=20 °C.](image)

The increase in the electrolyte content was investigated using the 1000 ppm CPAM in 0.34 M NaCl. The viscosity-time curves at three shear rates are shown in Figure (5.6). It can be observed that the viscosity behaviour of this polymer solution is completely different than that of the 1000 ppm CPAM in water. The relative viscosity (\(\eta_R\)) in the presence of
electrolyte increased slightly to about 1.1 at the shear rate of 500 s\(^{-1}\). On the other hand, it decreased to plateau values of 0.92 and 0.84 at the shear rates of 1000 s\(^{-1}\) and 1500 s\(^{-1}\), respectively. The salt decreases the repulsive forces between the charged monomer units in the chain, hence making the chain conform in a more coiled configuration. It has been found that the electrostatic interactions of this polymer (i.e. CPAM) are screened at fairly low salinity (Lauten and Nystrom, 2000). Hence, this coiled structure of the macromolecules has to be opened-up prior to the formation of the TEN. The stress required in the open-up stage of the chains in the 1000 ppm CPAM in 0.34 M NaCl could have been very high that the coiled chains could be damaged before opening-up. Consequently, a shear thinning behaviour was observed in the cases of the high shear rates (i.e. 1000 and 1500 s\(^{-1}\)). This thinning behaviour does not necessarily eliminate the possibility of the formation of TEN structures.

The difference between the viscosity behaviour of the CPAM in water and in the 0.34M NaCl could have been originated from the difference in the concentration of the two polymer solution in relation to the overlap concentration (\(c^*\)). To investigate this, the viscosity-time measurements were conducted for more concentrated solution of the CPAM in 0.34 M NaCl. Figure (5.7) shows the viscosity behaviour of the 5000 ppm CPAM in 0.34 M NaCl at three different shear rates. The relative viscosity (\(\eta_R\)) increased to a plateau value of 1.15 at the shear rate of 500 s\(^{-1}\). On the other hand, the relative viscosity (\(\eta_R\)) decreased to a plateau value of about 0.9 and 0.76 at the shear rates of 1000 and 1500 s\(^{-1}\), respectively. The viscosity at these shear rates (i.e. 1000 and 1500 s\(^{-1}\)) showed unstable, decreasing trend in the first 500 seconds of the measurements before decreasing sharply to a constant, stable value. The time required for such an event (i.e. the sharp decrease) was found to decrease with the increase in the shear rate. This result was reproducible but without a clear explanation. However, it has been found that some polymer solutions might undergo a pseudo-equilibrium state before decreasing suddenly to a constant viscosity (Le Meins and Tassin, 2001; Dupuis et al, 1994). This has been attributed to a shear-induced phase separation above a critical shear stress (shear rate). The pseudo-equilibrium stage might be the stage at which large aggregates are formed and destroyed until the critical time is reached (Dupuis et al, 1994). At the constant viscosity obtained after the critical time, only small aggregates persisted.

The viscosity-time curves of the 1000 ppm and 5000 ppm CPAM in 0.34M NaCl are another reason to possibly disregard the hydration of the aggregates which might have been present in the solution as a possible explanation for the shear thickening (anti-thixotropic) behaviour of some polymer solutions in the present study. This is because of the absence of
shear thickening behaviour with time even at the high shear rates using the 1000 ppm and 5000 ppm CPAM in 0.34 M NaCl. If hydration of aggregates was the cause of the shear thickening and the anti-thixotropic behaviour of the 1000 ppm CPAM in water solution from the viscosity-time curves in Figure (5.4), then it should have been expected in the cases of 1000 ppm and 5000 ppm CPAM in 0.34M NaCl, which is not the case as can be seen in Figure (5.6) and Figure (5.7), respectively.

Figure (5.7): The viscosity-time curves of the 5000 ppm CPAM in 0.34 M NaCl solution at three different shear rates using the cone-and-plate setup. The measurements were conducted at 20 °C.

The viscosity-time curves of the 1000 ppm PAM in water solution at different shear rates are shown in Figure (5.8). It can be observed that the same shear thickening behaviour that has been observed using the 1000 ppm CPAM in water solution can be observed for the 1000 ppm PAM polymer solution. It can also be observed that the increase in the viscosity with time is enhanced by the increase of the shear rate. In the same time frame of the applied shear rate (i.e. 10000 s), the maximum viscosity ($\eta_{MAX}$) obtained in the case of the 1000 ppm PAM in water solution did not show any decreasing trend, which has been observed in the case for the 1000 ppm CPAM in water solution. This can be an indication that the PAM has higher resistance to mechanical degradation compared to the CPAM. Also, it can be seen that at the shear rate of 5000 s$^{-1}$, the viscosity exhibited two stages of increase to a maximum
plateau region. This was reproducible but the justification for such behaviour is not obvious. It can be speculated that at such a high shear rate, the networks formed in solution interacted in a way to form larger networks as a result of physical bonds between the individual networks. This might have led to a significant increase in the relaxation time of such networks and hence more persistent structures. Hence, the second stage of increasing viscosity might be an indication of a stage of liquid-liquid phase separation. The increase in stress in such a situation may have led to a decreasing trend of viscosity with time after the second stage of increase to a maximum viscosity.

![Graph showing viscosity-time curves](image)

**Figure (5.8):** The viscosity-time curves of the 1000 ppm PAM in water solution at different shear rates using the cone-and-plate setup. The measurements were conducted at $T = 20^\circ C$.

The viscosity behaviour of the 500 ppm PAM in water solution at different shear rates is shown in Figure (5.9) in order to investigate the effect of decreasing the polymer concentration on the viscosity behaviour of the PAM in water solution. Even at this concentration, the shear thickening behaviour can be observed but to a lower degree than that of the 1000 ppm solution at a certain shear rate. Moreover, it can be observed that there is an obvious decreasing trend of the viscosity after reaching its maximum value at the shear rates
of 2500 and 5000 s\(^{-1}\). This was not as obvious in the case of the higher concentration (i.e. 1000 ppm). This might be due the fact that such a decrease in the case of the higher concentration was masked by the higher viscosity of the solution. Another reason might be that the degraded chains at the higher concentration might be still in the semi-dilute region and hence can entangle, forming new networks.

![Viscosity-time curves](image)

**Figure (5.9):** The viscosity-time curves of the 500 ppm PAM in water solution at different shear rates using the cone-and-plate setup. The measurements were conducted at \(T = 20^\circ C\).

The viscosity-time curves of the 10000 ppm PEO in water solution are shown in Figure (5.10) at three different shear rates. There was a slight increase of the viscosity in the case of the shear rates of 1500 and 2500 s\(^{-1}\). The relative viscosity (\(\eta_R\)) increased to 1.06 and 1.08 after 5000 s at the shear rates of 1500 and 2500 s\(^{-1}\), respectively. On the other hand, the PEO proved to be mechanically degradable as shown by the decrease in the viscosity with time at the shear rate of 5000 s\(^{-1}\) without showing any increasing trend. Hence, it can be concluded that such a polymer solution does not form significantly large TEN structures. This might be due to the relatively lower molecular weight of the polymer (compared to CPAM and PAM) and to the high degree of flexibility of the polymer as there are no side groups.
attached to the polymer. Both effects would be expected to give faster relaxation times, which is counter-productive of the TEN structures.

![Graph](image.png)

*Figure (5.10): The viscosity-time curves of the 10000 ppm PEO in water solution at different shear rates using the cone-and-plate setup. The measurements were conducted at 20 °C.*

### 5.3.3 Reversibility of the TEN Structures

The viscosity-time measurement at the shear rate of 2500 s\(^{-1}\) of the 1000 ppm PAM in water solution are used to study the reversibility of the TEN structures. There are two measurements shown in Figure (5.11): a continuous measurement and a measurement with rest intervals of 20 minutes using the same polymer sample (but different from the sample used in the continuous measurement). Comparing the measurements with the rest time in between with that of the continuous measurement, it can be observed that the viscosity behaviour is partly reversible before the viscosity reaches the plateau region. At the plateau region, the viscosity did not show any decrease after 20 minutes of rest.

The behaviour of the viscosity-time curve of the 1000 ppm PAM in water solution with the rest intervals can also be used as an argument against the hydration of polymer aggregates as a possible explanation of the shear thickening (anti-thixotropic) behaviour shown by the viscosity-time curves of some of the polymer solutions in this study at some shear rates (i.e. the 1000 ppm CPAM in water and the 1000 ppm PAM in water). This is because if the aggregates were hydrating and hence the viscosity of the polymer solution was
increasing with time, then this should have been *irreversible*. However, the viscosity-time measurements with 20 minutes rest times shown in Figure (5.11) are showing partly reversible behaviour before reaching the plateau region. This supports the formation of TEN structures as an explanation of such a shear thickening behaviour and in the author’s opinion excludes the hydration of aggregates as a possible mechanism. Hence, the anti-thixotropic behaviour shown in the flow and viscosity-time curves is attributed to the formation of shear-induced TEN structures, which are growing in size and/or number with time as well as becoming more persistent.

![Figure (5.11): The viscosity-time curves at the shear rate of 2500 s⁻¹ using the 1000 ppm PAM in water solution. The measurements were conducted at the temperature of 20 °C.](image)

Considering the measurements conducted with 20 minutes rest time, the viscosity decreased by about 20% the viscosity measured prior to the stoppage time for the first two rest intervals. This can indicate that at the same rest time of 20 minutes, the formed TEN structures underwent a relaxation process and hence disentanglements that may have resulted in TEN with smaller sizes. Once the shear was resumed, entanglements were reformed and hence the TEN structures were growing both in size and persistence. The run after the second stoppage interval was conducted during longer time to reach the plateau region. After the stoppage time of 20 minutes following this run, the viscosity starts at a value \( \eta_R = 2.13 \)
slightly higher than that reached in the previous run ($\eta_R = 2.07$) before decreasing with time of shear to the same value (i.e. the value obtained at the end of the previous run; $\eta_R = 2.07$). This might indicate that the TEN structures at the plateau region had been large enough to interact in a way to build some physical bonds during the quiescent stage. This indicates that the flow-induced liquid-liquid separation was possible with time of shear. However, it was found that very long stoppage times (60 hours) can be required to recover the initial state of a polystyrene solution (Magda et al., 1992).

![Figure (5.12): The viscosity-time curves at the shear rate of 2500 s$^{-1}$ using the 1000 ppm CPAM in water solution. The measurements were conducted at the temperature of 20°C.](image)

The behaviour of the viscosity during the period in which degradation of the polymer molecules and/or TEN structures is speculated, was found to be irreversible after 20 minutes of stoppage time. This is illustrated by a measurements conducted using the 1000 CPAM in water sheared at 2500 s$^{-1}$ as shown in Figure (5.12).

### 5.4 Summary and Conclusions

1. Rheological studies of the polymer solutions used in this study were conducted using a cone-and-plate setup. Flow and time curves were obtained to investigate the thixotropic (or anti-thixotropic) behaviour of these polymer solutions.
2. The 1000 ppm CPAM in water solution showed an obvious anti-thixotropic behaviour from both the flow and time curves. In the viscosity-time curves and at low shear rates, the viscosity of this solution increased to a maximum value before decreasing to a plateau value. This indicates that the 1000 ppm CPAM in water solution is mechanically degradable. At high enough shear rates above a critical value, the viscosity-time curves showed a consistent decrease in viscosity with time without showing any anti-thixotropic behaviour. This indicates that degradation occurs above a critical shear stress.

3. The flow curve of the 1000 ppm CPAM in 0.34 M NaCl has shown a slight shear thickening and anti-thixotropic behaviour above the shear rate of 1600 s^{-1}. However, the viscosity-time curves of this solution showed a shear thinning behaviour to plateau values at shear rates above the shear rate of 500 s^{-1}.

4. The flow curves of the 1000 ppm PAM in water solution has shown a slight shear thickening and anti-thixotropic behaviour above the shear rate of 1000 s^{-1}. However, the viscosity-time curves showed a strong anti-thixotropic behaviour at all shear rates up to 5000 s^{-1}. This polymer solution did not show any decreasing trend with time at all shear rates investigated except at 5000 s^{-1}.

5. The flow curves of the 10000 ppm PEO in water solution did not show any thixotropic or anti-thixotropic behaviour. However, the viscosity-time curves showed an increasing trend of viscosity with time but with very slow kinetics.

6. Two mechanisms for this anti-thixotropic behaviour have been presented: i) the formation of shear-induced transient entanglement networks; and ii) the shear-induced hydration/dissolution of polymer aggregates that might already have been present in solution. The experimental evidence supports the former hypothesis. The shear-induced hydration is effectively eliminated as the anti-thixotropic behaviour is (partly) reversible. It is hard to see why the polymer once dissolved, would re-associate once the shear is removed.

7. The formation of transient entanglement networks (TEN) depends on the polymer type, polymer charge (non-ionic such as PAM and PEO, cationic such as CPAM ), molecular weight, electrolyte concentration, polymer solution concentration, and the magnitude of the shear rate. These structures might grow in size and/or number leading to a possible liquid-liquid phase separation.

8. The formation of the TEN structures was found to be reversible in nature. The time required for the polymer solution to re-attain its initial state after being sheared at a
constant shear rate depends on the magnitude of the shear rate, and the period under which the polymer solution has been sheared. This relaxation time can range from few hours to few days.

9. The absence of any anti-thixotropic behaviour of a certain polymer solution does not necessarily exclude the formation of the TEN structures. However, these structures can be formed in sizes that are not significant enough to be manifested as a shear thickening behaviour in the flow curves and/or the viscosity-time curves. Also, high viscosity of polymer solutions can mask the shear thickening behaviour induced by any formed TEN structures.
6 INTERACTIONS BETWEEN GLASS SURFACES IN THE PRESENCE OF POLYMER SOLUTIONS DETERMINED USING MODIFIED ATOMIC FORCE MICROSCOPY

6.1 Introduction

The macroscopic behaviour of materials is determined by the forces between the microscopic constituents (Luckham, 2004). Hence, several techniques have been developed to measure these interaction forces such as mica surface forces apparatus and atomic force microscopy (AFM) (Israelachvili, 1991). Information and justifications drawn from these measurements can be crucial in understanding the microscopic world. A modified AFM apparatus was used in this study in order to measure the interaction forces in the presence of adsorbed polymer layers. The AFM measurements were conducted under static conditions in order to characterize the adsorption behaviour of the polymers used in this study from different solvents (0.01 M and 0.34 M NaCl for the CPAM and the PAM, and 0.01 M NaCl and 0.25 KNO₃ for the PEO) onto glass surfaces. Information such strength of adsorption energy (indicated by the time to obtain full-surface coverage) and the thickness of polymer monolayer adsorbed on glass surfaces can be obtained. This is crucial since adsorption of polymers occurs during the flow of polymer solutions through porous media (Sorbie, 1991). Also, the thickness of the polymer monolayer adsorbed in static conditions as measured from the AFM in this study is compared with the possible formation of polymer multilayers during the flow of polymer solutions through the single glass capillaries (Chapter 8, Section 8.3.1.3). The affinity of polymers to adsorb on glass indicated form the AFM measurements serves to possibly justify the formation of multilayers obtained in case of certain polymer solutions and the absence of such layers in the case of others using single glass capillaries, 2D and 3D models (Chapter 8). Before describing the experimental setup, different types of interaction forces will be summarized to help the reader through the discussion of the results.
6.2 Colloidal Forces

There are three main types of colloidal forces (Pashley and Karaman, 2004; Luckham, 2004; Israelachvili, 1991): Van der Waals interactions, electrical double-layer interactions, and steric interactions.

6.2.1 Van der Waals Forces

Van der Waals forces between the macroscopic surfaces are the same as those between atoms. In atoms, Van der Waals forces are attractive in nature and occur as dipole-dipole (Keesom interaction), dipole-induced-dipole (Debye interaction), and induced-dipole-induced-dipole (London or dispersion interaction) (Pashley and Karaman, 2004; Braithwaite, 1996; Israelachvili, 1991). Intuitively, for macroscopic surfaces, the Van der Waals interaction is the collective interaction between the atoms on the surfaces. The Van der Waals force of interaction \( F_{\text{VdW}} \) between a sphere of radius \( R \) and a flat surface at a distance \( X \) can be quantified using the following equation (Butt et al., 2005):

\[
F_{\text{VdW}} = \frac{A_H R}{6 X^2}
\]  

where \( A_H \) is the Hamaker constant, which is a material property.

6.2.2 Electrical Double-layer Interactions

If a charged interface exists in a polar solvent, then ions of opposite charge are attracted to the surface. The entropy prohibits the alignment of these ions on the surface and hence forming a crystal. Alternatively, ions will exist as a diffuse layer close to the charged interface. Double-layer interaction \( F_{\text{EDL}} \) can be expressed by the following relationship (Luckham, 2004):

\[
F_{\text{EDL}} = \alpha \psi^2 \exp(-\kappa X)
\]  

where \( \kappa \) is Debye-Huckel parameter.

The extent of the double-layer away from the solid-liquid interface (i.e. double-layer thickness) is determined by Debye length \( \kappa^{-1} \). The Debye length \( \kappa^{-1} \) is defined as the distance from the surface at which the surface potential \( \psi_0 \) has fallen to 1/e of its original value (Pashley and Karaman, 2004). It is known to decrease in the presence of electrolytes in the solvent above the surface, which can screen the charged interface. The following equation can be used to evaluate the Debye length \( \kappa^{-1} \) (Pashley and Karaman, 2004):

\[
\kappa^{-1} = \frac{1}{2} \left( \frac{D^2 \mu}{k_B T} \right)^{1/2}
\]
\[
\kappa^{-1} = \left\{ \frac{\varepsilon_0 \zeta kT}{q^2 \sum C_i(b) Z_i^2} \right\}^{1/2}
\] (6.3)

The Debye length of aqueous solutions at 25 °C can be stated by the following equation (Israelachvili, 1991):

\[
\kappa^{-1} = \begin{cases} 
0.304/\sqrt{[\text{NaCl}]} & \text{nm} \\
0.176/\sqrt{[\text{CaCl}_2]} & \text{nm} \\
0.152/\sqrt{[\text{MgSO}_4]} & \text{nm}
\end{cases}
\] (6.4)

where;

[NaCl]: the molar concentration of any 1:1 electrolyte (e.g. NaCl),
[CaCl_2]: the molar concentration of any 2:1 and 1:2 electrolytes (e.g. CaCl_2 and Na_2SO_4),
[MgSO_4]: the molar concentration of any 2:2 electrolytes (e.g. MgSO_4).

### 6.2.3 DLVO Theory

The combination of the Van der Waals and the double-layer interactions is known as the DLVO theory (after the originators Derjaguin, Landau, Verwey and Overbeek in the 1940’s) (Israelachvili, 1991). In the absence of polymer, the DLVO theory can be represented by a force-distance (F-X) curve as shown in Figure (6.1). This can be understood by the force felt by a microsphere as it is brought from infinity to the point of zero-separation (X_0). At long enough separation, the force exerted is zero. The repulsive interaction due to the double-layer interaction (F_{EDL}) will be felt first. Approaching the surface, the force (F) will increase monotonically until a point where the attractive Van der Waals force (F_{VdW}) will dominate and hence the total force (F) exerted will decrease sharply. At X_0 (i.e. hard contact) with the solid surface the force will increase suddenly to infinity. This collective interaction is true only if the repulsive, double-layer interaction is effective due to the presence of charged surfaces. In the absence of a double-layer (neutral surface or high electrolyte concentration), only the Van der Waals forces will be in effect. Once the particle is in a hard contact, it will stick to the surface in the minimum potential (see Figure (6.1)). A secondary minimum can exist at a certain salt concentration. The work required to separate (detach) the particle from the surface (at the primary minimum) is known as the work of adhesion (Israelachvili, 1991).
Figure (6.1): Schematic diagram showing the total interaction energy versus distance (X) of DLVO interaction; (a) no to very low salt concentrations, where the surfaces repel strongly starting at long distances, (b) with higher salt concentrations, where the interaction has a secondary minimum, increasing sharply due to the double-layer effect before decreasing again to the primary minimum, (c) pure attractive, Van der Waals interaction at very high salt concentration (or neutral surfaces).

6.2.4 Interactions in the Presence of Polymers

The presence of an adsorbing polymer in the system will induce new types of interactions, which can be superimposed upon the DLVO interaction. There are two opposite interactions in the presence of the adsorbed polymer: bridging-attraction and steric-repulsion (Braithwaite, 1996) as can be illustrated by Figure (6.2). Since the polymer adsorbed on a solid surface forms loops and tails extending away from the interface, the interaction on
approach will start due to the effect of these loops and tails (mostly tails). If one or both of the surfaces is *not* fully covered with the polymer (i.e. with vacant adsorption sites), the furthermost polymer segments from the other surface will adsorb on the available adsorption sites on the opposite surface hence grabbing it and pulling the surfaces together. This effect is called bridging-attraction. On the other hand, if both surfaces are fully covered, steric-repulsion will occur as the polymer layers between the two surfaces overlap inducing an increase in the osmotic pressure and a reduction in the polymer entropy.

![Bridging Attraction](image1.png) ![Steric Repulsion](image2.png)

*Figure (6.2): Particle interactions in the presence of adsorbing polymers.*

### 6.3 Experimental Section

#### 6.3.1 The Modified AFM

The force measurements in this study were conducted using an available modified AFM developed in the late 1990s (Luckham, 2004; Braithwaite, 1996). A sketch of the force-sensing apparatus with its main components is shown in Figure (6.3). The measurement of the colloidal interactions using AFM was first achieved by Butt (1991) and Ducker et al. (1991). A small, soft cantilever is used to sense the force at an interface. A microsphere (particle) of 2-30 µm in diameter is attached to the end of a cantilever. The interaction between the microsphere/particle and a flat surface is measured by monitoring the deflection of the cantilever in response to the interacting force. The deflection is determined using
optical beam deflection. A beam from a laser diode is focused onto the end of the cantilever and the position of the reflected beam is monitored by a position sensitive detector (PSD). The separation (X) between the particle and the sample surface is controlled by a piezo-electric ceramic of nanometer resolution. Both the piezo element and the PSD are fixed on an anti-vibration table since the measurements are very sensitive to any vibrations in the surrounding environment. The glass slide above the cantilever is used so that the surface of the solution is wetting the bottom surface of the slide. Consequently, the movement of the free surface, which might interfere with the output signal, is restricted. The amplified voltage driving the piezo element is generated by a function generator passing through a digital amplifier giving a working voltage range of ±150 V. The approach rate is controlled by the frequency \(f\) while the amount of compression and decompression is controlled by the magnitude of the amplified voltage.

---

**Figure (6.3): Schematic diagram of the modified AFM used to probe force interactions between surfaces (Braithwaite, 1996)**

The vertical and lateral signals from the PSD are amplified and captured along with the piezo-driving voltage using a commercial data acquisition card. In order to produce the final F-X profile, these data are analyzed using an Excel spreadsheet. The separation (X) is calculated by knowing the distance traveled by the surface for a given voltage to the piezo, which is obtained by calibration prior to the experiments. The force (F) can be calculated by
multiplying the cantilever spring constant \((k_s)\) and the distance \((X)\) traveled by the cantilever from its equilibrium position \(F = k_s \times X\). Detailed description of the calculations involved is available in the recent review of force measurements using AFM by Butt et al. (2005). In the presence of an adsorbed polymer layer, two assumptions are made first for AFM measurement analyses. First, the force at large separation \((X_a)\), where the cantilever is undeflected is assumed to be zero (i.e. cantilever at equilibrium position and \(F = 0\)); the second assumption is that the separation \((X)\) in the region at which the particle and the surface are moving together (constant compliance) is zero. Generally, the first assumption is valid. On the other hand, the second assumption is frequently incorrect (especially for polymeric systems) as a thin film of adsorbed material is squashed between the two surfaces even at full compression (Butt et al., 2005; Luckham, 2004).

**6.3.2 Procedure**

Glass particles of diameter around 25 \(\mu m\) (Jencons, UK) were carefully glued to the cantilevers. This process has been conducted through a microscope. The attached particle was visualized through the microscope to check that the glue was not covering the active glass surface of the tip. The particles were used as supplied without any further treatment. The interactions were measured between these particles on one side and a glass surface on the other. This flat surface was the bottom surface of a glass dish as shown in Figure (6.3). The dish was cleaned with RBS, an industrial surfactant, in an ultrasonic bath to remove any dirt/impurities that might interfere with the measurements and hence misleading the interpretations. First, the measurements were conducted in aqueous solvents (0.01 M NaCl, 0.34 M NaCl, and 0.25 M KNO₃) as a control and to establish the baseline for the next measurements in the polymer solution. This experiment also served to check whether the surfaces were clean. Since the double-layer repulsion can interfere with the interpretations regarding the adsorbed polymer layers, 0.01 M NaCl was the lowest salt concentration of the solvents used in the AFM experiments since it has been found to decrease the Debye length \((\kappa^{-1})\) substantially to less than 5 nm \((\kappa^{-1}=3\ \text{nm using Equation (6.4))}\) from the silica surfaces (Israelachvili, 1991). The measurements were started by placing the dish on the piezo and the cantilever (with the glass particle attached to it) was fixed to an arm lever, which extends horizontally above the dish as shown in Figure (6.3). The laser beam was then fixed on the upper surface of the end of the soft cantilever using a microscope. This laser beam should give a focused deflected beam, which is directed into the PSD as shown in Figure (6.3). Two
responses were acquired from the PSD, lateral and vertical which can be seen on the computer screen. The data points of these signals were retrieved every 1 ms so that any response can be closely monitored in a sweep of 10 s. Since the cantilever is not affected by any force while being far away from the surface (separation distance far longer than the distance covered by the continuously moving piezo), the vertical and lateral signals should be constant at zero (i.e. zero force of interaction). The vertical and the lateral signals were set to zero by moving the PSD vertically and horizontally until this was achieved and at that point the deflected laser signal was at the centre of the PSD. After ensuring sufficiently smooth signals from the vertical and lateral signals, the voltage to the piezo was switched on using a triangular signal from the signal generator, which was amplified by a factor of 30 using the amplifier. This makes the piezo moving up and down in a repetitive manner. The distance of this movement in each cycle was controlled by the driving voltage and the speed of movement (rate of approach and retraction) was controlled by the frequency. The glass dish was then filled with the required solvent. After that, the dish was lift up towards the particle attached to the cantilever in steps of nanometers until a point where an interaction was observed from the vertical signal of the PSD on the screen. It should be noted that the lateral signal should be constant at zero on interaction and this was used as a control as discussed below. The typical interaction curve between the glass particle and the glass surface in aqueous solvents is discussed in the next section (Section 6.3). The signals from this interaction were captured as raw voltage data, which were then analyzed using an excel spreadsheet in which calculations were performed to get the final force-distance (F-X) curves.

The force-distance curves obtained in solvent were used as baselines for the next measurements in the polymer solution. After the baseline has been established, the dish was lowered by a certain distance and the solvent was sucked out of the dish and the dish was refilled with dilute polymer solution. Dilute polymer solutions were used in the AFM measurements due to the measurements being affected by the hydrodynamic forces exerted on the soft cantilever by the viscous solutions (Butt et al., 2005). Both the surface and the particle on the cantilever were in contact with the polymer solution and hence adsorption of polymer should occur on both surfaces (the glass particle and the surface of the dish). The measurements were then conducted after different incubation times in polymer solutions using the same procedure described in solvents. These measurements were repeated at different sites on the surface of the dish at the same incubation time. Since the same particle on the cantilever was used, the behaviour of the approach and retraction force-distance curves
were generally not reproducible at the same incubation time because the adsorbed polymer layer on the particle could have been deformed on the first measurement as discussed below. As far as possible, it was ensured that the interaction conducted in the first measurement site at the given incubation time was obtained in the first compression-decompression cycle since it has been observed that the adsorbed polymer layers can be deformed on hard contact between the two surfaces (Braithwaite, 1996).

### 6.4 Results and Discussion

The raw data obtained during one cycle of the interaction (i.e. approach-retraction) between a glass particle and the glass surface in 0.01 M NaCl is shown in Figure (6.4). The F-X profile obtained from these data is shown in Figure (6.5). On approach, the force is zero until the point at about 38 nm separation at which the particle jumps-in to the approaching surface due to the spring elastic force being overcome by the attractive force between the particle and the surface. This attractive force is caused by the Van der Waals force (Butt, 1991). The force decreases to about -2 nN just before hitting the hard contact on approach ($X_{A0}$) and consequently increasing to infinity.

*Figure (6.4): An example of the raw data of one cycle (approach/retraction) obtained from the interaction between a glass particle and a glass surface in 0.01 M NaCl*
On retraction, adhesion between the particle and the surface causes the particle to stick with the moving surface until the bending of the cantilever induces a sufficient elastic force (-14.5 nN) to detach the particle away from the surface. The points shown below the point of -10 nN force in Figure (6.5) are not due to the force being in effect at separation more than zero. Instead, they are probably due to the twisting of the cantilever due to the high force of adhesion ($F_{ad}$) as has been observed in similar cases (Luckham, 2004). It can be observed that the curves on approach and retraction are wobbly when the surfaces are touching each other (i.e. hard contact at $X = 0$). This might be due to some minor, systematic vibrations from the surroundings, which could still have an effect on the measured signals. However, these wobbles do not cause any practical problem. For all the cases discussed below the base F-X profile of the baseline measurement is qualitatively similar to Figure (6.5).

![Figure (6.5): The force-distance (F-X) profile of the raw data shown in Figure (6.4)](image)

Before the discussion of the results in the presence of polymer solutions, several parameters should be defined:

$X_A$ : Distance on approach.

$X_{AR}$ : The distance at which steric-repulsion is observed on approach.

$X_{AJ-I}$ : Jump-in distance on approach.
$X_{A0}$ : The first point at zero-separation distance on approach ($F @ X_{A0} = F_{A0}$).

$X_R$ : Distance on retraction.

$X_{RJ-O}$ : Jump-out distance on retraction.

$F_{\text{ad}}$ : The adhesion force on retraction.

**Figure (6.6):** F-X plot of the approach and retraction obtained in 100 ppm CPAM in 0.01 M NaCl after 4 hours of adsorption. A semi-log plot is inserted to help in the determination of the starting point of the interaction as the scattered horizontal data points start to show an increasing trend towards higher force measurements.

### 6.4.1 CPAM Adsorption on Glass Surfaces

#### 6.4.1.1 CPAM in 0.01 M NaCl

The adsorption of CPAM dissolved into 0.01 M NaCl was monitored using the AFM measurements in 100 ppm solution. It was found that the adsorption of this low charged cationic polymer (10%) on the negatively charged glass surface was rapid and steric-repulsion was observed just after adding the polymer solution (usually in the measurements conducted after 1 hour of incubation). This has been expected since adsorption is driven by the strong electrostatic attraction between the positively-charged polymer molecules and the
negatively-charged glass surface. Figure (6.6) shows the F-X profile during both approach and retraction after 4 hours of incubation in the polymer solution. As can be seen, there is a slight hysteresis between the approach and the retraction curves. The steric-repulsion on approach and the absence of adhesion on retraction indicate full-surface coverage. On approach, the force departs from the zero value at a distance (X_{AR}) of 200 nm, increasing to 1.57 nN just before the hard contact (X_{A0}). On retraction, the force just before the hard contact is passed (F_{R0}) is 1.6 nN decreasing to zero at a distance of 141.2 nm. This hysteresis is probably caused by the layer being deformed (squashed) on compression (approach) and not decompressing fully on retraction (the retraction rate was 450 nm/s).

![Graph showing F-X profile](image)

**Figure (6.7):** F-X plot of the approach obtained in 100 ppm CPAM in 0.01 M NaCl after 4 and 30 hours of adsorption. A semi-log plot is inserted to help in the determination of the starting point of the interaction.

There has been no change in the F-X profile even after 30 hours of adsorption. The approach profile as shown in Figure (6.7) did not change significantly between the measurements conducted after 4 hours and 30 hours of adsorption. The X_{AR} is at 200 nm in the case of measurements after 4 hours. On the other hand, it is at 213 nm for the measurements conducted after 30 hours.
6.4.1.2 CPAM in 0.34 M NaCl

The interaction between a glass particle of diameter 25 µm and a flat glass surface was monitored in-situ of a 100 ppm CPAM in 0.34 M NaCl in order to investigate the effect of electrolyte on the adsorption of CPAM on glass. The AFM measurements showed very fast kinetics similar to those obtained in the case of adsorption from the CPAM in 0.01 M NaCl (i.e. full-surface coverage has been achieved in the measurement conducted after only 1 hour of incubation in the polymer solution). This indicates that the increase of sodium chloride concentration to 0.34 M in the solvent did not affect the electrostatically driven adsorption of this cationic polymer. The X_AR can be observed at 308 nm and the force increasing to a value of FA0 of 1.8 nN. Figure (6.8) shows the interaction after 1 hour of incubation in the polymer solution. The retraction curve shows a clear hysteresis from that of the approach. On retraction, the force drops to the value of zero at 27 nm separation. This might be due to the poor elasticity of the adsorbed polymer layer such that the decompression rate of the layer was less than the retraction rate (the retraction rate was 496 nm/s). The second and the third compression-decompression cycles, which are not presented here, showed almost the same
value of $X_{AR}$ (300 and 304 nm). Hence, it seems as if the layer was not affected by the multiple compressions. Moreover, this indicates that the approach-retraction hysteresis is due to the justification mentioned above (i.e. layer decompression rate being less than the retraction rate of the piezo). A number of AFM measurements were conducted in 2 days at different time intervals and showed almost no change from the curves shown in Figure (6.8). For example, Figure (6.9) shows a measurement conducted after 39 hours of adsorption.

![Figure (6.9): F-X plot of the approach and retraction obtained in 100 ppm CPAM in 0.34 M NaCl after 39 hours of adsorption. A semi-log plot is inserted to help in the determination of the starting point of the interaction on approach.](image)

**Figure (6.9):** F-X plot of the approach and retraction obtained in 100 ppm CPAM in 0.34 M NaCl after 39 hours of adsorption. A semi-log plot is inserted to help in the determination of the starting point of the interaction on approach.

### 6.4.1.3 Effect of Solvent Ionic Strength on the Adsorption of CPAM on Glass

In the case of the adsorption of a low-charged cationic polymer on a negatively charged surface, electrolytes can affect the polymer adsorption and the adsorbed layer thickness by two combined effects (Claesson et al., 2005; Shubin and Linse, 1995): at high electrolyte concentrations there will be (i) more coiled polyelectrolyte on the surface due to the screening of electrostatic interaction between the charged polymer segments and between the polymer and the surface, (ii) reduction in the number of bound fraction (i.e. trains' length), hence increasing the length of loops and tails. Both of these effects increase the adsorbed
layer thickness with the increase in the electrolyte concentration as illustrated in Figure (6.10). Indeed, this has been observed for the case of the CPAM adsorption on glass where the interpreted hydrodynamic layer thickness ($\delta_{\text{AFM}}$) increased from 106 nm in the case of 0.01M NaCl to 169 nm in the case of 0.34 M NaCl as discussed below (Section 6.4.4). However, this increase in thickness does not necessarily mean an increase in the adsorbed amount (Claesson et al., 2005; Shubin and Linse, 1995). This depends on the non-electrostatic polymer-surface affinity (Claesson et al., 2005) and the magnitude of the forces suggest that there may be less polymer adsorbed at high electrolyte concentrations in these experiments.

Figure (6.10): The effect of electrolyte on the conformation of a low-charged cationic polymer adsorbed on negatively charged surfaces (glass) under low (a) and high (b) electrolyte concentration.

6.4.2 PAM Adsorption on Glass Surfaces

6.4.2.1 PAM in 0.01 M NaCl

The adsorption of non-ionic, very high molecular weight (18 million Da.), polyacrylamide (PAM) on glass was monitored using the AFM in 50 ppm PAM in 0.01 M NaCl. The F-X
approach profiles of the measurements conducted at different times of adsorption are shown in Figure (6.11). Table (6.1) lists the values of $X_{AR}$ and $F_{A0}$ at different times of adsorption. The approach shows repulsion starting at about 160 and 185 nm for the measurements conducted after 18 and 26 hours, respectively. On the other hand, $X_{AR}$ is at about 150 and 100 nm for the measurements conducted after 46 and 69 hours, respectively. Moreover, the layer in the measurements conducted after 18 and 26 hours of adsorption seems to be denser than that formed after 46 and 69 hours of adsorption. This is reflected in the decrease of $F_{A0}$ from 2.6 nN in the first 26 hours to 1.2 nN after 46 hours of adsorption. These data are not what one would expect, but are repeatable and suggest that there is some rearrangement of the adsorbed polymer with time (and perhaps with the number of compressions the polymer layer has experienced).

Figure (6.11): A semi-log plot of $F$-$X$ profiles of the approach measurements conducted at different times of PAM adsorption on glass from the 50 ppm PAM in 0.01 M NaCl solution.
Table (6.1): Distance ($X_{AR}$) at which steric-repulsion was observed and force just before zero-separation ($F_{A0}$) at different times of PAM adsorption on glass from 0.01 M NaCl.

<table>
<thead>
<tr>
<th>Incubation time in solution (h)</th>
<th>$X_{AR}$ (nm)</th>
<th>$F_{A0}$ (nN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>160</td>
<td>2.6</td>
</tr>
<tr>
<td>26</td>
<td>184</td>
<td>2.6</td>
</tr>
<tr>
<td>46</td>
<td>150</td>
<td>1.2</td>
</tr>
<tr>
<td>69</td>
<td>100</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Figure (6.12): The F-X profiles on the retraction at different times of the PAM adsorption on glass from the 50 ppm PAM in 0.01 M NaCl.

Adhesion on retraction has been observed for all the measurements conducted in three days of adsorption as shown in Figure (6.12). The magnitude of the force of adhesion ($F_{ad}$) decreases consistently with time as shown in Figure (6.13). The change of the medium from 0.01 M NaCl to the polymer solution caused a sharp decrease in the $F_{ad}$ followed by slower decrease for the time after the addition of the polymer. This adhesion is an indication of the surface being not fully covered with the adsorbed polymer (Kappl and Butt, 2002; Braithwaite et al., 1997). Hence, bridging-attraction is anticipated on approach but this is not the case as discussed above where steric-repulsion has been observed on approach for all the
measurements. The repulsion (instead of bridging-attraction) on approach might be due to the slow rearrangement rate of the adsorbed chains which might be slower than the approach rate (the approach rate was 455 nm/s).

The above observations suggest that the adsorption of this very high molecular weight, polydisperse polyacrylamide on glass from the 0.01 M NaCl is weak and is accompanied by slow relaxation of the adsorbed macromolecules in the adsorbed polymer layer. The denser layer on the first 26 hours is probably due to the presence of low molecular weight molecules adsorbing along with the higher molecular weight molecules. As time passes, the low molecular weight macromolecules were displaced by the spreading action of the higher molecular weight macromolecules, which is suggested by the studies of many investigators on the adsorption kinetics (Mubarekyan and Santore, 2001a; Cohen-Stuart, 1998; Cohen-Stuart and Fleer, 1996). Moreover, the spreading of the high molecular weight macromolecules results in a better surface coverage and lower layer thickness. This is manifested in the delay of the start of interaction on approach after 48 hours accompanied by the decrease in the adhesion force ($F_{ad}$) with adsorption time as shown in Figure (6.13). The adhesion force is expected to disappear after a certain time as can be interpreted from Figure (6.13) but it is outside the scope of this study to wait for such an event.

![Figure (6.13): The force of adhesion ($F_{ad}$) obtained at different times during PAM adsorption on glass from the 50 ppm PAM in 0.01 M NaCl (the point at time=0 is the baseline case)](image-url)
6.4.2.2 PAM in 0.34 M NaCl

The effect of increasing the salt concentration on the adsorption of the PAM on glass was investigated using 0.34 M NaCl solvent. The F-X profiles of the approach at different times of incubation in a 50 ppm solution are shown in Figure (6.14). In solvent, the jump-in distance on approach ($X_{AJ-I}$) is 120 nm, which resulted in a force ($F_{A0}$) of -6 nN at the hard contact. After 1 hour of incubation in the solution, steric-repulsion on approach occurred at a separation of 25 nm, which resulted in a force of 0.1 nN at the hard contact. Almost identical approach profiles were obtained after 22 and 48 hours of adsorption. The values of $X_{AR}$ and $F_{A0}$ for these two profiles are 133 nm and 5 nN, respectively. The $X_{AR}$ and $F_{A0}$ increased significantly after 68 hours of adsorption to 150 nm and 14 nN, respectively. Generally, the values of the thickness of the adsorbed polymer layer obtained using the 0.34 M NaCl are less than those obtained using the 0.01 M NaCl (except after 68 hours of adsorption), which can be due to the screening effect of the PAM (with a finite degree of hydrolysis as stated in Chapter 5) and the negatively charged glass. This is the same reason for the significant increase in the density of the adsorbed polymer layer with the increase in the salt concentration. This is reflected in the increase of the $F_{A0}$ from 1.2 nN after 69 hours of adsorption in the 0.01 M NaCl solution to 14 nN after 68 hours of adsorption in the 0.34 M NaCl solution. Also, it is anticipated that the increase in the salt concentration has resulted in different adsorption kinetics. While the adsorbed polymer layer in the case of the PAM in 0.01 M NaCl experienced a spreading process, the increase of both $X_{AR}$ and $F_{A0}$ in the case of the PAM in 0.34 M NaCl indicates that the adsorbed polymer underwent a relaxation process, which allowed more polymer molecules from the solution to be adsorbed. The adsorption kinetics might have been relatively fast from the 0.34 M NaCl solution, which might have resulted in the trapping of the early adsorbing molecules.

The F-X profiles on retraction shown in Figure (6.15) at different incubation times in solution further supports that the adsorption of the PAM from the 0.34 M NaCl has faster kinetics (compared to the adsorption from the 0.01 M NaCl). The adhesion force on retraction disappeared after 48 hours of incubation time in solution. This is lower than the time required for the adhesion force to disappear in the case of the PAM in 0.01 M NaCl (more than 69 hours). The layer formed after 68 hours of incubation time in the PAM in 0.34 M NaCl seems to be elastic as can be observed from almost identical approach-retraction curves (without any adhesion on retraction) shown in Figure (6.16).
Figure (6.14): F-X plot of the approach profiles obtained in 50 ppm PAM in 0.34 M NaCl after different times of adsorption. A semi-log plot is inserted to help in the determination of the starting point of the interaction.

Figure (6.15): The F-X profiles on retraction at different times of the PAM adsorption on glass from the 50 ppm PAM in 0.34 M NaCl
Figure (6.16): F-X plot of the approach and retraction obtained in 50 ppm PAM in 0.34 M NaCl after 68 hours of adsorption.

Figure (6.17): The F-X profile of the approach of measurements conducted at different times of adsorption of PEO on glass from 500 ppm PEO in 0.01 M NaCl. A semi-log plot is inserted for the cases where steric-repulsion occurs to help in the determination of the starting point of the interaction.
6.4.3 PEO Adsorption on Glass Surfaces

6.4.3.1 PEO in 0.01 M NaCl

The adsorption of the PEO on glass from 0.01 M NaCl was monitored for 3 days. Some of the approach curves shown in Figure (6.17) as well as the retraction curves in Figure (6.18) show an interesting behaviour of the adsorption of the PEO on glass from the good solvent (0.01 M NaCl). The adsorption behaviour of the PEO on glass can be divided into three main stages with different force interactions during approach:

![Graph showing F-X profiles for PEO adsorption](image)

*Figure (6.18): The F-X profiles of the retraction measurements of the approach curves shown in Figure (6.17)*

1. **Purely attractive**: The attraction here might be due to the bridging-attraction on approach. This stage extended for about 24 hours of adsorption. The approach curves in this stage showed a “jump in” point at a certain distance ($X_{AJ-1}$) on approach. Generally, the jump-in distance ($X_{AJ-1}$) increased with the time of adsorption. Also, it was observed that the $X_{AJ-1}$ increased with the number of cycle of a measurement conducted in the same spot as shown in Figure (6.19) for the measurement conducted after 20 minutes of adsorption. The increase in the $X_{AJ-1}$ in the second cycle was accompanied by an increase in the magnitude of the attraction force on approach. On the other hand, there has been no
difference on retraction between the two cycles and show the same amount of adhesion. This can be explained by the “pull out” effect of the adsorbed macromolecules, which are bridging the two surfaces. Longer previously stretched chains would be met earlier in the subsequent cycle as has been demonstrated in the force interaction studies in the case of low surface coverage (Bremmell and Scales, 2004; Pederson and Bergstrom, 1999). This case is illustrated by Figure (6.20).

Figure (6.19): F-X profiles of the approach and retraction of two consecutive cycles obtained for 500 ppm PEO in 0.01 M NaCl after 20 minutes of adsorption

2. “Transition” stage: This stage can be included in the first stage, but due to its importance, it is discussed separately. The approach curve in this stage showed mixed responses from measurement to measurement and from cycle to cycle in the same measurement. Such mixed responses have been noticed between 24 and 47 hours after adsorption. Also, in some cases the increase in the jump-in distance ($X_{AI}$) was accompanied by an increase in adhesion to the point that no detachment on retraction was detected. Figure (6.21) presents some raw data of one of these cases. The adhesion force ($F_{ad}$) might have increased to the point forcing the particle to stick to the surface and hence moving together without detachment on retraction. The F-X curve of such a raw measurement is shown in Figure (6.22). The approach on the first
cycle shows a slight bridging-attraction at 100 nm. The force decreases to -1 nN at 64 nm from which repulsion is observed and the force starts to increase until the point of $X_{A0}$. The retraction curve of the first cycle shows very strong adhesion to a distance of 178 nm at which the particle driven by the cantilever might have snapped away from the surface. The approach curve on the second cycle shows strong bridging-attraction starting at a distance of 215 nm jumping-in in two stages which are characterized by two distinctive sets of points. The first set extends from 142 nm to 110 nm at an average attraction force of -7.5 nN. The second set of points extends from a distance of 50 nm to the zero-separation at an average force of -15 nN, which is twice the force at the first set. After this strong attraction on approach in the second cycle, the detachment between the particle and the surface was not possible as mentioned above. Moreover, there were measurements in this stage, where initial steric-repulsion was followed by bridging-attraction on the same approach as shown in Figure (6.23).

Figure (6.20): Schematic representation of bridging-attraction in two consecutive cycles. The first cycle starts at (a) with zero-force interaction. At point (b) the first bridging-attraction occurs leading to the constant compliance on compression at (c). Point (d) shows that the chains, which are bridging between the two surfaces are stretched on retraction. The second cycle of compression begins at point (e), bridging occur at point (f) earlier than in point (b) due to the previously stretched chains in point (d). Point (g) is the constant compliance region on the second cycle compression.
Figure (6.21): The raw data obtained of a measurement after 29 hours of PEO adsorption from the 500 ppm PEO in 0.01 M NaCl

Figure (6.22): F-X plot of the approach and retraction of two consecutive cycles of the raw measurement in Figure (6.21)
3. **Purely repulsive:** In this stage only steric-repulsion was observed on approach but still with adhesion on retraction. Pure steric-repulsion behaviour started after 47 hours of adsorption. The measurements showed repulsive interaction on approach and decreasing adhesion on retraction with time as shown in Figure (6.17) and Figure (6.18). After 52 hours of adsorption, the approach curve shows a repulsive response starting at a distance 67 nm increasing to 6.4 nN at $X_{A0}$. On retraction, two stages of adhesion can be seen in Figure (6.18). The first stage is from zero-separation to about 50 nm from the surface. The second stage shows a further decrease in the force (i.e. increase in adhesion) starting from 50 nm from the surface to 100 nm distance at which the particle snaps out of the surface. This suggests the existence of two adsorbed polymer layers of the same thickness (a monolayer on both surfaces). These layers act at different times during retraction. On the other hand, after 74 hours, the approach curve shows repulsion starting at 130 nm increasing to 2.4 nN at $X_{A0}$. On retraction, the curve shows a one stage adhesion. This adhesion force is almost the same as that measured at 52 hours and decreases gradually to zero at 90 nm from the surface. After 74 hours of adsorption, the experiment was stopped.

![Figure (6.23): F-X profile of the approach of measurements conducted after 24 hours of adsorption from the 500 ppm PEO in 0.01 M NaCl](image-url)
The above trend of the AFM measurements using the PEO in 0.01 M NaCl was reproducible. However, from the above description of the results, a number of observations and interpretations can be stated regarding the adsorption of PEO on glass from 0.01 M NaCl. Despite the high affinity of PEO to silica (Fleer et al., 1993), PEO adsorption on glass from the good solvent (0.01 M NaCl) shows low coverage denoted by the presence of a bridging-attraction on approach in the first 47 hours of adsorption as well as adhesion on retraction for the cases when steric-repulsion occurs on approach after 47 hours. Strictly speaking, the bridging-attraction on approach indicates the high affinity of PEO towards the silica surfaces mentioned above. The presence of the three stages in our measurements agrees with the theoretical predictions on the effect of polydispersity on polymer adsorption (Fleer et al., 1993). This polydispersity induces non-equilibrium stages during which exchange between the chains in solution and those adsorbed on the surface occurs (Mubarekyan and Santore, 2001a). The three stages listed above according to the AFM measurements are in qualitative agreement on the effect polydispersity on inducing these exchange kinetics (Fleer et al., 1993). Once the polymer solution comes into contact with the surface, the low molecular weight chains will preferentially adsorb on the surface due to their high diffusion. This can explain the bridging-attraction observed on approach during the first and second stages. This is probably due to the high affinity of the polymer towards the surface coupled with shorter rearrangement (relaxation) time. The mixed responses obtained in the second stage might be due to the presence of low and high molecular weight chains. It can occur that the measurement is conducted on an area where the chains have relaxation time enough to show repulsion and attraction during the same approach measurement as shown in Figure (6.23). Higher molecular weight in the third stage has a relaxation time longer than the approach rate hence only repulsion will be obvious. Relaxation of such high molecular weight polymer will make the adsorbed polymer chains forming longer loops and tails in expense of the segments in the bound fraction (i.e. trains). Moreover, such relaxation and spreading can form inter-chain entanglements in the adsorbed polymer layer (Mubarekyan and Santore, 2001a) hence increasing the surface coverage with time as indicated by the decrease in the force of adhesion ($F_{ad}$). Such surface kinetics have been observed to take up to 1 week in order to give a steady-state value of hydrodynamic layer thickness during the adsorption of narrowly distributed PEO in Millipore filters from a good solvent (Kawaguchi et al., 1984). The complexity of the high polydispersity, high molecular weight polymer in our measurements can make this time even longer.
6.4.3.2 PEO in 0.25 M KNO\textsubscript{3}

In order to investigate the effect of solvent on the adsorption of PEO on glass, 0.25 M KNO\textsubscript{3} solvent has been used. This solvent was used by Braithwaite et al. (1997); who investigated the adsorption of lower molecular weight PEO with a narrow polydispersity on glass using AFM. Figure (6.24) shows the approach curves obtained at 3 different times of adsorption in 500 ppm polymer solution. None of the approach curves showed any attraction except in some cycles following the first compression on the same measurement spot. Also, there has been gradual increase in the jump-in distance ($X_{AI}$) as well as an increase in the $F_{A0}$ with the increase in the adsorption time. On the other hand, slight adhesion on retraction occurred for the first 24 hours of adsorption as shown in Figure (6.25). After 24 hours of adsorption, no adhesion was detected and the hysteresis between the approach and retraction curves decreased with the time of adsorption. Hence, this can indicate a fully covered surface after 24 hours of adsorption which agrees with the study of Braithwaite et al. (1997). The hysteresis between the approach and retraction curves for the measurements conducted after 24 hours showed a decreasing trend until no hysteresis can be observed for the measurements conducted after 104 hours of adsorption as shown in Figure (6.26).

![Figure (6.24): The F-X profiles of the approach of measurements conducted at different times of PEO adsorption on glass from 500 ppm PEO solution in 0.25 M KNO\textsubscript{3}. A semi-log plot is inserted for the cases where steric-repulsion.](image-url)
Figure (6.25): The F-X profile of the retraction curves of the approach measurements shown in Figure (6.24)

Figure (6.26): The F-X profile of the approach and retraction of a measurement conducted after 104 hours of PEO adsorption on glass from 500 ppm PEO solution in 0.25 M KNO₃
A clear difference in the adsorption of PEO on glass from the 0.01 M NaCl and that from the 0.25 KNO₃ can be observed from the above measurements. Full surface coverage has been achieved after one day of adsorption using the 0.25 KNO₃, whereas full surface coverage has not been achieved even after about 4.5 days (104 hours) in the 0.01 M NaCl. Since both of these solvents are good solvents for PEO (Klein and Luckham, 1986; Fleer et al., 1993), this difference in the adsorption characteristics on glass cannot be attributed to the difference in the quality of the solvent. It has been indicated from experimental studies that shorter hydrodynamic layer thickness (EHT) of the adsorbed PEO on Millipore filters was obtained using good solvents (Kawaguchi et al., 1984) compared to the EHT using poor solvents (Kawaguchi et al., 1988). This has been explained in the work of Kawaguchi et al. (1988) according to the theoretical work of Cohen-Stuart et al. (1984) who attributed this solvent dependence to the tail sizes becoming shorter with increasing the solvent power. In the present study, the difference between the adsorption of the PEO from the 0.01 M NaCl and the 0.25 KNO₃ might be due to the difference in the adsorption of the different ions on the glass surface hence inducing different adsorption characteristics. Also, different salts can affect the interaction between the polymer chains in solution and hence their adsorption behaviour.

6.4.4 Hydrodynamic Layer Thickness

The force interaction using AFM in the presence of an adsorbed polymer layer can be used to measure the hydrodynamic layer thickness ($\delta_{\text{AFM}}$). Since the steric-repulsion on approach is due to the adsorbed polymer layer on the interacting surfaces, the start of such an interaction is mainly due to the tails, which are the furthermost segment protruding away from the surfaces. Hence, the hydrodynamic layer thickness ($\delta_{\text{AFM}}$) of the adsorbed polymer layer can be calculated as half this distance (i.e. $\delta_{\text{AFM}} = X_{\text{AR}}/2$) (Braithwaite and Luckham, 1997). The approach-retraction cycle of the AFM measurement, which can be used for such quantification of the adsorbed layer thickness should be the first cycle of the measurement on a new spot on the surface. It was found that the thickness of the adsorbed polymer layer using PEO ($M_W$ between 17 kDa to 668 kDa) on polystyrene lattices of diameters between 50 and 1000 nm, increased with the increase of the particle size (Baker et al., 1989). This curvature dependence of the EHT of the adsorbed polymer layer is outside the scope of this study and hence, identical EHT on the two surfaces was assumed in the calculation of the $\delta_{\text{AFM}}$. Table
(6.2) lists the hydrodynamic layer thickness ($\delta_{\text{AFM}}$) of the adsorbed polymer layers on glass of the polymer systems discussed above. These values were obtained from the last measurement (i.e. longest incubation time) in each case. Equilibrium was hard to establish for the PAM and PEO polymers due to the high polydispersity combined with high molecular weight. Equilibrium was obtained in the cases of CPAM adsorption on glass due to the high electrostatically-driven adsorption. Consequently, quantitative comparison with previous studies will not be attempted.

From the values of the $\delta_{\text{AFM}}$ of the adsorbed polymer layers listed in Table (6.2), several observations can be noticed. The increase in the NaCl concentration increases the $\delta_{\text{AFM}}$ of the adsorbed CPAM layer on glass. This has been observed previously and can be explained by the electrolyte affecting the interaction between the charged monomers in each polymer molecule as well as between the molecules (Claesson et al., 2005; Shubin and Linse, 1995). Also, electrolyte alters the degree of polymer-surface interaction. In the case of the CPAM adsorption on glass, the collective effect of increasing NaCl concentration is the increase in the hydrodynamic layer thickness ($\delta_{\text{AFM}}$).

Table (6.2): Hydrodynamic layer thickness ($\delta_{\text{AFM}}$) of the adsorbed polymer layers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>$c$ (ppm)</th>
<th>$\delta_{\text{AFM}}$ (nm ± 5 nm)</th>
<th>Incubation time (hs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPAM</td>
<td>0.01 M NaCl</td>
<td>100</td>
<td>106</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>0.34 M NaCl</td>
<td>100</td>
<td>169</td>
<td>39</td>
</tr>
<tr>
<td>PAM</td>
<td>0.01 M NaCl</td>
<td>50</td>
<td>48</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>0.34 M NaCl</td>
<td>50</td>
<td>75</td>
<td>68</td>
</tr>
<tr>
<td>PEO</td>
<td>0.01 M NaCl</td>
<td>500</td>
<td>65</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>0.25 KNO$_3$</td>
<td>500</td>
<td>171</td>
<td>104</td>
</tr>
</tbody>
</table>

The low adsorbed layer thickness ($\delta_{\text{AFM}}$) in the case of PAM on glass from 0.01 M NaCl suggests that this very high molecular weight polymer adsorbs on glass in a fairly flat conformation. This has not been expected due to the presence of a finite but small degree of hydrolysis of the amide group into acrylic acid (i.e. very weak negative charges) even for this non-ionic PAM (Denys, 2003). On the other hand, a similar flat conformation of PAM has been concluded from the force interaction study using AFM of very high molecular weight.
anionic PAM solutions adsorbing on silica conducted by Bremmell and Scales (2004). Moreover, a flat conformation of PAA adsorbed on a negatively charged Si₃N₄ surface was found by Laarz et al. (2001). The increase in the NaCl concentration from 0.01 to 0.34 M resulted in an increase in the adsorbed layer thickness from 47.5 nm to 70 nm. This might have been due to the increase in the adsorbed amount with the increase in the salt concentration.

The adsorbed layer thickness ($\delta_{\text{AFM}}$) of PEO on glass from the 0.01 M NaCl was lower than that from the 0.25 M KNO₃ in the time frame. This might be due to the difference in the adsorption of the different ions on glass, which might have induced different adsorption behaviour of the PEO molecules on the glass surfaces.

6.5 Summary and Conclusions

1. The effect of polymer adsorption on the force interactions between a glass microsphere/particle and a glass flat surface has been investigated using a modified atomic force microscopy (AFM). Three different ionic and non-ionic, linear, high molecular weight homopolymers have been used with different solvents. This was conducted to investigate the adsorption characteristics of these polymers from their respective solvents on glass. Information regarding the adsorption energy (indicated by the time at which full-surface coverage was observed) and the effective hydrodynamic thickness of adsorbed polymer monolayer can be obtained. This information is important in the study of the retention of polymer solutions in porous media since adsorption is one of the polymer retention mechanisms.

2. The adsorption of the cationic polyacrylamide (CPAM) on glass was found to be rapid due to electrostatic attraction between the positively charged polymer molecules and the negatively charged glass surface. Full surface coverage occurred after 1 hour of incubation time in the solution.

3. The adsorption of the CPAM from the 0.34 M NaCl was found to be rapid and full-surface coverage was achieved after 1 hour of adsorption. The increase in electrolyte concentration (NaCl) from 0.01 M to 0.34 M increased the hydrodynamic layer thickness ($\delta_{\text{AFM}}$) of the adsorbed CPAM layer from 106 to 169 nm.

4. The adsorbed molecules of the very high molecular weight non-ionic polyacrylamide (PAM) in 0.01 M NaCl adopted a flat conformation on the glass surfaces. Adsorption was slow and full surface coverage could not be achieved after almost 3 days of adsorption.
There was a decreasing trend in the adhesion forces measured with time suggesting an increase of surface coverage due to the spreading of the adsorbed macromolecules.

5. The adsorption of the PAM from 0.34 M NaCl on glass was found to be faster than adsorption from the 0.01 M NaCl. The adsorbed layer from the 0.34 M NaCl was found also to be denser than the layer formed from the 0.01 M NaCl. Moreover, the thickness of the polymer layer after about 68 hours of adsorption from the 0.34 M NaCl was higher than that from the 0.01 M NaCl. These differences in the adsorption characteristics as the result of the increase in the salt content are the result of the screening of the negatively charged glass surface.

6. The adsorption of the polyethylene oxide (PEO) on glass from the 0.01 M NaCl resulted in three-stage behaviour. The existence of these stages has been justified by the PEO being of a wide distribution. Full-surface coverage was obtained after 48 hours of adsorption.

7. The adsorption of the PEO on glass from the 0.25 M KNO₃ resulted in faster adsorption kinetics and a full surface coverage was obtained after 24 hours of adsorption. After that, exchange kinetics and relaxation of the adsorbed macromolecules increased the thickness of the adsorbed layer with time.

8. The difference between the adsorption characteristics of the PEO from the 0.01 M NaCl and the 0.25 M KNO₃ might have been due to the difference in the adsorption of the ions from the two solvents.
7 INVESTIGATING THE EFFECT OF FLOW RATE ON POLYMER ADSORPTION USING QUARTZ CRYSTAL MICROBALANCE WITH DISSIPATION MONITORING (QCM-D)

7.1 Introduction

In the previous chapter, AFM measurements have been presented of the adsorption of the high molecular weight polymers on glass surfaces from some solvents in the static conditions. This has been conducted to study the adsorption characteristics of these polymers on glass. However, the main objective of the present study has been to investigate the effect of the flow of the polymer solution on the adsorbed polymer layers and whether this would result in polymer adsorbed multilayers as has been indicated by several studies through capillaries (Grattoni et al., 2004; Kozicki et al., 1993; Hikmet et al., 1985; Cohen and Metzner, 1982; Kozicki et al., 1970) and porous media (Ogunberu and Asghari, 2006; Asghari, 2004; Chauveteau et al., 2002; Al-Sharji et al., 2001; Zitha et al., 1998; Kozicki et al., 1988). In the next chapter (Chapter 8), results from the flow of high molecular weight polymer solutions through single glass capillaries, 2D and 3D models are presented to investigate such multilayer formation. In this chapter, QCM-D technology is used to investigate whether the flow of the polymer solutions would induce any detectable effect on adsorption. Before the discussion of the QCM-D results, the measurement technique is briefly described followed by the description of the measurement procedure.

7.2 QCM-D Technology

Quartz crystal microbalance with dissipation monitoring (QCM-D) can be used to monitor the adsorption of polymer from solutions. In this technology, AT-cut quartz crystals are sandwiched between a pair of gold electrodes and excited to produce a shear mode oscillation (www.q-sense.com). The resonant frequencies of the crystals (fundamental and up to five harmonics) are recorded in real time. Once excited, the free mechanical oscillation can be monitored by measuring the decaying electric field. From the decay curve, the resonance frequency ($f$) and the dissipation ($D$) are extracted. If a layer is deposited on the surface of the
crystal, changes in the frequency \((\Delta f)\) and the dissipation \((\Delta D)\) allow one to characterize the adsorption processes and structural features of the adsorbed layer, in real time.

If the film is thin and rigid, the decrease in the frequency is proportional to the mass of the film. The mass added to the surface of the crystal (including the solvent incorporated into the layer) can be calculated using the Sauerbrey relation (www.q-sense.com):

\[
\Delta m = -\frac{v_q \rho_q \Delta f}{2f_0^2} \frac{n}{n} = -\frac{C \Delta f}{n} \tag{7.1}
\]

where,

- \(v_q\) : the speed of sound in the quartz crystal \((v_q = 3340 \text{ ms}^{-1})\)
- \(\rho_q\) : the density of the quartz \((\rho_q = 2.65 \text{ g cm}^{-3})\)
- \(f_0\) : the fundamental frequency \((f_0 = \frac{v_q}{2t_q})\) where \(t_q\) is the thickness of the quartz plate.
- \(C = 17.7 \text{ ng Hz}^{-1} \text{ cm}^{-2}\) for a 5 MHz quartz crystal.

\(n = 1, 3, 5, 7, 9, 13\) is the overtone number.

The thickness of the adhered layer \((\delta)\) can be obtained by dividing the mass by the density of the layer \((\rho_\ell)\). However, the Sauerbrey equation is strictly valid for adsorbed masses that are: (i) small, (ii) homogeneous, (iii) rigid, and (iv) couples with no slip. Hence, it is usually not valid for adsorbed polymer layers, which are viscoelastic in nature (i.e. not rigid). The viscoelasticity of the film will dampen the crystal oscillation due to the energy dissipated \((E_{\text{lost}})\) by the film. Hence, the dissipation \((D)\) is a measure of the viscoelasticity of the film and is defined as (www.q-sense.com):

\[
D = \frac{E_{\text{lost}}}{2\pi E_{\text{stored}}} \tag{7.2}
\]

where, \(E_{\text{stored}}\) is the energy stored in the oscillator.

The dissipation of the crystal can be measured by recording the response of a freely oscillating crystal that has been vibrated at its resonance frequency. Consequently, it is anticipated that thick, loosely bound layers dissipate energy more than thin, rigid ones. By measuring at multiple frequencies and using a viscoelastic model such as Voigt model, the adsorbed polymer layer can be fully characterized (www.q-sense.com). Information such as layer viscosity \((\eta)\) and thickness \((\delta)\) can be calculated after certain assumptions are made.
7.3 Information about Viscoelastic Adsorbed Layers

It has been stated above that the Sauerbrey relation cannot be used for viscoelastic layers such as adsorbed polymer layers in a liquid environment. Thus, for a purely viscous (Newtonian) bulk fluid, the relationship between the response and the fluid properties can be approximated by two simple equations:

\[
\Delta f = \frac{1}{\sqrt{\pi} v_s \rho_s} \sqrt{n f_0^3 \eta_b \rho_b} = 0.64 \times 10^{-7} \frac{m^2 s}{kg} \sqrt{n f_0^3 \eta_b \rho_b} \quad (7.3)
\]

\[
\Delta D = \frac{2}{\sqrt{\pi} v_s \rho_s} \sqrt{\frac{f_0}{n} \eta_b \rho_b} = 1.27 \times 10^{-7} \frac{m^2 s}{kg} \sqrt{\frac{f_0}{n} \eta_b \rho_b} \quad (7.4)
\]

where, \(\eta_b\) and \(\rho_b\) are the bulk liquid’s viscosity and density, respectively.

More complex models have been presented by Domack et al. (1997) and Voinova et al. (1999). These models establish a relationship between the properties of an adsorbed layer (thickness, \(\delta\); density, \(\rho\); shear viscosity, \(\eta\); and elastic shear modulus, \(\mu\)) immersed in bulk liquid on the one hand and the shifts in frequency and dissipation on the other hand as sketched in Figure (7.1). As a result of their work, Domack et al. (1997) have concluded that the acoustic thickness which can be obtained from QCM is similar (although somewhat lower) to the hydrodynamic thickness since it is most affected by the dilute outer tail of the segment density distribution of the adsorbed polymer layer. Moreover, the trapped film (even in the tails’ region or in between weakly adsorbing chains) is reflected in the acoustic thickness and hence appears as part of the film (Plunkett et al., 2003). Since the interest here is to investigate the effect of polymer solution flow rate on the hydrodynamic thickness of the residual polymer layer, the QCM-D seemed to be a valuable tool for such an investigation.

Based on these models, the changes in the frequency (\(\Delta f_n\)) and the dissipation (\(\Delta D_n\)) for the multiple overtones (n= 1, 3, 5, 7, 9, 11, 13) can be modelled using the software Q-Tools (Q-Sense, Sweden). Hence, the properties of the adsorbed layer can be deduced from such a model assuming parameters such as the bulk liquid viscosity (\(\eta_b\)) and density (\(\rho_b\)), and the adsorbed layer density (\(\rho\)).

For adsorbed polymer layers, the Voigt model may be used to fit the changes in the frequency and dissipation. A Voigt element is defined as a spring and dashpot in parallel under no slip conditions (Voinova et al., 1999). The adsorbed film is represented by a frequency-dependent complex shear modulus, \(G^*\) (Voinova et al., 1999):
Several assumptions are made to use the Voigt model to interpret $\Delta f$ and $\Delta D$ data. It is assumed that the polymer is covering the sensor’s entire active area, the adsorbed layer is homogeneous, and has a uniform thickness ($\delta_l$) and density ($\rho_l$). Also, it is assumed that the medium in which the sensor is resonating is a bulk Newtonian liquid. While the first assumption can be valid under the equilibrium conditions, the second assumption is contradicting the density profile of the adsorbed homopolymer on a solid surface. The density of the polymer segments is decaying with the normal distance from the surface (Fleer et al., 1993).

\[ G^* = G' + iG'' = \mu_l + i2\pi f \eta_l \]  

(7.5)

Figure (7.1): Diagram of the adsorbed polymer layer modelled by the Voigt viscoelastic model. The quartz crystal is covered by a thin film that can be described by $\rho_b$, $\mu_b$, $\eta_b$, and $\delta_l$ under no slip conditions. The film is covered by a bulk Newtonian liquid with $\rho_b$, and $\eta_b$ (Reproduced from Irwin et al., 2005).
7.4 Experimental Section

7.4.1 QCM-D E4

A QCM-D E4 (Q-Sense) was used to investigate the effect of flow rate of the polymer solution on the adsorbed amount ($\Gamma$) and the thickness ($\delta$) of the adsorbed polymer layer. QCM-D E4 consists mainly of a 4-sensor chamber as shown in Figure (7.2). The chamber is temperature controlled and the samples can be introduced using a peristaltic pump. The crystals can be placed and secured easily in the flow modules.

![Components of the QCM-D E4](www.q-sense.com)

Figure (7.2): Components of the QCM-D E4 (Picture from www.q-sense.com)

In the current experiments, all measurements were conducted at 20 ± 0.05 °C. Since QCM-D is a very sensitive device, one has to make sure that the crystals are cleaned properly. It has been found that there is a lack of reproducibility associated with the QCM-D (Munro and Frank, 2004). They have observed a variation of up to 10% for the $\Delta f$ and the $\Delta D$ measurements from run to run. Hence, care has to be taken in the preparation and the cleaning of the crystals as well as the flow cells prior to each experiment. This is more warranted in the case of polymer solutions since polymer solutions can adsorb irreversibly on the crystals’ surfaces. Crystals with gold (Au) and silica (SiO$_2$) surfaces were first cleaned in the following way:

1. The crystals were immersed in very dilute solution of sulfuric acid (H$_2$SO$_4$) and were placed in an ultrasonic bath for 30 minutes.
2. The crystals were then placed in deionized (DI) water in the ultrasonic bath. This was repeated three times with fresh DI water in each time.
3. The crystals were then washed with ethanol.
4. The crystals were finally placed under an ultraviolet (UV) source in an Ozone environment for about 10-15 minutes, to eliminate any retained polymer on the surfaces of the crystals.

### 7.4.2 Procedure

The flow measurements were planned so that the effect of the polymer solution flow rate on the adsorbed amount ($\Gamma$) and thickness ($\delta_{\text{QCM}}$) of the residual adsorbed polymer layer on the crystals could be determined. Due to the lack of reproducibility reported above, two flow rates of the polymer solutions were conducted in the same run, washing the solutions in between and at the end of the run.

The clean crystals were put and secured in the flow modules. The modules were then placed in the chamber. The chamber was covered and the flow of solvent at $Q_{w1} = 3\ \text{cm}^3/\text{h}$ was initiated. The baseline was then established by determining the fundamental frequencies ($f_0$) and dissipations ($D_0$). The measurements of the $\Delta f$ and the $\Delta D$ of the different overtones ($n = 1, 3, 5, 7, 9, 11, 13$) were then taken during the flow of the solvent. A time period was allowed so that temperature ($T$), the $f_0$, and the $D_0$ reach constant values. This was found to take different periods ranging from 30 to 60 minutes. The fundamental values of the frequency ($f_0$) and the dissipation ($D_0$) were then reset. The measurements of the $\Delta f$ and the $\Delta D$ during the solvent flow ($Q_w$) should give stable values at zero. This was tested for at least 10 minutes before the injection of the polymer solutions into the flow modules. After that, the polymer solutions were introduced to the respective modules at a flow rate ($Q_{p1}$) of $3\ \text{cm}^3/\text{h}$ for at least 1 hour. This period proved to be sufficient to reach steady state values of the $\Delta f$ and the $\Delta D$ during the polymer solution flow. The polymer was then washed with the solvent at a flow rate ($Q_{w2}$) of $3\ \text{cm}^3/\text{h}$ for about 40 minutes. This period of injection was chosen since about 30 pore volumes ($\text{PV} = 0.08\ \text{cm}^3$) of solvent were injected through the modules. After that, the polymer solutions were re-injected at a higher flow rate ($Q_{p2}$) of $15\ \text{cm}^3/\text{h}$ ($Q_{p2} = 3\ Q_{p1}$) for about 1 hour. Finally, the polymer solutions were washed with the solvent at $Q_{w3} = 3\ \text{cm}^3/\text{h}$ for 40 minutes.
7.5 Results and Discussion

7.5.1 Demonstration of the Procedure

The polymer/surface systems used in the QCM-D measurements are listed in Table (7.1). These polymer solutions were chosen to conduct the QCM-D measurements since they exhibit different thixotropic behaviour (the PEO solution does not exhibit any thixotropic behaviour while the CPAM solutions exhibit a strong anti-thixotropic behaviour) as well as different adsorption characteristics (e.g. weak and slow adsorption of the PEO on glass vs. strong and rapid adsorption of the CPAM on glass) as has been discussed in Chapter 5 and Chapter 6, respectively. It was anticipated that these differences between the two types of polymer would be manifested by different trends in the QCM-D measurements. Before going through the results and their discussion, an illustration of the procedure described above will the presented using the measured normalized frequency ($f_3/3$) and dissipation ($D_3$) measurements in the 3rd overtone for the PEO adsorption on gold (Au) from 5000 ppm solution in water as shown in Figure (7.3) along with a description of the different stages of the experiment.

Table (7.1): The polymer/surface systems used in the QCM-D measurements.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_W$ ($10^6$ Da)</th>
<th>Solvent</th>
<th>$c$ (ppm)</th>
<th>Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>4</td>
<td>H$_2$O</td>
<td>5000</td>
<td>Au</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>CPAM</td>
<td>6</td>
<td>H$_2$O</td>
<td>1000</td>
<td>Au</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SiO$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>SiO$_2$</td>
</tr>
</tbody>
</table>

The values of the $\Delta f_3/3$ and the $\Delta D_3$ were initially stable at zero during the initial stage, during which the solvent flow rate was 3 cm$^3$/h using a clean crystal (Region 1). After the introduction of the polymer solution at a flow rate of 3 cm$^3$/h (Region 2), the frequency ($\Delta f_3/3$) decreased showing an overshoot before decreasing again to a constant value of -5.06 Hz. This overshoot has been found elsewhere during the injection of polymer solutions through the QCM cells and has been attributed to the difference in viscosity between the displacing and the displaced liquids (Munro and Frank, 2004). On the other hand, the
dissipation ($\Delta D_3$) value increased to a constant value of about $8.76 \times 10^{-6}$. Washing the polymer solution with the solvent at a flow rate of 3 cm$^3$/h (Region 3) caused a slight increase in the frequency ($\Delta f_3/3$) to a value of -5.5 Hz whereas the dissipation ($\Delta D_3$) decreased to $4.16 \times 10^{-6}$ after washing with 30 pore volumes (PV) of the solvent. The slight increase in the $\Delta f_3/3$ (from -5.06 to -5.5 Hz) can be explained in terms of the viscoelastic nature of the polymer solution during its flow on the crystal. On the other hand, the decrease in the dissipation ($\Delta D_3$) (from $8.76 \times 10^{-6}$ to $4.16 \times 10^{-6}$) cannot be explained by the polymer being desorbed during the solvent flow since the $\Delta f_3/3$ did not show a significant decrease. Intuitively, this can be justified by the fact that the energy dissipated ($E_{\text{lost}}$) from the crystal increases with the increase in the viscosity of the bulk liquid. This has also been concluded by the QCM-D study of Munro and Frank (2004). The re-injection of the polymer solution at a flow rate of 15 cm$^3$/h (Region 4) caused a slight decrease in the $\Delta f_3/3$ to -5.3 Hz and an increase of the ($\Delta D_3$) to $9.22 \times 10^{-6}$. Finally, the steady state values of the $\Delta f_3/3$ and the $\Delta D_3$ after the second period of washing (Region 5) were -5.46 Hz and $4.45 \times 10^{-6}$, respectively.

![Figure (7.3): Normalized frequency ($\Delta f/n$) and dissipation ($\Delta D$) measurements of the 3rd overtone of the PEO/Au system showing the procedure conducted: (1) $Q_{w1} = 3$ cm$^3$/h, (2) $Q_{p1} = 3$ cm$^3$/h, (3) $Q_{w2} = 3$ cm$^3$/h, (4) $Q_{p2} = 15$ cm$^3$/h, (5) $Q_{w3} = 3$ cm$^3$/h.](image-url)
7.5.2 The Sauerbrey Relation

The Sauerbrey relation and the Voigt model have been used to calculate the adsorbed amount \((\Gamma)\) and thickness \((\delta_{QCM})\) of the residual polymer layer after the polymer solution wash out. Analysis of the \(\Delta f\) and the \(\Delta D\) measurements while polymer solution flow through the module is avoided here, primarily because it does not serve our objective as well as being a very complex task. This complexity is due to the viscoelasticity of the polymer solutions and the interference of this with the \(\Delta f\) and \(\Delta D\) measurements during polymer solution flow (Munro and Frank, 2004). Hence, no comparison will be attempted between the different responses during the polymer solution flow and that during the solvent flow.

As discussed previously, the Sauerbrey relation is valid for thin, rigid films where the \(\Delta f\) values of the different overtones are similar when normalized (i.e. \(\Delta f/n\)). This was the case in the measurements conducted using the PEO and CPAM solutions, which resulted in the normalized the \(\Delta f\) for the different overtones being within 5 Hz for the case of the 1000 ppm CPAM on SiO\(_2\) shown in Figure (7.4). Hence, the Sauerbrey relation can still be applied (Irwin et al., 2005), and will be attempted for all the measurements conducted in this study.

![Graph](image)

*Figure (7.4): Normalized frequency \((\Delta f/n)\) and dissipation \((\Delta D)\) measurements of \(n = 3, 5,\) and 7 of 1000 ppm CPAM/SiO\(_2\) showing the different stages of the run as in Figure (7.3)*
Table (7.2) summarizes the values of the adsorbed amount ($\Gamma_{\text{QCM-S}}$) obtained and calculated using the Sauerbrey relation for the polymer/surface systems listed in the Table (7.1). The $\Delta f/n$ and the $\Delta D$ values used for this purpose (i.e. in the Sauerbrey relation; Equation 7.1) were the values of the third overtone after the injection of 30 pore volumes (PV) of solvent. The third overtone can give a better indication of the adsorbed amount ($\Gamma_{\text{QCM}}$) and thickness ($\delta_{\text{QCM}}$) since it is giving information at a greater depth away from the surface (www.q-sense.com). It can be seen from Table (7.2) that $\Delta f/3$ and hence $\Gamma_{\text{QCM-S}}$ shows mixed trends regarding the effect of the polymer solution flow rate. On the other hand, $\Delta D_3$ shows a consistent increase with flow rate by different percentages in all cases investigated. The increase in the $\Delta D$ is mostly associated with an increase in layer thickness (not necessarily $\Gamma$) hence dissipating more energy.

Table (7.2): Normalized 3rd overtone frequency ($\Delta f/3$) and dissipation ($\Delta D_3$) change after the injection of 30 PVs of solvent at 3 cm$^3$/h. These values are listed for different polymer/surface systems and after flow of polymer solution at 3 and 15 cm$^3$/h. Values of the adsorbed amount ($\Gamma_{\text{QCM-S}}$) are calculated using the Sauerbrey relation.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta f/3$ (Hz)</th>
<th>$\Delta D_3$ ($\times 10^6$)</th>
<th>$\Gamma_{\text{QCM-S}}$ ($\pm 0.03$ mg/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 cm$^3$/h</td>
<td>15 cm$^3$/h</td>
<td>3 cm$^3$/h</td>
</tr>
<tr>
<td>5000 ppm PEO/Au</td>
<td>-5.5</td>
<td>-5.46</td>
<td>4.16</td>
</tr>
<tr>
<td>5000 ppm PEO/SiO$_2$</td>
<td>-6.10</td>
<td>-7.43</td>
<td>4.10</td>
</tr>
<tr>
<td>1000 ppm CPAM/Au</td>
<td>-1.31</td>
<td>-1.35</td>
<td>5.26</td>
</tr>
<tr>
<td>1000 ppm CPAM/SiO$_2$</td>
<td>-3.27</td>
<td>-3.37</td>
<td>2.82</td>
</tr>
<tr>
<td>100 ppm CPAM/SiO$_2$</td>
<td>-4.9</td>
<td>-3.86</td>
<td>2.35</td>
</tr>
</tbody>
</table>
Figure (7.5): Adsorbed layer thickness ($\delta_{\text{QCM-S}}$) calculated using the Sauerbrey relation and assuming a layer density ($\rho$) of 1000 kg/m$^3$ after washing with 30 PVs of solvent at 3 cm$^3$/h. The thicknesses shown are calculated based on the 3rd overtone after injection of the polymer solution at 3 and 15 cm$^3$/h.

The adsorbed amount ($\Gamma_{\text{QCM-S}}$) has not shown a substantial change on increasing the polymer flow rate for the case of PEO/Au and CPAM/Au systems. It should be noted that the error of the Q-sense E4 in the measurement of $\Gamma_{\text{QCM-S}}$ is around 1-3 ng/cm$^2$ (0.01-0.03 mg/m$^2$) (www.q-sense.com), the $\Gamma_{\text{QCM-S}}$ increased by around 22% in the case of the PEO/SiO$_2$ system. On the other hand, it decreased by almost the same percentage (21%) in the case of the dilute solution of the CPAM (100 ppm) on a SiO$_2$ surface. It is interesting to note that the adsorbed amount calculated here for the PEO/SiO$_2$ system is in the range obtained by Dijt et al. (1990) for the same system, although they used reflectometry.
Figure (7.6): Adsorbed layer thickness ($\delta_{QCM-V}$) obtained using the Voigt model and assuming a layer density ($\rho_l$) of 1000 kg/m$^3$ during the injection of solvent at 3 cm$^3$/h after injection of the polymer solution at 3 and 15 cm$^3$/h for the 5000 ppm PEO/SiO$_2$.

The hydrodynamic layer thickness ($\delta_{QCM-S}$) can be calculated by assuming a homogeneous layer of density $\rho_l$=1000 kg/m$^3$ (i.e. the density of the deionized water). Figure (7.5) shows the $\delta_{QCM-S}$ values obtained for the different systems with an error of 0.03 nm (error in $\Gamma$ = 0.03 mg/m$^2$). It can be observed that the $\delta_{QCM-S}$ values obtained using the Sauerbrey relation, are unrealistically small. This might be due to the rigidity of the adsorbed polymer layer inherently assumed in this relation, hence neglecting the parts of the adsorbed layer which are not coupled with the oscillating crystals (mainly the tails) and the water entrapped.

### 7.5.3 The Voigt Model

It is known that the Sauerbrey relation can fail to apply for adsorbed polymer layers due to the basic assumptions upon which this relation has been derived (www.q-sense.com). Q-Sense E4 is supplied with a Voigt model program, which can be used to obtain some information of the adsorbed polymer layers such as layer thickness ($\delta_{QCM-V}$), viscosity ($\eta_l$),
and stress. In the following results obtained using the Voigt model in this study using Q-Tools, the following assumptions have been made:

*Properties of the bulk liquid (DI water):*

\[ \eta_b = 0.001 \text{ Pa.s} \]

\[ \rho_b = 1000 \text{ kg/m}^3 \]

*Table (7.3): Adsorbed layer thickness ($\delta_{\text{QCM-V}}$) and adsorbed amount ($\Gamma_{\text{QCM-V}}$) as obtained using the Voigt model*

<table>
<thead>
<tr>
<th>System</th>
<th>$\delta_{\text{QCM-V}}$ ($\pm 0.03 \text{ nm}$)</th>
<th>% increase</th>
<th>$\Gamma_{\text{QCM-V}}$ ($\pm 0.03 \text{ mg/m}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 cm$^3$/h</td>
<td>15 cm$^3$/h</td>
<td>3 cm$^3$/h</td>
</tr>
<tr>
<td>5000 ppm PEO/Au</td>
<td>5.40</td>
<td>5.64</td>
<td>4.4</td>
</tr>
<tr>
<td>5000 ppm PEO/SiO$_2$</td>
<td>5.45</td>
<td>6.47</td>
<td>18.7</td>
</tr>
<tr>
<td>1000 ppm CPAM/Au</td>
<td>24.74</td>
<td>26.28</td>
<td>6.2</td>
</tr>
<tr>
<td>1000 ppm CPAM/SiO$_2$</td>
<td>3.66</td>
<td>4.00</td>
<td>9.3</td>
</tr>
<tr>
<td>100 ppm CPAM/SiO$_2$</td>
<td>3.84</td>
<td>4.16</td>
<td>8.3</td>
</tr>
</tbody>
</table>

In the absence of information regarding the density of the adsorbed polymer layers ($\rho_l$), the thickness calculations were overestimated by assuming that the layer density ($\rho_l$) is the same as the water density (i.e., 1000 kg/m$^3$). This can be safely made since the adsorbed polymer layers consist mainly of solvent in between the porous structure of the adsorbed polymer layer. Since the main objective of this QCM-D study was to investigate the effect of the polymer solution flow rate on the adsorbed amount and thickness of the adsorbed polymer layer, rigorous analysis was not needed. Figure (7.6) shows the behaviour of the adsorbed layer thickness ($\delta_{\text{QCM-V}}$) of the PEO on SiO$_2$ surface as calculated using the Voigt model during the two polymer wash-out stages (i.e., after polymer solution flow rates at 3 and 15 cm$^3$/h). The initial layer thickness of around 8 nm shown in the Figure (7.6) was due to the viscosity and density of the bulk liquid being affected by the displaced polymer. The layer thicknesses ($\delta_{\text{QCM-V}}$) after washing with 30 PVs of solvent after the flow of polymer at 3 and 15 cm$^3$/h are 5.45 and 6.47 nm, respectively. This increase of the layer thickness ($\delta_{\text{QCM-V}}$) is due to the increase of polymer solution flow rate by 5 folds. Such a trend was observed for the other polymer/surface systems studied as listed in Table (7.3). The values in the table are
the values obtained after the injection of 30 PVs of solvent. The Table (7.3) shows the consistent direct relationship between the polymer solution flow rate and the adsorbed layer thickness \( \delta_{QCM-V} \) (and consequently the adsorbed amount, \( \Gamma_{QCM-V} \)). Hence, it can be concluded that increasing the flow rate of polymer solution is associated with an increase in the adsorbed layer thickness as well as the adsorbed amount. The very high values of the adsorbed amount listed in the Table (7.3) reflects that the QCM-D measurements sense the total amount of the trapped film as has been indicated by Plunkett et al. (2003).

Making a comparison between the values of the adsorbed layer thickness obtained using the Sauerbrey relation \( \delta_{QCM-S} \) with those obtained using the Voigt model \( \delta_{QCM-V} \), one can lean to support the latter values since they can represent the actual situation. This is due to the Voigt model taking into account the viscoelasticity of the adsorbed polymer layer. Also, the values obtained using the Sauerbrey relation are very small and do not seem realistic if the high electrostatic attraction energy deriving the adsorption of the CPAM on the SiO\(_2\) as was demonstrated by the AFM measurements in Chapter 6 for instance, coupled with the high molecular weight of the polymer, were taken into account. Also, the values of the adsorbed layer thickness obtained using AFM \( \delta_{AFM} \) are far higher than those obtained using QCM-D from the Voigt model \( \delta_{QCM-V} \). The hydrodynamic layer thickness of this system was found to be 106 ± 5 nm using the AFM measurements, while it does not exceed 4.2 nm using the QCM-D. This can be attributed to the difference in the measurement techniques as well as the errors involved in assumptions made in the Voigt model. While AFM measurements are force measurements, the QCM-D measurements are measurements of the polymer mass. The thickness obtained from the AFM has been \textit{direct} from the force-distance curves, while the thickness obtained from the QCM-D measurements are based on using the Voigt model with assumptions. Also, the thickness obtained from the QCM-D measurements might indicate primarily the thickness of the loops while the tails might not been coupled in the measurements and hence not accounted for in the \( \delta_{QCM-V} \). On the other hand, the adsorbed layer thickness obtained from the AFM measurements is indicating the extent of the tails (i.e. the hydrodynamic layer thickness). Moreover, the effect of the flow of the polymer solutions even at the lower flow rate (i.e. 3 cm\(^3\)/h) in the QCM-D measurements can induce the adsorption of the elongated polymer molecules in a flat conformation (McGlinn et al., 1988).

Adsorption-entanglement has been proposed since 1973 by Hand and Williams and has been investigated by Hikmet et al. (1985) and can justify the increase in the adsorbed polymer layer thickness with the increase in the polymer solution flow rate in the case of
concentrated solutions ($c > c^*$). Also, this can be concluded from the QCM-D work of Munro and Frank (2004), who found that the adsorbed layer thickness ($\delta_{\text{QCM}}$) reached a plateau value with respect to concentration in the case of the low molecular weight polyacrylamide ($10^4$ Da.) injected at the same flow rate using the QCM-D measurements on a gold surface. On the other hand, they found that the $\delta_{\text{QCM}}$ increased linearly and sharply with concentration using the high molecular weight polyacrylamide ($10^6$ Da.). In the present study, the adsorption of the CPAM from both dilute and semi-dilute solutions in water was found to result in almost the same layer thickness on SiO$_2$ surfaces at the same solution flow rate using the Voigt model to obtain the layer thickness from the QCM-D measurements. Consequently, multilayer formation as a result of adsorption-entanglement can be excluded using the CPAM in water solutions in the present study.

**7.6 Summary and Conclusions**

1. QCM-D was used to investigate the effect of polymer solution flow rate on the adsorbed amount ($\Gamma_{\text{QCM}}$) and thickness ($\delta_{\text{QCM}}$) of the residual polymer layer.

2. Increasing the flow rate of the polymer solution by 5 fold caused mixed trends of the $\Delta f$ measurements of the polymer/surface systems investigated whereas $\Delta D$ increased with the flow rate for all the systems.

3. In this study, the Sauerbrey and the Voigt models were used to estimate the layer thickness of the adsorbed polymer layers from the QCM-D measurements. The Sauerbrey relation failed since the calculated thickness values of the adsorbed polymer layers unrealistically low. This is because of the rigidity assumption upon which the use of this relation has been based. Hence, the Voigt model which is used to model the QCM-D measurements of viscoelastic systems such as polymer solutions resulted in somehow trustworthy thickness values.

4. Using the adsorbed layer thicknesses from the Voigt model, all polymer/surface systems showed that increasing the flow rate of the polymer solutions caused an increase in the adsorbed layer thickness ($\delta_{\text{QCM-V}}$) and consequently the adsorbed amount ($\Gamma_{\text{QCM-V}}$). However, the values obtained were low and do not give any indication of multilayer formation as a result of polymer solutions’ flow through the QCM-D cells.
5. It is believed that the QCM-D is actually measuring the thickness of the loops of the adsorbed polymer rather the thickness of the tails, which is measured by hydrodynamic (flow through capillaries) techniques. Also, the QCM-D measures directly the adsorbed amount and not the thickness of the layer. The use of the Voigt model to calculate the thickness of the adsorbed polymer layers from these measurements can give results based on certain assumptions which may not be valid.
8 FLOW OF POLYMER SOLUTIONS THROUGH MODELS OF POROUS MEDIA

8.1 Introduction

The study of flow of fluids through porous rocks is very complex. Usually, interpretations are drawn from the measurement of the pressure during flow through the rock cores at a constant flow rate, or visa versa. Many factors can affect the flow such as grain and pore sizes, degree of heterogeneity, presence of clay particles, and surface chemistry. Hence, the flow of already complex (non-Newtonian) systems such as polymer solutions through rocks is a very challenging matter. Polymer solution properties such as the polymer type (anionic, non-ionic, or cationic), molecular weight, chain flexibility, solvent type and quality (good, poor), and concentration can affect the flow of such solutions through rocks. Hence, conclusions from a study of the flow of polymer solutions through rocks cannot be generalized since they are valid only for the specific polymer/rock system investigated. Consequently in this work, simple models of porous media were used to study the flow of polymer solutions as this some control of the pore size and the pore surface chemistry can be achieved. Moreover, these models can allow flow visualization. These models range in complexity from the very simple (e.g. single capillaries) to more complex (e.g. bead packs) as has been described in Chapter 2. In this study, the models used in the flow experiments were single glass capillaries of rectangular cross-sectional area (1D model), a 2D model comprised of an etched glass plate and a flat plate sintered onto it, and a glass bead pack (3D model).

In this chapter, the results from the flow experiments of different polymer solutions through the 1D, 2D, and 3D models will be presented and discussed in the context of mobility reduction ($R_m$) during polymer solution flow, and permeability reduction ($R_k$) after polymer solution flow. The mobility reduction is a result of the rheology polymer solutions during the flow through porous media, while the permeability reduction is due to the irreversible retention of the polymer in the porous media after flow. Polymer adsorption and mechanical entrapment as irreversible retention mechanisms have been discussed in Chapter 2 (Section 2.5). In the case of the capillary flow experiments, parameters such as apparent viscosity ($\eta_a$) of the polymer solutions and the effective hydrodynamic thickness (EHT) of the residual adsorbed polymer layers will be quantified. Flow visualization was not attempted mainly
because of the difficulty involved in distinguishing between the polymer and the solvent. The results from the rheological study, and the AFM measurements of the polymer systems used in these flow experiments, as has been presented in chapters 5 and 6, respectively, along with the results obtained from these models have been used to draw some conclusions regarding the mechanisms of polymer retention in porous media.

8.2 Experimental Section

8.2.1 Polymer Solutions

Capillary flow experiments were conducted using four different polymer solutions, which are listed in Table (8.1). The procedure followed in the preparation of these solutions has been described in detail in Chapter 5. In brief, the solutions were filtered through a series of Millipore filters of 8 \( \mu \)m and 3 \( \mu \)m at a flow rate of 6 cm\(^3\)/min. The polymer solutions were not filtered through the 1.2 \( \mu \)m filters as has been suggested by Chauveteau and Kohler (1980) because of the possible polymer degradation of these very high molecular weight polymers under divergent flow. After the filtration was complete, the solutions were allowed to stand for another day in order to erase any memory effects of the filtration before conducting any flow experiments. It should be noted here that the deionized (DI) water used to prepare the solvents for the capillary flow measurements as well as the 2D and 3D experiments was degassed by heating to a temperature of 60-70 °C and subsequently putting it in an ultrasonic bath. This is important since the formation of micron-size air bubbles can be a problem.

Table (8.1): The polymer solutions used in the capillary flow experiments.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( M_w ) (×10(^6) Da)</th>
<th>Solvent</th>
<th>c (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPAM</td>
<td>6</td>
<td>water</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.34 M NaCl</td>
<td>1000</td>
</tr>
<tr>
<td>PAM</td>
<td>18</td>
<td>water</td>
<td>1000</td>
</tr>
<tr>
<td>PEO</td>
<td>4</td>
<td>water</td>
<td>5000</td>
</tr>
</tbody>
</table>
The polymer solutions listed in Table (8.1) have shown different adsorption characteristics on glass as has been discussed in Chapter 6 (i.e. electrostatic attraction in the case of CPAM from water and 0.34 M NaCl solvents and non-electrostatic adsorption in the cases of PAM and PEO from water). Also, the 1000 ppm CPAM in water and the 1000 ppm PAM in water solutions were found to exhibit an obvious anti-thixotropic behaviour, which was attributed to the formation of flow-induced transient entanglement networks (TEN) as has been indicated from the rheological measurements discussed in Chapter 5. However, the 1000 ppm CPAM in 0.34M NaCl did not show any sign of such behaviour, and the effect of these TEN structures in the case of the 10000 ppm PEO in water solution was negligible. This will prove to be crucial in rationalizing the capillary, 2D, and 3D flow measurements below. The increase in the salt content in the case of the CPAM solutions was found to affect both the rheology of such solutions and the adsorbed layer thickness determined using the AFM as has been discussed in Chapter 6. The concentrations of the polymer solutions used in the flow through the single capillary models were chosen to be in the semi-dilute region (i.e. above the polymer overlap concentration as has been shown in Chapter 5).

The 2D model experiments were conducted using three polymer solutions: 1000 ppm CPAM in water; 1000 ppm CPAM in 0.34 M NaCl; and 500 ppm PAM in water. The concentration of the polyacrylamide (PAM) solution was decreased in order to decrease the pressure required for the flow without exceeding the maximum pressure which could be read by the transducer (i.e. 1200 mbar) due to the very high molecular weight of this polymer (18 million Da.). However, this concentration is still in the semi-dilute region (c* = 290 ppm). Only two polymer solutions were used in the 3D flow experiments: the 1000 ppm CPAM in water and the 500 ppm PAM in water.

![Figure (8.1): Schematic diagram showing the dimensions of the rectangular, glass capillaries.](chart)

*Figure (8.1): Schematic diagram showing the dimensions of the rectangular, glass capillaries.*
8.2.2 Capillary Flow Experiments

The flow of solvent and polymer solutions through micro-scale, single, glass capillaries was studied mainly to quantify the residual effective hydrodynamic thickness (EHT) of the adsorbed polymer after the flow of the polymer solutions at different flow rates. The capillaries were supplied by CAMLAB and have a rectangular cross-sectional area \((a \times b)\) of \(0.5 \times 0.05\) mm and a length \((L)\) of 50 mm as shown in Figure (8.1). Prior to use, the capillaries were sonicated in dilute RBS detergent to remove any impurities/dirt that can interfere with the measurements and then rinsed with a large volume of deionized water.

![Schematic diagram of the constant-flow capillary setup.](image)

The experimental setup consists of a syringe pump (SAGE Instruments Model 352) which has a minimum flow rate of 0.15 cm³/h, two pressure transducers (a differential transducer; Trans GE Druck (UK) LPM9381 with a pressure range 0-200 mbar and an absolute transducer; Druck LTD (UK) PDCR22 with a pressure range of 0-1200 mbar). While one end of the differential pressure transducer was connected to the flow system, the other end was open to atmosphere since it was assumed that the pressure at the flow outlet is the atmospheric pressure. It has been possible to measure the pressure during the flow of solvents at all flow rate values using the differential transducer, which has a better sensitivity to the low pressure drops observed in these experiments, especially at the lowest solvent flow rate (i.e. 0.15 cm³/h). There were rare cases where the pressure has been above the limit of this differential transducer and the other transducer has to be used in the measurements (e.g. flow...
of some polymer solutions at 1.5 and 3 cm$^3$/h). The glass capillary was connected to the syringe pump and the transducers in the flow setup as shown in Figure (8.2).

Flow of solvent at different rates (0.15, 0.3, 0.6, 1.0, 1.5, and 3 cm$^3$/h) was conducted prior to polymer solution injection. The measurements in Volts from the pressure transducers were recorded in the computer, which is connected to the pressure transducers via a USB data acquisition device (Data Shuttle/USB) supplied from iotech (USA).

The Reynolds number was calculated using Equation (2.4) to check the applicability of Darcy’s Law. The hydraulic radius ($d_p$) and velocity ($v$) were calculated using the following equations (www.engineeringtoolbox.com):

$$d_p = \frac{2a \times b}{(a + b)} \quad \text{and} \quad v = \frac{Q}{a \times b} \quad (8.1)$$

This resulted in a maximum Reynolds number of 3 at the highest flow rate of water (i.e. 3 cm$^3$/h). This value is above unity but the flow should still be viscous flow since it has been found that the flow is still Darcian for Reynolds number up to 10 (www.wikipedia.org). This implies the validity of the Darcy Law using all solutions in the range of flow rates in this study (0.15 to 3 cm$^3$/h) since they have viscosity values higher than water (Reynolds number is inversely proportional to viscosity).

![Figure (8.3): Schematic of the different components of the flow setup downstream the pressure transducers.](image-url)
Table (8.2): Dimensions of the setup components downstream the transducers shown in Figure (8.3).

<table>
<thead>
<tr>
<th>Components Name</th>
<th>ID (mm)</th>
<th>OD (mm)</th>
<th>L (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube 1</td>
<td>0.8</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>Needle</td>
<td>0.495</td>
<td>0.813</td>
<td>5</td>
</tr>
<tr>
<td>Tube 2</td>
<td>0.76</td>
<td>0.8</td>
<td>4</td>
</tr>
<tr>
<td>Tube 3</td>
<td>0.76</td>
<td>0.8</td>
<td>4</td>
</tr>
</tbody>
</table>

The pressure values measured using the transducers have to be dominated by the resistance to flow from the capillary. This implies that the contribution of other components of the flow setup downstream the pressure transducer to the pressure readings should be negligible. The flow setup downstream the transducers consists of 3 tubes, a needle and the capillary in the following order: polyethylene tube (Tube 1), needle, polyethylene tube (Tube 2), the capillary, polyethylene tube (Tube 3) as shown in Figure (8.3). The inner diameter (ID), outer diameter (OD), and length of these parts are listed in Table (8.2). The capillary is connected to Tube 2 and Tube 3 by polyethylene tubes with an inner diameter (ID) of 0.5 mm and lengths of 0.5 cm. The capillary is fitted so that these small tubes (i.e. tubes with ID of 0.5 mm) do not contribute to the pressure drop. The capillary, the 0.5 mm tubes and the 0.76 mm tubes are glued together. Table (8.3) shows the pressure drops in each part of the flow setup downstream the pressure transducers at different flow rates using the nominal dimensions. These were calculated using water, 1000 ppm CPAM in water and 1000 ppm PAM in water at a temperature of 20 °C. The viscosity values of the polymer solutions at this temperature were obtained from Figure (5.2) at the calculated shear rates using equation (8.5) below. This was achieved assuming that the viscosity obtained from the cone-and-plate setup is the same as that during the flow of the polymer solutions through the capillary.

Table (8.3) shows the dominance of the pressure drop in the capillary which can be measured using water (the contribution of the other components are only contributing 0.6% to the total pressure drop). The contribution of the other components can increase by using the polymer solutions especially at the lower flow rates. This is due to the shear thinning behaviour of the polymer solutions and the higher shear rates in the capillary compared to those calculated in the tubes and the needle. However, the main objective of the capillary measurements was to measure the EHT of any adsorbed polymer layers after polymer solutions flow using the pressure measurements during water/solvent flow before and after
polymer solutions flow. As can be seen in Table (8.3), the contribution to the pressure drop of the other components of the apparatus is less than 1%.

**Table (8.3): Values of pressure drop (Pa) calculated in the different components of the capillary flow setup downstream the pressure transducers, as shown in Figure (8.3), using nominal dimensions.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Water</th>
<th>1000 ppm CPAM in water</th>
<th>1000 ppm PAM in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q (cm³/h)</td>
<td>0.15</td>
<td>3.0</td>
<td>0.15</td>
</tr>
<tr>
<td>ΔP (Pa)</td>
<td></td>
<td></td>
<td>ΔP (Pa)</td>
</tr>
<tr>
<td>Tube 1</td>
<td>0.58</td>
<td>11.63</td>
<td>71.95</td>
</tr>
<tr>
<td>Needle</td>
<td>1.42</td>
<td>28.33</td>
<td>94.73</td>
</tr>
<tr>
<td>Tube 2</td>
<td>0.20</td>
<td>4.08</td>
<td>25.04</td>
</tr>
<tr>
<td>Tube 3</td>
<td>0.20</td>
<td>4.08</td>
<td>25.04</td>
</tr>
<tr>
<td>ΔPTOTAL (Pa)</td>
<td>2.4</td>
<td>48.1</td>
<td>216.7</td>
</tr>
<tr>
<td>ΔP Capillary (Pa)</td>
<td>400.8</td>
<td>8016</td>
<td>4080</td>
</tr>
<tr>
<td>ΔP_TOTAL/ΔP Capillary (%)</td>
<td>0.6</td>
<td>0.6</td>
<td>5.3</td>
</tr>
</tbody>
</table>

The steady state values of pressure at the different solvent flow rates (Q_w) through a fresh capillary (i.e. clean capillary before any polymer solution flow) were used to obtain the dimensions of the capillary. Since the width (a) of the capillary is ten times its height (b), the width and length of the capillary were fixed and the capillary height before polymer solution flow (b_before) was calculated from the slope of ΔP/Δη versus Q_w plots using the best line fit. The viscosity of the solvent at the different flow rates is taken into account since a slight change of temperature can induce significant errors. Using Darcy equation:

\[
Q = \frac{k}{L} \frac{ΔP}{Δη} = \frac{C}{L} \frac{ΔP}{Δη}
\]  

(8.2)

where,

\[
C = \text{Conductance} = \frac{k}{L} \frac{ΔP}{Δη} = \frac{b^3a}{12} (m^4)
\]

for a rectangular cross-section (Sisavath et al., 2001)

b : the height of the capillary (m),
a : the width \((5 \times 10^{-4} \text{ m})\), and

L : the length \((5 \times 10^{-2} \text{ m})\).

Hence, the slope of \(\Delta P/\eta\) vs \(Q_w\) is \(L/C\) from which \(b_{\text{before}}\) can be calculated. The capillary flow measurements were conducted at room temperature. The temperature change during each experiment using a certain polymer solution was generally no more than 2 °C as was measured with a thermocouple with its readings recorded in the computer via the USB data acquisition device. The viscosity of water was corrected for temperature using the following equation (The Handbook of Chemistry and Physics, 64th ed.):

\[
\log_{10} \frac{\eta_T}{\eta_{20}} = \frac{1.3272 (20 - T) - 0.001053(T - 20)^2}{T - 105}
\]

(8.3)

where,

\(\eta_T\) : is the viscosity of water at a certain temperature (T), and

\(\eta_{20}\) : is the viscosity of water at 20 °C \((\eta_{20} = 1.002 \text{ mPa.s})\).

Also, the viscosity of the 0.34 M NaCl solvent was calculated using the following equation (Laliberte, 2007):

\[
\eta_T = \exp \left( \frac{v_1(1 - w_w)^v_1 + v_3}{(v_4(T + 1)(v_5(1 - w_w)^v_5 + 1)} \right)
\]

(8.4)

where,

\(w_w\) : Mass fraction of water,

\(T\) : Temperature (°C).

The constants \(v_1, v_2, v_3, v_4, v_5,\) and \(v_6\) have the following values for the aqueous NaCl solutions:

<table>
<thead>
<tr>
<th>(v_1)</th>
<th>(v_2)</th>
<th>(v_3)</th>
<th>(v_4)</th>
<th>(v_5)</th>
<th>(v_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.222</td>
<td>1.3229</td>
<td>1.4849</td>
<td>0.0074691</td>
<td>30.78</td>
<td>2.0583</td>
</tr>
</tbody>
</table>

The apparent shear rate \((\gamma_a)\) which corresponds to a certain solvent flow rate was calculated using the following equation (Erickson et al, 2002):

\[
\gamma_a = \frac{6Q_w}{ab^2}
\]

(8.5)

where, the height (b) in this equation was substituted by the height calculated of a fresh capillary \((b_{\text{before}})\). After the determination of \(b_{\text{before}}\), the polymer solution was injected starting at the lowest flow rate (i.e. 0.15 cm³/h). This initial flow of polymer solution was allowed to last for at least 12 hours in order to allow a certain time for the adsorption. From the
measurements of the pressure (ΔP) during polymer solution flow, the ‘apparent’ viscosity (ηₐ) of the polymer solution can be calculated using the Darcy equation (i.e. Equation 8.2). In this calculation, the height of the capillary (b) was substituted by the value bₜₚ. After that, the polymer solution was washed out by injecting the solvent at a flow rate of 0.15 cm³/h. After reaching the steady state value of pressure, the solvent flow rate was stepped up to 0.6 cm³/h and then to 1.5 cm³/h allowing a steady state value of pressure to be obtained at each flow rate. The wash out steps started with the lowest flow rate (i.e. Q_w of 0.15 cm³/h) since the shear stress values at the higher flow rates can induce irreversible deformation and/or destruction of the adsorbed polymer layer. The capillary was then flushed with the solvent at very high flow rate in order to destroy any polymer layers. The capillary dimensions (i.e. the height) after this flush step have been found to be equal to the bₜₚ indicating the destruction of any possible formation of polymer multilayers. The same procedure was repeated at the higher polymer solution flow rates (i.e. 0.3, 0.6, 1, 1.5 and 3 cm³/h).

After the flow of polymer solution at a certain flow rate, the steady-state pressure drop (ΔP) measurements at different solvent flow rates (Q_w) were used to obtain the height of the capillary after polymer solution flow (bₜₚ). The ΔP/η versus Q_w plots were used to obtain the bₜₚ in the same way followed to obtain bₚ before as discussed above. The effective hydrodynamic thickness (δ_CAP) of the adsorbed polymer layer can be calculated after every flow rate of the polymer solution using the following equation:

\[
\delta_{CAP} = \frac{b_{before} - b_{after}}{2}
\]  

(8.6)

The calculation of the δ_CAP of the polymer layer using this equation is based on the following assumptions:

1. The difference in apparent capillary height (bₚ before –bₜₚ) is due to the formation of an adsorbed polymer layer covering the whole internal surface of the capillary.

2. The adsorbed polymer layer is homogeneous and incompressible with a uniform thickness.

3. Since the width of the capillary (a) is ten times the height (b), then the width can be regarded as being unaffected by the adsorbed polymer layer (i.e. a is constant with a value of 0.5 mm).
8.2.3 2D Model Flow Experiments

A picture of the 2D model used in the flow experiments is shown in Figure (8.4). This 2D model has random porous structures that were produced by etching a pattern into a glass plate and a flat plate sintered onto it. The pore sizes vary from 60 μm to 250 μm, and the pore volume (PV) is about 100 μl. The model has a length of 11.5 cm and a width of 5.5 cm. However, there is no information regarding the height of the model.

*Figure (8.4): The 2D model: (a) a sketch of the model; the grains are shown in black and the channels (i.e. the pores) in white, (b) an actual picture of the model. Each division on the sides of the pictures is 1 mm. In (b), the light grey areas are the grains and the dark grey are the pores.*
The same experimental setup used to conduct the capillary flow experiments was used for the 2D model flow experiments substituting the syringe pump by Model 355 (SAGE Instruments) since it can pump at higher flow rates than the Model 352. First, the 2D model was cleaned by saturating it with acetone for about 5 hours. The model was then flushed with the acetone and subsequently dried at 80 °C. The clean model was then saturated and flushed with the solvent. After that, the solvent was injected at flow rates of 9.26, 18.53, 27.79, 37.06, and 46.32 cm³/h while recording the pressure (ΔPₜₜ). The polymer solution was then injected at the lowest flow rate (9.26 cm³/h) while recording the pressure (ΔPₚ). At least 100 PVs of the polymer solution were injected through the model. The polymer solution was then displaced by the solvent at a flow rate of 9.26 cm³/h. After the pressure reading (ΔPₜₜ) reached a steady state value, the solvent flow rate was stepped up to higher flow rates (i.e. 18.53, 27.79, 37.06 and then 46.32 cm³/h) allowing a steady state pressure value (ΔPₜₜ) to be obtained at each flow rate. Finally, the model was flushed with the solvent at a very high flow rate and the same procedure was repeated for other values of the polymer solution flow rate (i.e. Qₚ of 18.53, 27.79, 37.06, and 46.32 cm³/h).

From the values of pressure measured at the steady state conditions for a certain flow rate of the solvent and the polymer solution, the following parameters were calculated (Sorbie, 1991):

1. Mobility reduction (Rₘ)

\[
Rₘ = \left( \frac{\frac{k}{\eta}}{\frac{k}{\eta}_\text{polymer}} \right) = \left( \frac{\Delta P_\text{polymer}}{\Delta P_\text{before}} \right) \text{ at same flow rate} \tag{8.7}
\]

2. Residual permeability reduction (Rₖ)

\[
Rₖ = \frac{k_{\text{before}}}{k_{\text{after}}} = \frac{(\Delta P/\eta)_{\text{after}}}{(\Delta P/\eta)_{\text{before}}} \tag{8.8}
\]

where the Rₖ after each polymer solution flow at a certain solution flow rate was obtained by plotting the steady-state pressure drop (ΔP/η) versus solvent flow rate (Qₜ), which is a linear relationship with a slope m, where:

\[
m = \frac{L}{kA} \tag{8.9}
\]

The viscosity of the solvent (η) has been included in the plot since the viscosity of the solvent was different from time to time due to the slight change in temperature, which was measured along with the pressure. Equations (8.3) and (8.4) have been used to obtain the viscosity value at the average measurement.
temperature for water and 0.34 M NaCl, respectively. The slope of these plots (i.e. \( \Delta P/\eta \) versus \( Q_w \)) after every flow rate of the polymer solutions was divided by the slope of the plot obtained using freshly cleaned model prior to any polymer solution flow (i.e. \( R_k = m_{\text{after}}/m_{\text{before}} \)).

### 8.2.4 3D Model Flow Experiments

The 3D model used in this study to conduct the flow of polymer solutions was a pack of Perpox with dimensions of 22.5 cm × 10 cm × 0.6 cm. A schematic of the pack with its components is shown in Figure (8.5). The pack has two inlets and two outlets, separated from the packing material by a mesh screen. There is one channel perpendicular to the flow direction at the inlet and another at the outlet in order to establish the liquid front at the inlet. In these experiments, the pressure (\( \Delta P \)) was measured using a manometer using the same flowing liquid, which was connected to one of the inlets, using the other inlet for liquid injection with one of the outlets being sealed.

This pack was packed with spherical glass beads of diameter in the range 212 to 250 \( \mu \text{m} \) supplied by Jencons (UK). The glass beads were poured inside the pack from the removable side of the pack. After the pack was filled with the glass beads, the pack was sealed tightly using the fitted screws.

![Schematic drawing of the Perpox pack used as a 3D model in the flow experiments](image)

*Figure (8.5): Schematic drawing of the Perpox pack used as a 3D model in the flow experiments*
It was ensured that the pack was full without any regions of loose beads. CO₂ injection was then conducted to check any possible leakage. After that, the pack was saturated with the solvent. The CO₂ injection before the flow of the solvent helped in prohibiting the entrapment of air bubbles since water is more miscible with CO₂ than air. It was found that the pore volume (PV) of the pack using the bead sizes stated above was in the range of 60-65 cm³, which resulted in a porosity of 0.45. After making sure that the pack was fully saturated with the solvent, the solvent was injected at different flow rates of 60, 120, 240, and 360 cm³/h. The steady state values of pressure (ΔP_before), which were measured using the manometer, were recorded at each solvent flow rate. After that, 200 cm³ (PV = 3.1 to 3.3) of polymer solution was injected at a flow rate of 60 cm³/h while recording the pressure (ΔP_polymer) at different time intervals. It was found that this volume of polymer solution was sufficient to reach a steady-state condition for most of the measurements as discussed below. The polymer solution was then displaced by the solvent at a flow rate of 60 cm³/h. After the pressure reading (ΔP_after) had stabilized (usually after injecting 5 PVs of the solvent), the solvent flow rate was stepped up to higher flow rates (i.e. Q_w at 120, 240 and 360 cm³/h) recording the steady-state value of pressure (ΔP_after) at each solvent flow rate. These measurements were conducted at a temperature of 20 °C. The mobility reduction (R_m) and the permeability reduction (R_k) at the steady-state conditions were calculated using the same equations stated above [i.e. Equations (8.7) and (8.8)]. The permeability reduction was calculated using the slope of ΔP versus Q_w before and after polymer solution flow (i.e. R_k = m_after/m_before). The same procedure was conducted at higher flow rates of the polymer solution (i.e. Q_p at 120 and 240 cm³/h).

8.3 Results and Discussion

8.3.1 Capillary Flow

8.3.1.1 Apparent Capillary Height (b_before) of the Fresh Capillaries

As an example, the results of four capillary flow experiments are presented in this chapter; one experiment for each of the polymer solutions listed in the Table (8.1). Table (8.4) lists the steady state pressure measurements recorded at different solvent flow rates in the fresh capillaries. Higher measurement fluctuation around the steady state value was observed at the lowest solvent flow rate (i.e. 0.15 cm³/h) as compared to the pressure measurements at the
higher flow rates. This might have been due to pressure values being at the lower sensitivity limit of the differential pressure transducer. Figure (8.6) shows the $\Delta P/\eta$ versus $Q_w$ plot of the capillary used in the 1000 ppm CPAM in water experiment. A linear relationship can be observed between the $\Delta P/\eta$ and $Q_w$ with a slope of $1.08 \times 10^{10}$ cm$^{-3}$. Since this slope equals $L/C$ from Equation (8.2) and the capillary length ($L$) and width ($a$) are fixed, $b_{\text{before}}$ was calculated to be 48.07 $\mu$m. The same procedure was followed in all capillary flow experiments to calculate the height of the capillaries before and after each polymer solution flow at a certain solution flow rate. The values of $b_{\text{before}}$ in the four flow experiments are listed in Table (8.4) and seem to differ from capillary to capillary, which might be due to slight variations in the manufacture of the capillary. The nominal height of the capillary as supplied by the manufacturer is 50 $\mu$m, but the values obtained from the current measurements were in the range 48.1 to 52.6 $\mu$m. The calculated heights of the capillaries $b_{\text{before}}$ have been used in Equation (8.6) to calculate the apparent shear rates at different solvent/solution flow rates and the results are listed in Table (8.5). The flow through these capillaries in the flow rate range from 0.15 cm$^3$/h to 3 cm$^3$/h has allowed a wide range of shear rate to be investigated (the range from $180$ s$^{-1}$ to $4328$ s$^{-1}$).

![Graph](image)

*Figure (8.6): The plot of $\Delta P/\eta$ versus $Q_w$ of the fresh capillary used to conduct the flow of the 1000 ppm CPAM in water. An exact linear relationship can be observed and the slope was determined from the best fit of trend line.*
Table (8.4): The steady-state pressure measured at different solvent flow rates ($Q_w$) through fresh capillaries before polymer solution flow in the four experiments. The results of the $b_{before}$ for each capillary are also listed.

<table>
<thead>
<tr>
<th>$Q_w$ (cm$^3$/h)</th>
<th>1000 ppm CPAM in water</th>
<th>1000 ppm CPAM in NaCl</th>
<th>1000 ppm PAM in water</th>
<th>5000 ppm PEO in water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta P$ (kPa)</td>
<td>$T$ ($^\circ$C)</td>
<td>$\Delta P$ (kPa)</td>
<td>$T$ ($^\circ$C)</td>
</tr>
<tr>
<td>0.15</td>
<td>0.424</td>
<td>23.3</td>
<td>0.446</td>
<td>20.3</td>
</tr>
<tr>
<td>0.3</td>
<td>0.876</td>
<td>22.3</td>
<td>0.767</td>
<td>20.4</td>
</tr>
<tr>
<td>0.6</td>
<td>1.734</td>
<td>22.4</td>
<td>1.497</td>
<td>20.5</td>
</tr>
<tr>
<td>1</td>
<td>2.906</td>
<td>22.5</td>
<td>2.316</td>
<td>20.6</td>
</tr>
<tr>
<td>1.5</td>
<td>4.280</td>
<td>22.6</td>
<td>3.577</td>
<td>20.7</td>
</tr>
<tr>
<td>3</td>
<td>8.351</td>
<td>23.0</td>
<td>7.139</td>
<td>21.0</td>
</tr>
</tbody>
</table>

$b_{before}$ ($\mu$m) 48.07 52.70 51.68 49.3

Table (8.5): The apparent shear rate ($\gamma_a$) calculated at different solvent/solution flow rates using the values of $b_{before}$ in Table (8.4).

<table>
<thead>
<tr>
<th>$Q_w$ (cm$^3$/h)</th>
<th>1000 ppm CPAM in water</th>
<th>1000 ppm CPAM in NaCl</th>
<th>1000 ppm PAM in water</th>
<th>5000 ppm PEO in water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma_a$ (s$^{-1}$)</td>
<td>$\gamma_a$ (s$^{-1}$)</td>
<td>$\gamma_a$ (s$^{-1}$)</td>
<td>$\gamma_a$ (s$^{-1}$)</td>
</tr>
<tr>
<td>0.15</td>
<td>216</td>
<td>180</td>
<td>187</td>
<td>206</td>
</tr>
<tr>
<td>0.3</td>
<td>433</td>
<td>360</td>
<td>374</td>
<td>411</td>
</tr>
<tr>
<td>0.6</td>
<td>866</td>
<td>720</td>
<td>749</td>
<td>823</td>
</tr>
<tr>
<td>1</td>
<td>1443</td>
<td>1200</td>
<td>1248</td>
<td>1371</td>
</tr>
<tr>
<td>1.5</td>
<td>2164</td>
<td>1801</td>
<td>1872</td>
<td>2057</td>
</tr>
<tr>
<td>3</td>
<td>4328</td>
<td>3601</td>
<td>3744</td>
<td>4114</td>
</tr>
</tbody>
</table>
Figure (8.7): (a) The behaviour of total pressure drop ($\Delta P$) during the flow of the 1000 ppm CPAM in water through the capillary at different flow rates (shear rates). (b) The corresponding apparent viscosity ($\eta_a$) behaviour. The measurements were conducted at 23 °C.
8.3.1.2 Apparent Viscosity ($\eta_a$) of the Polymer Solutions

The behaviour of the total pressure drop measured during the flow of the 1000 ppm CPAM in water solution through the capillary at different solution flow rates is shown in Figure (8.7 a). The behaviour of the calculated ‘apparent’ viscosity ($\eta_a$) from these pressure values is also shown in Figure (8.7 b). It can be observed that it takes a certain time for the steady state value of the pressure readings at a certain flow rate to be reached. This time decreases with the flow rate. The steady-state pressure values recorded during the flow of the different polymer solutions through the glass capillaries are listed in Table (A.1) in Appendix-A. The steady-state apparent viscosity calculated from the capillary flow measurements during the flow of the different polymer solutions are listed in Table (8.6). It can be observed that the apparent viscosity is fairly constant with flow rate (shear rate) for the 1000 ppm CPAM in 0.34 M NaCl, which is consistent with the rheology of this polymer solution above the shear rate of 100 s$^{-1}$ as has been shown in Figure (5.2). However, significant shear thinning behaviour can be observed during the capillary flow of the other three polymer solutions through the glass capillaries. The shear thickening behaviour, which has been observed by different degrees in the cone-and-plate flow curves of these polymer solutions (except for the PEO in water solution) cannot be observed during the flow of these solutions through the glass capillaries. An exception is the viscosity calculated during the flow of 1000 ppm CPAM in water through the capillary at the flow rate of 3 cm$^3$/h. Comparison between the apparent viscosity values calculated from the capillary flow with the viscosity values obtained from the cone-and-plate rheology measurements of the 1000 ppm CPAM in water is shown in Figure (8.8). The values of the apparent viscosity at a certain apparent shear rate ($\gamma_a$) obtained from the capillary flow measurements are generally lower than those obtained from the rheometer. This has been found to be the case for all the polymer solutions investigated. The might be attributed to the differences in the flow regimes through the different flow systems and hence inducing different effects in the bulk solution. It can be observed from Figure (8.8) that the magnitude of the difference between the two values (i.e. the viscosities obtained from the rheometer and the capillary at a certain shear rate) in the case of the 1000 ppm CPAM in water is generally increasing with shear rate, except for the highest shear rate value.
Table (8.6): The apparent viscosity of the polymer solutions calculated at different polymer solution flow rates from the steady-state pressure measurements during the flow through glass capillaries. The average room temperature during the measurements is shown in between brackets.

<table>
<thead>
<tr>
<th>$Q_p$ (cm$^3$/h)</th>
<th>1000 ppm CPAM in water (23 °C)</th>
<th>1000 ppm CPAM in NaCl (21 °C)</th>
<th>1000 ppm PAM in water (22 °C)</th>
<th>5000 ppm PEO in water (21.5 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\eta_a$ (mPa.s)</td>
<td>$\eta_a$ (mPa.s)</td>
<td>$\eta_a$ (mPa.s)</td>
<td>$\eta_a$ (mPa.s)</td>
</tr>
<tr>
<td>0.15</td>
<td>9.86</td>
<td>3.20</td>
<td>9.34</td>
<td>20.22</td>
</tr>
<tr>
<td>0.3</td>
<td>7.08</td>
<td>2.88</td>
<td>-</td>
<td>16.73</td>
</tr>
<tr>
<td>0.6</td>
<td>5.51</td>
<td>2.64</td>
<td>5.74</td>
<td>14.91</td>
</tr>
<tr>
<td>1.0</td>
<td>4.92</td>
<td>2.55</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.5</td>
<td>3.54</td>
<td>2.41</td>
<td>4.41</td>
<td>12.24</td>
</tr>
<tr>
<td>3.0</td>
<td>4.14</td>
<td>-</td>
<td>-</td>
<td>6.16</td>
</tr>
</tbody>
</table>

Figure (8.8): The apparent viscosity ($\eta_a$) obtained during the flow of the 1000 ppm CPAM in water solution through the capillary at different solution flow rates (shear rates). These values are compared to the viscosity values obtained using the cone-and-plate system for the same solution at 23°C. The errors in the apparent viscosity ($\eta_a$) measurements obtained from the capillary flow are indicated by the error bars.
The above results from the apparent viscosity using the capillary flow measurements could be considered to be a further support for the formation of transient entanglement networks (TEN) during the flow of the high molecular weight polymer solutions, which has been concluded in Chapter 5. It has been stated in Chapter 5 that the formation and sizes of such structures are shear-rate dependent. Moreover, such structures have to grow and/or accumulate enough to produce the apparent shear thickening effect observed from the flow curves in the case of the 1000 ppm CPAM in water as well as the 1000 ppm CPAM in 0.34 M NaCl and the 1000 ppm PAM in water solutions. Also, it has been found that such structures are time-dependent and the viscosity-time curves presented in Chapter 5 (Figures 5.4 and 5.8) have shown that both the 1000 ppm CPAM in water and the 1000 ppm PAM in water solutions have shown an apparent shear thickening behaviour with time. On the other hand, the 10000 ppm PEO in water solution has shown a very slight increase of the viscosity with time. However, the 1000 ppm CPAM in 0.34 M NaCl has not shown such an increase in the viscosity with time. On the contrary, it has shown an initial shear thinning behaviour with time followed by a constant-viscosity. The domination of shear thinning behaviour observed during the flow of the 5000 ppm PEO in water through the capillary is consistent with the monotonic shear thinning behaviour of this solution at higher concentration (10000 ppm) as has been observed in Figure (5.2). However, the relatively strong shear thinning behaviour in the cases of the 1000 ppm CPAM in water, the 1000 ppm PAM in water in the capillary flow experiments can be related to the decrease in the solution residence time in the capillary with the increase in flow rate. Hence, even if the transient entanglement networks did exist during the flow of these solutions, they might not have been allowed to grow and/or accumulate enough to be detected by the capillary experiments and hence showing the otherwise shear thickening behaviour, which was observed using the cone-and-plate rheometer measurements. This is particularly true in the case of the 1000 ppm CPAM in water which showed a noticeable shear thickening behaviour above 1000 s\(^{-1}\) from the rheometer measurements as shown in the Figure (8.8). The apparent shear thickening behaviour observed at the highest shear rate during the capillary flow of this solution was probably due to the formation of large vortices at the entrance of the capillary and not a real thickening behaviour of the polymer solution.
Table (8.7): The effective hydrodynamic thickness ($\delta_{CAP}$) obtained for different polymer solutions after different solution flow rates ($Q_p$)

<table>
<thead>
<tr>
<th>$Q_p$ (cm$^3$/h)</th>
<th>1000 ppm CPAM in water</th>
<th>1000 ppm CPAM in NaCl</th>
<th>1000 ppm PAM in water</th>
<th>5000 ppm PEO in water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta_{CAP}$ (nm)</td>
<td>$\delta_{CAP}$ (nm)</td>
<td>$\delta_{CAP}$ (nm)</td>
<td>$\delta_{CAP}$ (nm)</td>
</tr>
<tr>
<td>0.15</td>
<td>577</td>
<td>184</td>
<td>269</td>
<td>23</td>
</tr>
<tr>
<td>0.3</td>
<td>653</td>
<td>-</td>
<td>-</td>
<td>323</td>
</tr>
<tr>
<td>0.6</td>
<td>368</td>
<td>69</td>
<td>104</td>
<td>214</td>
</tr>
<tr>
<td>1</td>
<td>1804</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.5</td>
<td>-</td>
<td>247</td>
<td>292</td>
<td>454</td>
</tr>
<tr>
<td>$\delta_{AFM}$ (nm)</td>
<td>106</td>
<td>169</td>
<td>48</td>
<td>65</td>
</tr>
</tbody>
</table>

8.3.1.3 Effective Hydrodynamic Thickness ($\delta_{CAP}$)

The steady-state pressure values conducted during the wash out stages at different solvent flow rates ($Q_w$) are listed in Tables (A.2), (A.3), (A.4) and (A.5) in Appendix-A after the flow of the different polymer solutions at different solution flow rates ($Q_p$). The slopes of the $\Delta P/\eta$ versus $Q_w$ plots after each polymer solution flow rate have been used to calculate the height values of the capillaries ($b$) after the flow of the polymer solution ($b_{after}$), which are listed in Tables (A.2), (A.3), (A.4) and (A.5) in Appendix-A. The effective hydrodynamic thickness ($\delta_{CAP}$) calculated from the capillary flow measurements using Equation (8.6) are listed in Table (8.7) after the flow of polymer solutions through the capillary at different flow rates. It should be noted here that the errors calculated for the values of $b_{before}$ and $b_{after}$ were negligible (less than 0.3 nm), thus giving rise to negligible errors in the values of the effective hydrodynamic thickness from the capillary measurements ($\delta_{CAP}$). The table also shows the thickness of the adsorbed monolayer obtained for these solutions on glass using the AFM measurements in Chapter 6 (Section 6.4.4). Generally, the hydrodynamic thickness values from the capillary flow experiments are very high compared to the adsorbed layer thickness obtained using the AFM. This might be due to the effect of polymer solution flow which might give rise to the formation of polymer multilayers as has been discussed in Chapter 4 (Section 4.1.3). However, the thicknesses obtained from the capillary flow of the 1000 ppm CPAM in 0.34 M NaCl were relatively low (between 69 and 247 nm) and comparable with
the thickness obtained from the AFM measurements (169 nm). On the other hand, the flow of the 1000 ppm CPAM in water have resulted in very high values of the effective hydrodynamic thickness ranging from 360 nm to 1804 nm, when the measured thickness of the monolayer has been around 106 nm using the AFM measurements. The thickness values from the capillary flow measurements from the other two solutions (the 1000 ppm PAM in water and the 5000 ppm PEO in water) were lower than those obtained using the 1000 ppm CPAM in water solution but generally several fold of the monolayer thickness obtained from the AFM measurements. These values of the adsorbed layer thickness from the capillary flow measurements using these polymer solutions were reproducible and showing the same indication of multilayer formations; with the 1000 ppm CPAM in water showing the most significant values. If one accepts the idea of polymer multilayer formation from the glass capillary flow experiments, then the question would be about the cause of such an apparent multilayer adsorption especially in the case of the 1000 ppm CPAM in water. The answer to this question would be logically one of the previously proposed mechanisms such as adsorption-entanglement (AE), adsorption-gel (AG), and/or flow-induced adsorption (FIA).

Adsorption-entanglement can be excluded as a possible mechanism since if it were the cause for such an effect during the flow of the 1000 ppm CPAM in water, then it would be more probable in the case of the 1000 ppm CPAM in 0.34 M NaCl. This is because of the longer tails and loops of the adsorbed polymer layer from such solution (as has been indicated from higher thickness of the adsorbed monolayer from the CPAM in 0.34 M NaCl as compared to the one formed from the CPAM in water using the AFM measurements) coupled with the screening of the charged monomers in the polymer chains making the probability of entanglements between the flowing and the adsorbed polymer molecules higher. But this was not the case and the values of the $\delta_{CAP}$ obtained in the case of the 1000 ppm CPAM in 0.34 M NaCl were not indicating multilayer formation and were much lower than those obtained using the 1000 ppm CPAM in water.

The adsorption-gel (AG) and the flow-induced adsorption (FIA) have been proposed as two different mechanisms but the possibility of these mechanisms being the same mechanism cannot be excluded since the microscopic origin of these mechanisms has not been stated. The FIA, as proposed by Zitha et al. (1998), is different than that proposed by Chauvetreau et al. (2002). Chauvetreau et al. (2002) described the FIA as being equivalent to the AE, as has been proposed and described by Hikmet et al. (1985), whereas Zitha et al. (1998) have proposed it as a mechanism by which polymer chains can adsorb individually.
and/or collectively from the flowing polymer solution. If one supports this view (i.e. the FIA as described by Zitha et al., 1998); then one would wonder about the microscopic origin of the collective adsorption induced by the flow of the polymer solution. This microscopic origin can be something related to the microscopic events in the bulk solution which can have its results at the interface as a formation of multilayers. The capillary flow experiments have been extended to the flow of the polymer solutions through the 2D models. The results from the 2D models will be presented and discussed before the proposal of the possible mechanism of multilayer formation during the flow of high molecular weight polymer solutions through systems in which mechanical entrapment is not possible.

![Figure (8.9): The plot of ΔP/η versus Q_w of the fresh 2D model before the flow of the 1000 ppm CPAM in water. An exact linear relationship can be observed and the slope was determined from the best fit of trend line.](image)

8.3.2 2D Model

The steady-state pressure measurements obtained from the 2D flow measurements using the three polymer solutions (i.e. the 1000 ppm CPAM in water, the 1000 ppm CPAM in 0.34 M NaCl, and the 500 ppm PAM in water) are listed in Tables (A-6) to (A-8) in Appendix-A along with the average temperature during the measurements. The plot of ΔP/η versus Q_w
before the flow of the 1000 ppm CPAM in water is shown in Figure (8.9). The slope of the plot can be used to calculate the product $kA$ since there is no information on the cross-sectional area ($A$) of the 2D model. The slope ($m$) of the $\Delta P/\eta$ versus $Q_w$ plot in Figure (8.9) equals $L/kA$ where $L$ is 11.5 cm and hence $kA$ can be calculated ($kA = L/m$). The calculated $kA$ values for the same model cleaned as described above are listed for the three different 2D experiments in Table (8.8). This product (i.e. $kA$) differed from experiment to experiment which might have been due to experimental error since the values are within 5% of the average value of $2.06 \times 10^{-6}$ cm$^4$. The slope after the flow of a certain polymer solution was divided by the slope obtained before the flow of that polymer solution (i.e. not the average of the three listed in Table (8.8)). This was done because the objective of these measurements has been to investigate whether the flow of any polymer solution at different flow rates would induce a change in the 2D model permeability compared to the initial permeability before the flow of that specific solution.

Table (8.8): The permeability-area product ($kA$) values obtained from the $\Delta P/\eta$ vs. $Q_w$ plots before the use of the 2D model to flow the three polymer solutions

<table>
<thead>
<tr>
<th>Polymer Solution</th>
<th>$kA$ (cm$^4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 ppm CPAM in water</td>
<td>$2.06 \times 10^{-6}$</td>
</tr>
<tr>
<td>1000 ppm CPAM in 0.34 M NaCl</td>
<td>$2.16 \times 10^{-6}$</td>
</tr>
<tr>
<td>500 ppm PAM in water</td>
<td>$1.99 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

The mobility reduction ($R_m$) values during the flow of the three polymer solutions through the 2D model at different polymer solution flow rates are shown in Figure (8.10). It can be observed that the $R_m$ curve for the 1000 ppm CPAM in water solution looks like a “bell” shape with a maximum at a solution flow rate of 27.79 cm$^3$/h. The maximum value of the $R_m$ was thought to be a result of some problems in the flow system such as trapped air bubbles or some other particulates; however this was reproduced twice indicating a real effect. The $R_m$ values obtained at the other polymer solution flow rates (for the 1000 ppm CPAM in water solution) were virtually constant around 15. On the other hand, the $R_m$ for the 1000 ppm CPAM in 0.34 M NaCl is almost constant at around 2.5. This can be correlated with the almost constant apparent viscosity values for the same polymer solution (i.e. the 1000 ppm CPAM in 0.34 M NaCl) obtained during the flow through the glass capillary as listed above in the Table (8.6). The mobility reduction during the flow of the 500 ppm PAM
in water is slightly but consistently increasing with the polymer solution flow rate with an overshoot at the highest flow rate (i.e. $Q_p$ of 46.32 cm$^3$/h). This polymer solution is showing an obvious shear thickening behaviour during the flow through the 2D model. This might have been due to the relatively long relaxation time of this very high molecular weight polymer, which can result in the extension of the macromolecules during flow. The already extended polymer molecules might have enhanced the formation of TEN structures with the increase in the flow rate of the polymer solution through the 2D model.

![Graph](image)

*Figure (8.10): The mobility reduction ($R_m$) of three polymer solutions obtained at different polymer solutions’ flow rates ($Q_p$) through the 2D model. The errors in the $R_m$ values are shown by the error bars.*

The permeability reduction ($R_k$) values obtained after the flow of the three polymer solutions at different polymer solution flow rates through the 2D model are listed in Table (8.9). The permeability reduction values in the case of the 1000 ppm CPAM in 0.34 M NaCl and the 500 ppm PAM in water are almost one indicating no effect of polymer flow in reducing the permeability of the 2D model. On the other hand, the flow of the 1000 ppm CPAM in water solution through the model reduced the permeability of the model by 10% to 20%. This reduction is very small, but it is above the experimental errors and hence can be indicative since it is occurring just in the case of the 1000 ppm CPAM in water solution. This
polymer solution has been found to induce significant change in flow resistance to solvent after solution flow through the glass capillaries, which has been attributed to multilayer formations. The maximum permeability reduction obtained in this case (i.e. for the 1000 ppm CPAM in water through the 2D model) was after the flow of the polymer solution at 27.79 cm$^3$/h, which is the same flow rate at which this same polymer shows a maximum in the mobility reduction, as can be observed from Figure (8.10). This can indicate that the same cause of the change in the mobility reduction is responsible for the change in the permeability reduction. Since detectable permeability reduction has been only induced by the 1000 ppm CPAM in water; this cannot be explained by the effect of a polymer monolayer. This is because the AFM measurements have shown that the CPAM in 0.34 M NaCl forms a thicker layer on glass surfaces than when the CPAM is adsorbed from water. Since the 1000 ppm CPAM in 0.34 M NaCl has not induce higher permeability reduction compared to the 1000 ppm CPAM in water, then the formation of multilayers during the flow of the latter through the 2D model might have been responsible for such effect.

Table (8.9): Permeability reduction calculated after the flow of different polymer solutions through the 2D model at different solution flow rates

<table>
<thead>
<tr>
<th>$Q_p$ (cm$^3$/h)</th>
<th>1000 pm CPAM in water</th>
<th>1000 ppm CPAM in 0.34 M NaCl</th>
<th>500 ppm PAM in water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_k$ (No)</td>
<td>$R_k$ (No)</td>
<td>$R_k$ (No)</td>
</tr>
<tr>
<td>9.26</td>
<td>1.10</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>18.53</td>
<td>1.09</td>
<td>1.08</td>
<td>0.98</td>
</tr>
<tr>
<td>27.79</td>
<td>1.20</td>
<td>1.01</td>
<td>1.01</td>
</tr>
<tr>
<td>37.06</td>
<td>1.12</td>
<td>-</td>
<td>0.99</td>
</tr>
<tr>
<td>46.32</td>
<td>1.13</td>
<td>0.99</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Mechanical entrapment is not possible during the flow of the polymer solutions through the single glass capillaries and the 2D model. Also, adsorption entanglement mechanism has been excluded as the possible mechanism for multilayer formation during the flow of the polymer solutions through the glass capillaries. Also, mechanisms such as adsorption-gel and flow-induced adsorption do not explain fully the microscopic origin of the multilayer formation. In this study, the flow of the 1000 ppm CPAM in water has been found to cause multilayer formation of polymer in the single glass capillaries as well as indication
of such formations during the flow of this polymer solution through the 2D model. It is proposed here that the transient entanglement networks (TEN) formed during the flow of the 1000 ppm CPAM in water might have been the origin of the multilayer formation. In Chapter 5, it has been concluded that such large structures can be formed during the flow of the 1000 ppm CPAM in water. Also, it has been concluded that the TEN structures were too small to be observed in the rheological behaviour of the 1000 ppm CPAM in 0.34M NaCl. On the other hand, it has been found that the 1000 ppm PAM in water solution can produce such large structures, which might have been responsible for the obvious shear thickening behaviour during the flow of this polymer solution through the 2D model. However, the 1000 ppm PAM in water solution has not shown a significant value of the $\delta_{\text{CAP}}$ after the flow through the glass capillaries and permeability reduction of almost one after the flow through the 2D model. The high adsorption energy in the case of the CPAM in water (electrostatic attraction) compared to the weak adsorption of the PAM on glass as has been indicated by the AFM measurements in Chapter 6 may have been the factor that promoted the multilayer formation in the case of the 1000 ppm CPAM in water. Hence, two main steps can be proposed for the multilayer formation in the simple systems (i.e. where mechanical entrapment is not possible; such as the flow through the capillaries and the 2D model in this study):

1. The formation of micron-size gel-like structures in the bulk of the polymer solution as a result of polymer solutions flow, and
2. The deposition (adsorption) of such structures on the solid-liquid interface.

Consequently, two criteria for a certain polymer solution/surface system should be satisfied in order to produce the multilayer adsorption in simple systems:

1. The presence of certain qualities in the polymer solution that can promote the formation of the TEN. High molecular weight, more extended polymer molecules, and an increase in polymer concentration have been found to be some of the parameters that can promote the formation of the TEN provided that the shear rate is high enough to create the entanglements between the flowing chains. The studies of Kishbaugh and MucHugh (1993a,b) are a strong support of the formation of TEN structures, which might grow up to 5 $\mu$m in size.

2. The polymer-surface-solvent system has to permit sufficient adsorption energy so that the formed TEN structures in the bulk solution can adsorb at the liquid-solid interface.
In the case of the 1000 ppm CPAM in water solution, the above criteria are fulfilled. The cationic polymer has a more extended conformation of the chains in solution especially with the absence of any salt that can screen the charged monomers and hence make the chains attain more coiled conformation, as can be predicted in the case of the CPAM in the 0.34 M NaCl. Since the concentration of the 1000 ppm CPAM in water was in the semi-dilute regime, chains have been already entangled in the quiescent state. Hence, low shear would be sufficient to increase the degree of entanglement, since it would induce a higher degree of extension to the already extended chains, as well as forcing these chains together by the hydrodynamic effects and hence possibly forming micron-size TEN structures. Also, the TEN structures have been suggested as the cause of the obvious shear thickening behaviour of the 1000 ppm CPAM in water solution (as has been investigated using the rheological measurements in Chapter 5). The presence of a surface of opposite charge (negatively charged glass surface) would induce sufficiently high adsorption energy for these entangled formations (i.e. TEN structures) to be deposited (adsorbed) on the glass surface as mentioned above.

In light of such a mechanism, the 1000 ppm CPAM in 0.34 M NaCl and the 5000 ppm PEO in water might not have induced significant multilayers during the flow through the glass capillaries because neither of these solutions have shown significant antithixotropic behaviour. Hence, TEN structures of significant sizes might not have been formed during flow, although the CPAM adsorption from the 0.34 M NaCl has shown strong electrostatic attraction from the AFM measurements. On the other hand, the 1000 ppm PAM in water has not induced significant multilayer formations after the flow through the glass capillaries and the 500 ppm solution has not induced any permeability reduction after the flow through the 2D model in spite of the evident antithixotropic behaviour shown from the viscosity-time curves using this polymer solution. This might have been due to the weak adsorption energy of this polymer on glass from water as has been observed from the AFM measurements using the PAM in water solution. Hence, both criteria listed above (i.e. formation of shear-induced TEN structures in significant sizes and sufficiently high adsorption energy) have to be satisfied so that the flow of the polymer solution through simple systems can induce multilayer formation.

The above mechanism (the adsorption of TEN structure formed during flow) is essentially the FIA mechanism proposed by Zitha et al. (1998), but they did not speculate as to the microscopic source of the collective adsorption and hence the multilayer formation. Here, the present study has attempted to explain the microscopic source of such adsorption in
light of the TEN and hence the formation of polymer multilayer. Also, in order to distant this picture from the AE picture proposed by Chauveteau et al. (2002) as being the FIA, this mechanism will be called transient entanglement networks adsorption (TENA).

One of the studies that have concluded the AE mechanism as a result of capillary flow and AFM experiments using different high molecular weight polyacrylamide solutions is the study of Grattoni et al. (2004). In the absence of rheology measurements of their solutions, it can be speculated that the solutions used (expected to be in the semi-dilute regime) might have the ability to form the TEN structures. The full-surface coverage shown by their AFM measurements might indicate sufficiently high adsorption energy, which might have caused any TEN structures formed in the bulk solutions during flow to adsorb on the surface of the glass capillaries and the flow channel used for the AFM measurements. In addition, the presence of the divalent Ca\(^{2+}\) ions in their solutions might have also played an important role in the formation of the TEN structures since they can significantly reduce the electrical double-layer repulsion between the chains and hence increasing the ability of these polymer solutions to form entanglements. Also, the same ions can create higher adsorption energy due to their bridging ability between the negatively charged glass surface and the negatively charged polymer chains (Mennella et al, 1999; Needham et al., 1974).

The study of Al-Sharji et al. (2001) was conducted using the same type of 2D model as that used in the experiments of the current study. Also, the same polymer (i.e. CPAM) was used but with a different solvent which also contained two divalent ions (Ca\(^{2+}\), and Mg\(^{2+}\)). They have concluded of polymer multilayers formed behind the grains (in the stagnant areas) from their measurements, as well as using a microscope to visualize such polymer multilayers. These multilayer formations were found to be prohibited by making the surface of the model hydrophobic. In the case of the hydrophilic case, the mobility reduction was found to increase with the increase in the polymer solution flow rate. On the other hand, the permeability reduction was found to be almost constant and around 2.5 at all the polymer solution flow rates. However, the mobility reduction was found to be constant at the different polymer solution flow rates in the case of the hydrophobic model. Also, the permeability reduction was found to be unity in this case. They have attributed this multilayer formation to the adsorption-entanglement (AE) mechanism. From the viewpoint of the current study, the multilayer formations observed in this study (i.e. Al-Sharji et al., 2001) could have been attributed better to the adsorption of the transient entanglement networks (TENA). Actually, the study of Al-Sharji et al. (2001) strongly supports the TENA mechanism rather than adsorption entanglement, AE. The proper location of the multilayers which could be
attributed to the AE mechanism as described by Hikmet et al. (1985) and Chauveteau et al. (2002) is around the converging region, upstream from the pore-throats. The mere visualization of these multilayers behind the grains can suggest a mechanism other than the AE with the TENA mechanism being the best candidate. The transient networks formed during the flow of the polymer solution used in the flow experiments of Al-Sharji et al. (2001) through the 2D model might have been driven by the hydrodynamic forces to the stagnant regions behind the grains, where they adsorbed and accumulated. The absence of these formations in the case of the hydrophobic model provides further support to the TENA hypothesis, since the system in this case did not satisfy the second criteria for the TENA mechanism, which is the requirement of sufficient adsorption energy for the TEN.

### 8.3.3 3D Model

Given that the porosity of the packs has been around 0.45, the Reynolds number calculated using Equation (2.5) using water was around 0.075 at the highest flow rate used in the 3D model experiments (i.e. 360 cm³/h). This is below unity and hence the flow through these packs has been in the creep flow regime (Chapter 2; Section 2.4) in which Darcy equation (Equation 8.2) applies. Moreover, the values of the flow of the Reynolds number during the flow of the polymer solutions would be always below this value (up to the flow rate of 360 cm³/h) since the viscosity of the polymer solutions is higher than that of water.

The pressure measurements at steady-state during the flow of solvent before and after polymer solutions flow at different flow rates are listed in Tables (A.9) and (A.10) in Appendix-A for the 1000 ppm CPAM in water and the 500 ppm PAM in water solutions respectively. The permeability of each pack before any polymer solution flow (k_before) was obtained from the plot of ΔP versus Q_w before polymer solution flow through the pack. These plots are shown in Figure (8.11) for the packs used in the flow experiments of the 1000 ppm CPAM in water and the 500 ppm PAM in water. The permeabilities of the two packs used in the flow experiments of the 1000 ppm CPAM in water and the 500 ppm PAM in water have been calculated from slopes of the ΔP versus Q_w, which are shown in Figure (8.11) from the equation of the best line fit in both cases; giving rise to permeability values of 38 µm² and 101 µm² for the packs used in the 1000 ppm CPAM in water and the 500 ppm PAM in water experiments, respectively. This difference might have been because of the random packing of the glass beads being in the range of 212 µm and 250 µm.
Figure (8.11): $\Delta P$ versus $Q_w$ before the flow of the polymer solutions through the glass bead packs. The equations of the best line fit are shown in the figure for each case.

Figure (8.12): Pressure behaviour during the flow of the 1000 ppm CPAM in water through the 3D model at different polymer solution flow rates.
The behaviour of pressure recorded during the flow of the 1000 ppm CPAM in water and the 500 ppm PAM in water solutions are shown in Figures (8.12) and (8.13), respectively. It can be observed that the 1000 ppm CPAM in water solution has reached almost steady-state values at the different flow rates. On the other hand, the 500 ppm PAM in water solution has reached a steady-state pressure values at the two lower flow rates ($Q_p$ of 60 and 120 cm$^3$/h), but it can be observed that the pressure at the higher flow rate (240 cm$^3$/h) is increasing without fully leveling off even after about 3.2 pore volumes of polymer have been injected through the pack. This behaviour above a critical shear rate has been observed by several investigators during the flow of high molecular weight polymer solutions through porous media (Ogrunberu and Asghari, 2006; Szabo, 1972; Zitha et al, 2001; Zaitoun and Chauveteau, 1998; Zitha et al, 1995; Dominguez and Willhite, 1977; Szabo, 1975; Chauveteau and Kohler, 1974). Some of these studies have attributed this steady increase of pressure with time of flow to the dynamic formation of polymer multilayers (Szabo, 1972), decrease of accessible pore volume due to mechanical entrapment (Dominguez and Willhite, 1977; Szabo, 1975), bridging-adsorption (Zaitoun and Chauveteau, 1998), and flow-induce adsorption (Zitha et al., 1998). The possible cause of such pressure behaviour in this study
will be explained after the discussion of the mobility and permeability reduction results from the two packs.

![Graph showing the mobility and permeability reduction results from the two packs.](image)

**Figure (8.14):** The mobility reduction ($R_m$) of the 1000 ppm CPAM in water and the 500 ppm in water is shown during the flow of these polymer solutions through the 3D models at three polymer solution flow rates ($Q_p$). The permeability reduction ($R_k$) values are shown after every polymer solution flow rate in the two cases. The errors in these parameters are shown by the error bars at each point.

The mobility reduction ($R_m$) values during the flow of the 1000 ppm CPAM in water solution and the 500 ppm PAM in water solution at three different solution flow rates ($Q_p = 60, 120$ and $240$ cm$^3$/h) are shown in Figure (8.14). It can be observed that the mobility reduction values have steadily decreased from 51 at solution flow rate of 60 cm$^3$/h to 38 at solution flow rate of 240 cm$^3$/h in the case of the 1000 ppm CPAM in water. On the other hand, the mobility reduction values have been around 100 for the lower solution flow rates of the 500 ppm PAM in water (i.e. 60 and 120 cm$^3$/h) before decreasing to 51 at the highest solution flow rate (240 cm$^3$/h). It should be noted that the pressure value used to obtain the mobility reduction at the highest solution flow rate in the case of the 500 ppm PAM in water was the pressure reading at the end of the measurements since the pressure was showing a consistent increasing trend. However, the mobility reduction values for the 500 ppm PAM in
water solution at the two lower flow rates are almost twice those calculated for the 1000 ppm CPAM in water solution at the same solution flow rates. This might have been due to the fact that the permeability of the pack used for the 500 ppm PAM in water has been 2.7 times that of the pack used for the 1000 ppm CPAM in water. Hence, the effective shear rates in the first pack might have been much lower than those in the second pack, hence giving rise to higher viscous resistance for the PAM solution (higher apparent viscosity) as compared to the CPAM solution during flow.

This general shear thinning behaviour of the flow of the above polymer solutions through the bead packs is contrary to most of the polymer solution flow studies conducted through packed materials (e.g. Chauveteau et al., 2002; Kauser et al., 1999; Zitha et al., 1998; Saez et al., 1994), which have obtained shear thickening behaviour of the polymer solutions used, as has been discussed in Chapter 3. The apparent shear thinning behaviour might has been due to the polymers becoming mechanically degraded with the increase in the flow rate. It has been found from the rheology of the 1000 ppm CPAM in water solution that it can be mechanically degraded even with simple shear system (i.e. cone-and-plate). This depends on the magnitude of the shear rate as well as the time during which the polymer molecules and/or networks are subjected to the shear. The flow through the glass beads being extensional in nature can induce such degradation at relatively low flow rates. It has been demonstrated that the molecules in the high molecular weight polymer solutions can be ruptured in the mid-point during the extensional flow regimes (Keller and Odell, 1985). Also, the higher values of shear stress during the flow through the bead packs might have prohibited the formation of sizable TEN structures that can induce the otherwise shear thickening behaviour.

The permeability reduction ($R_k$) values calculated after the flow of the 1000 ppm CPAM in water solution and the 500 ppm PAM in water solution at three different solution flow rates ($Q_p = 60, 120$ and $240 \text{ cm}^3/\text{h}$) are also shown in Figure (8.14). These values are around 1.6 after the two lower flow rates of the 1000 ppm CPAM in water solution ($Q_p$ of 60 and 120 cm$^3$/h). The permeability reduction has increased to 2.7 after the polymer solution flow at 240 cm$^3$/h. This polymer solution would be expected to induce such magnitudes of permeability reduction since it has been found to form polymer multilayers during the flow of this solution through the glass capillaries and the 2D models. On the other hand, the PAM in water solutions used in the flow through the glass capillaries and the 2D models has not shown such multilayer formation. Surprisingly, relatively high permeability reduction values after the flow of the 500 ppm PAM in water solution have been obtained after different
polymer solution flow rates. The $R_k$ value obtained at the lowest solution flow rate (i.e. $Q_p = 60 \text{ cm}^3/\text{h}$) was 4.6 increasing to 5.4 at the solution flow rate of 120 cm$^3$/h before decreasing to 4.9 after polymer solution flow rate of 240 cm$^3$/h. The permeability reduction values obtained after the flow of the 500 ppm PAM in water solution were much higher than those obtained after the flow of the 1000 ppm CPAM in water.

This is the first time in which the PAM in water solutions have induced such a significant residual resistance to the solvent flow in this study since it has not been observed in the cases of the flow of this polymer solution through the glass capillaries and the 2D model. Hence, the mechanism responsible for such an effect using the bead pack model must be different than the TENA mechanism stated above for the capillary and the 2D model, since the PAM adsorption from water on glass surfaces has been found to be weak, as has been indicated from the AFM measurements (Chapter 6). The 1000 ppm PAM in water has shown antithixotropic behaviour of from the viscosity-time curves in Chapter 5. The retention of this polymer through the bead pack must have been induced by another mechanism and not merely through the adsorption of the TEN structures (i.e. the TENA mechanism).

As discussed above, the mechanism responsible for relatively high permeability reduction induced by the flow of the 500 ppm in water solution after the flow through the glass bead pack cannot be the mere adsorption of the transient entanglement networks (i.e. the TENA mechanism). The only factor by which the bead packs differ from the glass capillaries and the 2D model is the possibility of the polymer molecules and/or aggregates being physically entrapped. Hence, a possible cause for the high permeability reduction induced by the 500 ppm in water solution as well as the 1000 ppm CPAM in water solution might have been the mechanical entrapment of the formed transient entanglement networks (TEN) in the small pores and pore throats. This requires sufficiently large TEN structures, which are comparable to the size of these small pores and pore throats. Also, the TEN structures can be forced by the hydrodynamic forces between the glass beads in the case of pores and pore throats with sizes larger than the formed TEN, as can be illustrated in Figure (8.15). The mechanism which is proposed by this study to account for the residual resistance in both cases (i.e. the flow of the 1000 ppm CPAM in water and 500 ppm in water solutions through the bead pack) we will call the transient entanglement network entrapment (TENE). Entrapment is a better description of the mechanism during the flow of polymer solutions through the bead pack and rocks since it includes both the physical entrapment and adsorption. If two polymer solutions can induce the formation of TEN structures with the same sizes (below the pore size), the polymer solution with higher adsorption strength will
have advantage in inducing higher permeability reduction, as illustrated in Figure (8.15). The higher permeability reduction in the case of the 500 ppm PAM in water as compared to the 1000 ppm CPAM in water might indicate the large contribution of mechanical entrapment of the TEN structures to the retention of the polymer solutions in porous media. Although the adsorption energy of the CPAM on glass is higher than the PAM on glass from water, the 1000 ppm CPAM in water might be mechanically degradable as has been indicated from the viscosity-time measurements of this polymer as has been discussed in Chapter 5. Hence, the size of the TEN structures in the case of the 500 ppm PAM in water might have been much larger than those formed in the 1000 ppm CPAM solution at the same flow rate. The dominance of the mechanical entrapment concluded from this study is consistent with the study of Cohen and Christ (1986), who found that adsorption contribution to the retention of polymer in porous media, is about 35% only as compared to the mechanical and hydrodynamic retention. Moreover, the consistent increase in pressure with time during the flow of the 500 ppm PAM in water through the bead pack at the highest flow rate conducted in this study (i.e. 240 cm³/h) may have been due to the formation of larger TEN structures that could have induced blockage of the smaller pores. Hence, the accessible pore volume would be consistently decreased with time of flow rate as more and more pore volume would be rendered inaccessible.

Figure (8.15): Schematic illustration of the transient entanglement network entrapment (TENE) during the flow of polymer solutions through porous media (e.g. glass bead pack), (a) polymer solution with high adsorption energy (e.g CPAM in water), (b) polymer solution, with weak adsorption energy (e.g. PAM in water). The flow direction is into the page.
In some cases, the $R_k$ was measured after leaving the 3D model locked without any flow of the solvent for a certain period. This resulted in lower values of the $R_k$ as compared to the initial values (measured just after polymer solution flow). Two examples of such cases are presented in Table (8.10) after the flow of the 500 ppm PAM in water at 60 cm$^3$/h and 240 cm$^3$/h. The permeability reduction decreased from 4.6 to 2.7 after the pack was locked without flow for 15 hours in the case of polymer solution flow at 60 cm$^3$/h. On the other hand, the permeability reduction calculated from the measurement conducted after 15 hours at no flow conditions was 2.3 decreasing from 4.9 after the flow of the polymer solution at 240 cm$^3$/h. The TENE mechanism can give a better justification to this observation. Since the mechanically entrapped networks are made up of entangled polymer chains, some of these chains can undergo a relaxation process resulting in cases of disentanglement of the weakly entangled chains. Hence, the entrapped network would be affected as a decrease of its size and hence inducing a decrease in the $R_k$ value with time.

<table>
<thead>
<tr>
<th>$Q_p$ = 60 cm$^3$/h</th>
<th>$Q_p$ = 240 cm$^3$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_k$ Initial</td>
<td>$R_k$ After 15 h</td>
</tr>
<tr>
<td>4.6</td>
<td>2.7</td>
</tr>
<tr>
<td>$R_k$ Initial</td>
<td>$R_k$ After 15 h</td>
</tr>
<tr>
<td>4.9</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Chauveteau et al. (2002) used the CPAM in 0.34 M NaCl in their flow experiments through a SiC bead pack. The CPAM used in their experiments is nominally the same polymer as that used in the current experiments. They found that this polymer shows an increasing mobility reduction with the polymer solution flow rate using dilute polymer solution. In their calculations of the effective hydrodynamic thickness (EHT), they have assumed that the residual resistance to flow is due to an adsorbed polymer layer only. They did not consider the possibility of the mechanical entrapment as the primary cause of this resistance (Sorbie, 1991; Cohen and Christ, 1986), which might have been the cause of the relatively high values of the EHT obtained even at the low polymer solution flow rates (about 0.8 µm). This value was found to increase after a critical polymer solution flow rate (shear rate) up to an EHT of about 1.8 µm. Also, the apparent EHT was found to increase with the increase in the solvent flow rate. Since the relatively high EHT obtained from their study
cannot be attributed to the formation of a monolayer, they have attributed this to the FIA mechanism, which they described to be equivalent to the AE mechanism. Regardless, their results from using the CPAM in 0.34 M NaCl can indicate some important conclusions from the viewpoint of this study.

Here, it has been found that a concentrated solution of the CPAM in 0.34 M NaCl has not shown significant formation of the TEN structures as well as not inducing any significant residual effects in the capillary and 2D flow experiments. On the other hand, the Chauveteau et al. (2002) study has shown the ability of this solution to induce a residual resistance to flow in a bead pack made of Silicon Carbide (SiC) grains using a dilute solution of CPAM in 0.34 M NaCl. This might indicate the role of elongational flow of polymer solutions through porous media. It has been found that even very dilute high molecular weight polymer solutions (in the range of few ppms) can induce a shear thickening behaviour during the flow through porous media, which has been attributed to the formation of transient entanglement networks (Torres et al., 2002; Kauser et al., 1999; Saez et al., 1994). Given the fine SiC particles (18 to 50 µm) used in the study of Chauveteau et al. (2002), it is expected that the flow was highly elongational and hence the coiled conformation of the CPAM in 0.34 M NaCl underwent a coil-stretch transition which might have promoted the formation of the TEN structures and hence the mechanical entrapments of these networks (i.e. the TENE mechanism). The sizes of the TEN structures formed under these conditions might have been comparable to the sizes of the pores and pore throats of the SiC packs. Also, the consistent increase of the pressure with time during the flow of polymer solutions after a critical polymer solution flow rate, which can be observed from their study, can be well explained using the TENE mechanism. This consistent increase in the pressure with time has been noticed also by several studies using high molecular weight polymer solutions during the flow in porous media (Ogrunberu and Asghari, 2006; Szabo, 1972; Zitha et al, 2001; Zaitoun and Chauveteau, 1998; Zitha et al, 1995; Dominguez and Willhite, 1977; Szabo, 1975; Chauveteau and Kohler, 1974). It is likely that the pore sizes in the study of Chauveteau et al. (2002) were in the range of the sizes of the TEN formed during flow at a certain polymer solution flow rate. Hence, blockage of the smaller pores could occur at sufficiently high polymer flow rates (i.e. higher TEN sizes). This blockage of the pores would induce an increase in the apparent shear rate in the remaining, accessible pores and hence the blockage of the smallest pores would in turn promote the formation of the TEN in larger sizes and hence the blockage of larger and larger pores. Hence, the consistent increase in the pressure
with time at a certain polymer solution flow rate would be observed since the accessible pore volumes would be consistently decreased. The consistent increase of pressure at a constant flow rate during the flow of polymer solutions through porous media of pore sizes in the range of the fully stretched chains has been attributed to bridging-adsorption mechanism (Zitha et al, 2001; Zaitoun and Chauveteau, 1998; Zitha et al, 1995). However, this mechanism cannot account for large residual resistances exhibited in porous media of intermediate permeabilities (where the fully stretched chains were smaller than the pore sizes). Hence, mechanisms such as the FIA have been suggested by Chauveteau et al. (2002). However, the TENE mechanism can best explain the different effects exhibited during and after the flow of the polymer solutions through porous media. Moreover, the TENE mechanism can give a new insight into the results of some previous studies regarding the polymer solution flow through porous media, as will be explained in the next chapter.

8.4 Summary and Conclusions

1. The flow through actual porous media such as rocks can be a very complex matter; hence models of porous media are used to avoid dealing with such complexities. In this study, single capillary models (1D) as well as 2D models and bead packs (3D model) were used in the flow experiments of different polymer solutions.

2. The effective hydrodynamic thickness (EHT) values obtained using the 1000 ppm CPAM in water solution flow through the glass capillaries, which were in the range of 370 to 1800 nm after the flow of the polymer solution with flow rates in the range 0.15 cm$^3$/h to 1.0 cm$^3$/h, which were much higher than the thickness of the monolayer adsorbed on glass as have been indicated from the AFM measurements using this polymer solution (thickness of 106 nm). The same multilayer formation but to lesser extent has been observed from the capillary flow measurements of the 1000 ppm PAM in water and 5000 ppm PEO in water. On the other hand, the values of the EHT from the flow of the 1000 ppm CPAM in 0.34 M NaCl through the glass capillaries have not indicated multilayer formation.

3. The flow of the 1000 ppm CPAM in water solution was found to induce detectible permeability reduction after the flow through the 2D model at different polymer solution flow rates from 9.26 to 46.32 cm$^3$/h, whereas the 1000 ppm CPAM in 0.34 M NaCl and the 500 ppm PAM in water have not been found to induce any permeability reduction.
4. The possible multilayer formation during the flow of a high molecular weight polymer solution through simple systems in which mechanical entrapment is not possible (such as the glass capillaries and the 2D model) was attributed to the transient entanglement networks adsorption (TENA) mechanism. Two main steps have to occur to induce the TENA mechanism in the flow of any polymer solution through porous systems in which mechanical entrapments is not possible: first, micron-size, gel-like, transient entanglement networks (TEN) have to be formed in sufficient sizes in the bulk of the polymer solution as a result of polymer solution flow. The second criterion is the presence of sufficient adsorption energy between these TEN structures and the solid surface so that the deposition (adsorption) of such structures can occur at the solid-liquid interface.

5. The flow of polymer solutions through porous media in which mechanical entrapment is possible, any significant permeability reduction can be attributed primarily to the mechanical entrapment of the TEN structures into the entrapment sites (small pores and pore throats and at the grain-grain interface). Multilayer adsorption in such systems can also occur provided that the adsorption energy of the polymer-solvent-surface system is sufficiently high, although the contribution of the mechanical entrapment is likely to be the most dominant factor. The mechanism proposed in this case is the transient entanglement network entrapment (TENE) which includes both the mechanical and the adsorption entrainment mechanisms.

6. It has been found that the proposed mechanisms (i.e. the TENA and the TENE) can explain many flow anomalies of the polymer solutions through porous media. These two mechanisms (especially the TENE) can give new insight of many previous studies conducted on the flow of polymer solutions through porous media.
9 CONCLUSIONS AND RECOMMENDATIONS

9.1 Introduction

In this chapter, the overall conclusions from this study will be presented. These conclusions will be used to give a new prospective of the polymer retention in porous media. The results obtained from previous studies will be explained in light of the mechanisms proposed in this study for the retention of polymers in the porous media (i.e. the TENA and TENE). Also, the parameters which can contribute for more successful application of the high molecular weight polymer solutions for water shut-off in the oil fields will be discussed. Finally, recommendations regarding further investigations, which can be conducted to give further understanding of the proposed TENE mechanism, will be proposed.

9.2 Overall Conclusions

Summary of the conclusions drawn from this study will be listed in this section. The focus here is on the experiments conducted in this study, which has been discussed starting from Chapter 5.

1. Two polymer solutions (i.e. 1000 ppm CPAM and PAM in water) used in this study have shown a significant anti-thixotropic behaviour from the rheological study using the cone-and-plate system. On the other hand, the 10000 ppm PEO in water solution showed only very slight anti-thixotropic behaviour from the viscosity-time curves. However, the 1000 CPAM in 0.34 M NaCl solution has not shown such behaviour. The anti-thixotropic behaviour has been attributed to the formation of shear-induced transient entanglement networks (TEN). The size of such networks depends on the type and charge of the polymer, molecular weight, electrolyte concentration in the solvent, polymer concentration, and the magnitude of the shear rate. The TEN structures can be diversely affected by the increase of the shear stress above a critical value for a certain system due to the mechanical degradation of the individual chains as well as the possibly present TEN structures. Hence, there is a critical shear rate above which only small TEN structures can persist due to the destruction of the large structures by the high values of shear stress. Also, the absence of an obvious anti-thixotropic behaviour for a certain
polymer solution does not exclude the possibly of the formation of the TEN but with insignificant sizes.

2. The AFM measurements have shown that the CPAM from water solution adsorbs strongly on the negatively-charged glass surfaces. The same strong adsorption of the CPAM has been observed from the 0.34 M NaCl solvent. It was observed that the effective hydrodynamic thickness (EHT) of the CPAM obtained from the AFM measurement in the case of the 0.34 M NaCl was higher than that obtained in water. This is due to the screening effect increasing with the increase in the NaCl content. This screening effect would result in more coiled polymer chains on the glass surface as well as a decrease in the attractive forces between the positively-charged polymer and the negatively-charged glass surface; hence, longer loops and tails can be formed. On the other hand, weak adsorption on the glass surfaces of both PAM and PEO from water has been observed. It took three and two days for the full surface coverage to be observed in the cases of PAM and PEO, respectively.

3. Using the Voigt model, the QCM-D measurements have shown that increasing the flow rate of the polymer solutions by five times induced a slight increase in the adsorbed layer thickness of the PEO and the CPAM on silica and gold surfaces. The thickness obtained for dilute and a semi-dilute CPAM solution at the same flow rates. Consequently, adsorption-entanglement (AE) mechanism was not concluded to be occurring as a result of the flow of semi-dilute CPAM in water solutions through the QCM-D cells.

4. The flow of the 1000 ppm CPAM in water solution through glass capillaries resulted in relatively high values of apparent EHT (several times the thickness of the monolayer obtained using the AFM). Hence, multilayer formation can be concluded as a result of the flow of the 1000 ppm CPAM through the glass capillaries. Such high values of the EHT were not obtained in the case of the 1000 ppm CPAM in 0.34 M NaCl. On the other hand, multilayer formation has been concluded from the flow of the 1000 ppm PAM and the 10000 ppm PEO in water solutions through the glass capillaries.

5. The flow of the 1000 ppm CPAM in water solution induced a significant residual resistant to the flow of the solvent through the 2D glass model. On the other hand, the 1000 ppm CPAM in 0.34 M NaCl and the 500 ppm PAM in water solutions did not induce such a significant residual resistance. The detected permeability reduction after the flow of the 1000 ppm CPAM in water solutions has been attributed to mulilayer formation in the 2D model.
6. This multilayer formation after the flow of the 1000 ppm CPAM in water solution through the glass capillaries and the 2D model has been attributed to the adsorption of the large TEN structures in the case of the 1000 CPAM in water solution. These structures have been concluded as a cause of the obvious antithixotropic behaviour of this polymer solution. The high adsorption energy of this polymer on glass from water solutions can force these structures formed during flow to be adsorbed on the inner surfaces of the glass capillaries and the 2D model.

7. The retention of the polymer in the glass bead packs (3D models) was found to be dominated by the physical entrapment of the TEN structures in the small pores and in the grain-grain contacts. The sizes of the TEN structures were speculated to grow in the range of the pore sizes; hence, blockage of the smaller pores was possible. The residual resistance to solvent flow might be due to both adsorbed polymer layers and the mechanical entrapment as in the case of the 1000 CPAM in water solution. On the other hand, the mechanical entrapment is the main mechanism in the case of the weakly adsorbing polymers such as the case of the 500 ppm PAM in water solution.

8. The adsorption of the TEN structures in the case of the flow of polymer solutions through systems, in which mechanical entrapment is not possible such as the glass capillaries and the 2D model used in the present study, is speculated by this study to be the cause of the formation of polymer multilayers at the liquid-solid interfaces. This mechanism has been called the transient-entanglement network adsorption (TENA). On the other hand, in the systems where the mechanical entrapment of the TEN structures is possible (bead packs and actual rocks); the mechanism responsible for the residual flow resistance is called the transient-entanglement networks entrapment (TENE).

9.3 Transient Entanglement Network (TEN) Entrapment

The formation and growth of the transient entanglement networks (TEN) have been found to be responsible for the anti-thixotropic behaviour of the high molecular weight polymer solutions as has been presented and discussed in Chapter 5 of this thesis. Moreover, the adsorption and the mechanical entrapment of these TEN structures have been found to be the cause of the residual resistance to the solvent flow after polymer solution injection through different models of porous media as has been discussed in Chapter 8. The measurements of the colloidal forces using AFM in the presence of polymers has been presented and discussed in Chapter 6. Using the AFM, the affinity of the polymers to adsorb on the glass surfaces has
been found to be crucial for the study of the polymer entrapment in the porous media. QCM-D measurements have been conducted in order to investigate the effect of increasing the flow rate of the polymer solution on the adsorption of the polymers on silica and gold surfaces. This has been discussed in Chapter 7.

The main conclusion of this study regarding the entrapment of the polymers in porous media is that the polymers can be entrapped in aggregates called the transient entanglement networks (TEN). In flowing systems where mechanical entrapment is not possible, entrapment by adsorption of the TEN structures can occur only if the polymer-solid attraction energy is sufficiently high. This mechanism has been called the transient entanglement networks adsorption (TENA). The results from studies of Grattoni et al. (2004), and Al-Sharji et al. (2001) have been found to be explained best by the TENA mechanism as has been discussed in Chapter 8 (Sections 8.3.1.3 and 8.3.2, respectively). On the other hand, the entrapment of the TEN by adsorption and/or mechanical entrapment can occur in porous media where mechanical entrapment is possible (i.e. bead packs and actual rocks). This mechanism has been called the transient-entanglement networks entrapment (TENE). The results from the study of Chauveteau et al. (2002) using dilute solutions of the CPAM in 0.34 M NaCl have been found to be better explained by the TENE mechanism rather that the flow-induced adsorption (FIA), which they have explained as being equivalent to adsorption-entanglement mechanism (AE). This has been discussed in Chapter 8 (Section 8.3.3). The main difference between the TENA mechanism and the AE mechanism is the order of microscopic events. In the TENA mechanism, entanglement of the polymer molecules to form the TEN structures occurs before the adsorption, whereas the reverse occurs in the AE mechanism.

Apart from the above three studies (i.e. Grattoni et al., 2004; Chauveteau et al., 2002; Al-Sharji et al., 2001) that can be explained better by the proposed mechanisms in this study (i.e. TENA and TENE), it is the belief of the author that the results from several other studies regarding the flow and retention of polymers in porous media can be better explained and understood in the light of these mechanisms (i.e. TENA and TENE). The interpretation of adsorbed polymer layers with an EHT far higher than a monolayer has been obtained in literature during the flow of polymer solutions through capillaries of different materials (Kozicki et al., 1993; Cohen and Metzner, 1982; Thomas, 1976; Kozicki et al., 1970) as has been summarized in Chapter 4 (Section 4.1.3). The results of Cohen and Metzner (1982) can be explained by the TENA mechanism since the TEN structures from the concentrated polyacrylamide solution used in their study can adsorb on the hydrophilic surfaces. However,
the adsorption energy in the case of the hydrophobic capillaries might not have been sufficient to allow the adsorption of the formed structures. The EHT of the adsorbed polymer layers ranging from 4 to 180 µm obtained during the flow of high molecular weight polymer solutions through capillaries in the study Kozicki et al. (1970) has been attributed to the adsorption-gel (AG) mechanism. However, the microscopic source of these multilayers was not explained. It is the belief of the author that these layers might have been caused by the adsorption of the TEN structures formed during the flow of the polymer solutions. The transition from the AG formation to the slip effect above a critical shear stress from their results correlates the criticality of the shear thickening behaviour of the 1000 ppm CPAM in water solution in Chapter 5. Also, the critical capillary diameter below which no AG formation was obtained by Kozicki et al. (1970), which was independent of the polymer solution concentration, might have been due to the high magnitudes of shear stress in the narrow capillaries (i.e. shear stress already above the critical value). Moreover, the larger TEN structures formed in the higher concentrations of the polymer solutions used in their study might explain the higher EHT obtained for the higher polymer concentrations using the same capillary diameter. Also, the adsorption of the TEN structures formed during the flow of very dilute polymer solutions through glass capillaries in the study of Kozicki et al. (1993) might explain the AG layers, as these structures can be formed even for such dilute solutions, which was concluded by the visualization study of Vrahopolou and McHugh (1987).

The interpretation of polymer multilayers, formed during the flow of high molecular weight polymer solutions through different porous media was concluded by several studies (e.g. Ogunberu and Asghari, 2006; Asghari, 2004; Chauveteau et al., 2002; Zitha et al., 1998; Kozicki et al., 1988; Thomas, 1976; Szebo, 1975; Szebo, 1972; Kozicki et al., 1967). These studies concluded the existence of adsorbed polymer multilayer as a result of the flow of dilute solutions of high molecular weight polymers. However, Szebo (1975) has attributed part of the residual resistance to the mechanical entrapment of the polymer in the narrow pores and pore throats, which was supported by the study of Thomas (1976). Hence, the bridging-adsorption (BA) mechanism was proposed by several studies as a mechanism for polymer entrapment in low permeability porous media in which the pores and pore throats were in the range of the fully extended polymer chains (Zitha et al., 2001; Zaitoun and Chauveteau, 1998; Zitha et al., 1995). However, Chauveteau et al. (2002) have proposed the flow-induced adsorption (FIA) mechanism to account for the residual flow resistance of solvents flowing through silicon carbide (SiC) porous medium with pores and pore throats of
sizes larger than the fully extended polymer molecules (i.e. bridging-adsorption mechanism was not possible). Also, Chauveteau et al. (2002) have listed several observations regarding some flow studies, which previously proposed the BA mechanism. These observations could not be fully explained by the BA mechanism, which was the motivation for proposing the new mechanism (i.e. the FIA) in their work. The FIA explained in their study was the same as the adsorption-entanglement mechanism (AE) previously explained by Hikmet et al. (1985). The same mechanism (i.e. the FIA) has been investigated by Asghari (2004) and Ogunberu and Asghari (2006). From the view point of this study, the AE mechanism (and the FIA as proposed by Chauveteau et al., 2002) proposed to account for the formation of polymer multilayers is giving an ideal picture, which stay short of explaining the real and complex picture of the flow and retention of polymers in porous media. The main assumption which gave the interpretation of thick, adsorbed, polymer multilayer in porous media was that mechanical entrapment was not possible as the dimensions of the pores and pore throats were larger than the fully extended polymer chains. This assumption can be proven unrealistic since it has been found that mechanical and hydrodynamic entrapment can account for about 65% of the overall polymer retention even in a porous media of medium permeability (Cohen and Christ, 1986). Also, making the same approach of this study (i.e. comparing the flow of polymer solutions through capillaries and packed beds), one can conclude that the interpretation of super-micron EHT in the case of packed beds in some studies was due to lumping the adsorption and mechanical entrapment mechanisms in the adsorption effect only. The is evident if one compares the EHT values obtained from the study of Thomas (1976) and from the studies of Asghari (2004) and Ogunberu and Asghari (2006) using comparable polymer solutions of anionic polyacrylamide. Thomas (1976) measured values of EHT of the adsorbed polymer layers in the range of 0.2 to 0.3 µm using flow through glass capillary bundles. On the other hand, Asghari (2004) and Ogunberu and Asghari (2006) interpreted adsorbed polymer layers of EHT in the range of 1 to 11 µm from the flow of similar polymer solutions through sand packs.

The more realistic mechanisms of adsorption and entrapment of the TEN structures (i.e. TENA and TENE) proposed by this study can explain the residual resistance to solvent flow depicted as being adsorbed multilayers by the studies mentioned above. The high residual resistance to solvent flow after polymer solution flow through porous media can be explained by the adsorption and/or the mechanical entrapment of the TEN structures. The mechanical entrapment in the porous media is possible only if the sizes of the TEN structures

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formed during flow of the polymer solutions are large enough to be entrapped. Deminguez and Willhite (1977) found that the mechanical retention was more pronounced (i.e. higher flow resistance) in the second section of the core which was just after the entrance section. This can be understood in light of the results of Chin et al. (1989), who concluded the formation of fully elongated polymer chains after enough periodic extension of polymer molecules. Hence, the formation of larger TEN structures can be observed only after a certain length along the porous medium for certain polymer solutions. The decrease in retention in the subsequent section (i.e. after the second section) observed in their study can be attributed to the mechanical degradation of the TEN structures and/or individual chains especially after the partial blockage of the previous section, which can induce an increase in the shear stress. This can be further explained by the results obtained by Szabo (1975), who concluded that the polymer retention decreased exponentially from the inlet to the outlet of the core which has been investigated using two different concentrations (1200 and 600 ppm) as shown in Figure (9.1). This decrease in polymer retention can be explained by the decrease of the sizes of the formed TEN structures by the mechanical degradation with the time of flow (i.e. distance from the inlet). The sizes of the structures formed were higher in the case of the higher concentration (i.e. 1200 ppm) compared to those from the lower concentration curve at the same core distance from the inlet. It can be speculated that the TEN sizes using the 1200 ppm polymer solution at a distance of 9 cm from the inlet were the same TEN sizes at the inlet (distance of 0) using the 600 ppm solution. It should be observed that the curve of the 600 ppm solution starting from the inlet identically fits the 1200 ppm curve starting from the distance of 9 cm as drawn in Figure (9.1).

Other observations such as the vague hydrodynamic retention mechanism (Sorbie, 1991) can be explained and comprehended more clearly by the mechanism proposed in this study (i.e. the TENE). Figure (9.2) obtained from the study of Chauveteau and Kohler (1974) will be used as an example of how the TENE can give a better understanding of the hydrodynamic retention of the polymers in porous media. The hydrodynamic retention during the flow of the polymer solution through porous media is the migration and accumulation of the polymer in the stagnant areas. Figure (9.2) below indicates that the polymer concentration decreased at the time at which the flow rate was increased from 3 m/day to 10.3 m/day. At the flow rate of 10.3 m/day, the polymer concentration measured at the outlet initially decreased before increasing to its initial value. It is speculated that the increase in the flow rate of the polymer induced an increase of the sizes of the TEN structures in the polymer
solution and the subsequent migration of these structures to the stagnant areas of the porous media in which they may underwent a relaxation process (i.e. disentanglement). The process of formation and relaxation of the TEN structures can reach a steady state after a certain time, which resulted in the increase of the polymer concentration at the outlet to its initial value. The decrease of the flow rate to its initial value (i.e. 3 m/day) induced an increase of the polymer concentration followed by a decrease to its initial value. The increase of the concentration is expected to be due to the migration of the hydrodynamically trapped polymer to the main polymer stream and hence appearing at the outlet. Another observation from Figure (9.2) is the effect of the increase of the polymer solution flow rate on the measured mobility reduction ($R_m$). The steady state $R_m$ value at the higher flow rate is lower than that at the lower flow rate in the initial stage. In the last stage, the $R_m$ value regained its initial value at the flow rate of 3 m/day. It decreased to lower values after 8 days and 30 minutes break periods. This can be explained by the effect of the disentanglement of the outer parts of the entrapped TEN structures with time as has been experimentally obtained in this study (Chapter 8, Section 8.3.3).
9.4 Use of Polymer Solutions for Water Shut-off/Conformance

The disproportionate permeability reduction (DPR) induced by the flow of polymer solutions through porous media has been described in Chapter 1. This effect is used to reduce water production from an oil well without affecting the oil production. This technology is called water shut-off or conformance. In this study, transient-entanglement networks entrapment (TENE) has been proposed as the mechanism responsible for inducing the DPR effect. The presence of very thick adsorbed polymer layers on the pore surfaces and/or the blockage of the smaller pores would reduce the pore diameters as well as reducing the accessible pore volume. Consequently, water flow would be greatly restricted since water is flowing on the surface of the pores and through the smaller pores in a water-wet medium. On the other hand, slight effect to the oil phase would be induced by the TENE mechanism since oil is flowing in the middle of the larger pores. This supports the segregated oil and water pathways justification from the DPR effect (Nilsson et al., 1998; Liang and Seright, 1997; Liang et al., 1995). However, steric and lubrication effect, wettability change, and polymer layer swelling and shrinking discussed in Chapter 1, might cause the DPR effect in combination with the segregated oil and water pathways.

The DPR effect of a certain polymer solution should be optimized to cause significant reduction in water production without affecting the oil production. Hence, the sizes of the
TEN structures formed during flow of the polymer solution should be optimized. Moreover, the polymer/surface system should provide sufficient adsorption energy for these structures to be adsorbed and/or entrapped. The parameters affecting the TENE mechanism can be categorized into the following classes:

1. **Polymer solution:** This includes polymer type, charge, molecular weight, solvent quality and salt content, and polymer concentration. Generally, it is speculated that the sizes of the TEN structures increase with the polymer charge, molecular weight, and polymer concentration. Charged polymers are more extended in good solvents, which enhance the formation of the TEN structures. However, the interaction between the polymer chains will be hindered due to the electrostatic repulsion between the chains. Hence, the salt content in the solvent should be optimized to screen the charged polymers without losing much of the extended conformation of the polymer chains in the solution.

2. **Reservoir properties:** The degree of the DPR effect can be a function of the pore sizes and pore-size distribution of the porous media (i.e. permeability). The TEN structures formed under certain conditions can cause complete blockage of the low-permeability porous media. On the other hand, partial blockage can occur in the case of medium- to high-permeability porous media. Also, the temperature of the formation can affect the properties of the polymer solution and hence the formation and entrapment of the TEN structures. Moreover, the mixing between the polymer solution and the reservoir brine can affect the properties of the polymer solution and hence the degree of the DPR effect.

3. **Surface chemistry:** This is part of the reservoir properties but due to its importance it is listed separately. The surface chemistry and wettability can affect the adsorption stage of the TENE mechanism. The charge of the surface should be opposite the charge of the polymer in order to provide sufficient electrostatic attraction force for the TEN structures to be adsorbed (Mennella et al., 1999). It should be taken into consideration that the salt content intended to enhance the formation of the TEN structures can screen the surface charge as well and hence it may reduce the adsorption affinity of these structures. On the other hand, the presence of multivalent salt ions was found to enhance the adsorption of the polymer solution by bridging between the charged polymer chains and the charged surface (Needham et al., 1974; Mennella et al., 1999).

4. **Flow rate:** It has been observed in this study that the increase in the flow rate of the polymer solution would increase the size and persistence of the TEN structures. However, there is a critical upper limit for the flow rate above which the related stress would cause the destruction of any formed structures. In the application of the polymer solution for the
water shut-off, two criteria are important: the size and the persistence of the TEN structures, and the depth of the penetration. The degradability of the polymer by flow should be closely investigated since it would determine the effectiveness of the application (i.e. the depth of penetration). Moreover, the flow rates of oil and water during production may affect the degree of the DPR effect causing the DPR effect to be diminished at the high flow rates (Ganguly et al., 2003). Hence, these flow rates during production should be optimized to give the best DPR application.

Two of the above parameters for water conformance application are out of control: reservoir properties and surface chemistry. On the other hand, the polymer solution with certain properties can be applied at an optimized flow rate to obtain the best DPR effect. It is believed that the understanding of the polymer entrapment by the TENE mechanism proposed in this study will help in conducting more successful field applications of the polymer solutions for water conformance. Moreover, the field application of the polymer solutions in chemical flooding will benefit tremendously from such an understanding.

9.5 Recommendations

The adsorption and entrapment of the transient entanglement networks (TEN) proposed in this study for the first time need further investigations using various polymer-solid systems. Here, several suggestions for such investigations will be listed in order to further examine and understand the mechanisms proposed in this mechanism (i.e. the TENA and the TENE):

1. Visualization using techniques such as birefringence and dichroism in order to follow the formation and growth of the TEN structures during flow in the bulk polymer solutions used in this study. The effect of polymer concentration, solvent quality and electrolyte content on the formation and sizes of the TEN structures can be investigated and visually quantified.

2. Visualization techniques of the events at the liquid-solid interfaces such as neutron reflectometry, infrared flow cells, and ellipsometry can be implemented to probe the adsorption of the TEN structures during the flow of the polymer solutions.

3. The above visualization techniques can be used during the flow of the polymer solutions through simple capillaries, sinusoidal channels, and 2D models. The elongational flow can be controlled in the sinusoidal and 2D models by controlling the ratio of diameters of the pores and pore-throats.
4. Different polymers with solvents of different qualities can be used to test the formation and the growth of the sizes of the TEN structures during flow at a constant flow rate. Polyelectrolytes are the proper candidates for such an investigation. Since the formation of the TEN structures depends on the conformation of the polymer chains in solution, the conformation of the polyelectrolytes can be controlled by the changing the salt content. In order to compare between the different polymer solutions with different salt contents, the polymer concentrations should be multiples (or fractions) of the overlap concentration (c*). Also, the effect of the molecular weight on the formation of the TEN structures should be investigated. Narrowly distributed polymer can be implemented in such an investigation.

5. Since the formation and growth of the TEN structures is affected by the hydrodynamic forces in the flow systems, special attention should be given to study the migration of particles in certain flow systems. Also, the adsorption and entrapment of the TEN structures might be affected (either positively or negatively) by the migration of these structures in a certain flow field.

6. The mechanical degradation of the high molecular weight polymer solutions should be thoroughly investigated under various flow conditions since the formation and size of the TEN structures can be adversely affected in the case of mechanically degradable polymers.

7. The affinity of the different polymers to adsorb on a certain solid surface can be investigated using the AFM technique in order to measure the colloidal forces in the presence of the polymer solution using different solvents. This has been found to be critical in the adsorption and entrapment of the TEN structures.

8. After the formation of the TEN structures in the bulk of a certain polymer solution has been visualized and the size of these structures has been quantified, as well as the adsorption of the polymer on a certain surface has been characterized, the effect of the polymer solution during the flow through 3D models of different grain sizes, permeability, and heterogeneity can be more deeply understood in the context of the adsorption and/or mechanical entrapment of the TEN structures. Moreover, the residual resistance should be investigated at different time intervals (up to months) after the flow of the polymer solution in order to study the disentanglement mechanism of these structures and hence a possible decrease of the residual resistance to flow.

9. The synthesis of new polymers, which can provide successful application in the oil fields for water conformance, should be conducted in light of the new understanding of the
TENE mechanism. These polymers should produce stable TEN structures under optimum flow conditions. Also, they should be resistant to mechanical degradation and stable under the reservoir pressure and temperature.
APPENDIX-A: PRESSURE AND TEMPERATURE DATA FROM THE CAPILLARY, 2D, AND 3D MODEL EXPERIMENTS

A.1 Capillary Flow Measurements

Table (A.1): The steady-state pressure drop (kPa) recorded during the flow of the polymer solutions through the glass capillaries.

<table>
<thead>
<tr>
<th>$Q_w$ (cm$^3$/h)</th>
<th>1000 ppm CPAM in water</th>
<th>1000 ppm CPAM in NaCl</th>
<th>1000 ppm PAM in water</th>
<th>5000 ppm PEO in water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta P$ (kPa)</td>
<td>$\Delta P$ (kPa)</td>
<td>$\Delta P$ (kPa)</td>
<td>$\Delta P$ (kPa)</td>
</tr>
<tr>
<td>0.15</td>
<td>4.438</td>
<td>1.092</td>
<td>3.381</td>
<td>8.359</td>
</tr>
<tr>
<td>0.3</td>
<td>6.371</td>
<td>1.971</td>
<td>-</td>
<td>14.006</td>
</tr>
<tr>
<td>0.6</td>
<td>9.916</td>
<td>3.607</td>
<td>8.307</td>
<td>24.713</td>
</tr>
<tr>
<td>1</td>
<td>14.766</td>
<td>5.800</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.5</td>
<td>15.939</td>
<td>8.232</td>
<td>15.943</td>
<td>50.723</td>
</tr>
<tr>
<td>3</td>
<td>37.293</td>
<td>-</td>
<td>-</td>
<td>51.071</td>
</tr>
</tbody>
</table>

Table (A.2): The steady-state pressure drop (kPa) recorded during solvent flow after the flow of the 1000 ppm CPAM in water solution through the glass capillaries at different solution flow rates. The temperature values at which these measurements have been conducted are listed.

<table>
<thead>
<tr>
<th>$Q_w$ (cm$^3$/h)</th>
<th>$Q_p$ = 0.15 cm$^3$/h</th>
<th>$Q_p$ = 0.3 cm$^3$/h</th>
<th>$Q_p$ = 0.6 cm$^3$/h</th>
<th>$Q_p$ = 1.0 cm$^3$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta P$ (kPa)</td>
<td>$T$ ($^\circ$C)</td>
<td>$\Delta P$ (kPa)</td>
<td>$T$ ($^\circ$C)</td>
</tr>
<tr>
<td>0.15</td>
<td>0.519</td>
<td>22.0</td>
<td>0.592</td>
<td>22.8</td>
</tr>
<tr>
<td>0.6</td>
<td>1.872</td>
<td>22.1</td>
<td>1.945</td>
<td>23.0</td>
</tr>
<tr>
<td>1.5</td>
<td>4.588</td>
<td>22.2</td>
<td>4.465</td>
<td>23.0</td>
</tr>
<tr>
<td>$b_{before}$ ($\mu$m)</td>
<td>46.92</td>
<td>46.76</td>
<td>47.34</td>
<td>44.46</td>
</tr>
</tbody>
</table>
Table (A.3): The steady-state pressure drop (kPa) recorded during solvent flow after the flow of the 1000 ppm CPAM in 0.34 M NaCl solution through the glass capillaries at different solution flow rates. The temperature values at which these measurements have been conducted are listed.

<table>
<thead>
<tr>
<th>$Q_w$ (cm$^3$/h)</th>
<th>$Q_p = 0.15$ cm$^3$/h</th>
<th>$Q_p = 0.6$ cm$^3$/h</th>
<th>$Q_p = 1.5$ cm$^3$/h</th>
<th>$Q_p = 3.0$ cm$^3$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta P$ (kPa)</td>
<td>$T$ (°C)</td>
<td>$\Delta P$ (kPa)</td>
<td>$T$ (°C)</td>
</tr>
<tr>
<td>0.15</td>
<td>0.429</td>
<td>20.8</td>
<td>0.385</td>
<td>21.0</td>
</tr>
<tr>
<td></td>
<td>0.401</td>
<td>21.5</td>
<td>0.426</td>
<td>21.0</td>
</tr>
<tr>
<td>0.6</td>
<td>1.545</td>
<td>21.0</td>
<td>1.499</td>
<td>21.1</td>
</tr>
<tr>
<td></td>
<td>1.534</td>
<td>21.6</td>
<td>1.469</td>
<td>21.7</td>
</tr>
<tr>
<td>1.5</td>
<td>3.602</td>
<td>21.1</td>
<td>3.574</td>
<td>21.2</td>
</tr>
<tr>
<td></td>
<td>3.644</td>
<td>21.6</td>
<td>3.571</td>
<td>21.9</td>
</tr>
<tr>
<td>3</td>
<td>7.297</td>
<td>21.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$b_{before}$ (µm)</td>
<td>52.33</td>
<td>52.56</td>
<td>52.20</td>
<td>52.89</td>
</tr>
</tbody>
</table>

Table (A.4): The steady-state pressure drop (kPa) recorded during solvent flow after the flow of the 1000 ppm PAM in water solution through the glass capillaries at different solution flow rates. The temperature values at which these measurements have been conducted are listed.

<table>
<thead>
<tr>
<th>$Q_w$ (cm$^3$/h)</th>
<th>$Q_p = 0.15$ cm$^3$/h</th>
<th>$Q_p = 0.6$ cm$^3$/h</th>
<th>$Q_p = 1.5$ cm$^3$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta P$ (kPa)</td>
<td>$T$ (°C)</td>
<td>$\Delta P$ (kPa)</td>
</tr>
<tr>
<td>0.15</td>
<td>0.454</td>
<td>22.6</td>
<td>0.419</td>
</tr>
<tr>
<td></td>
<td>0.426</td>
<td>21.7</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>1.476</td>
<td>22.7</td>
<td>1.414</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>3.456</td>
<td>22.9</td>
<td>3.457</td>
</tr>
<tr>
<td></td>
<td>3.595</td>
<td>21.7</td>
<td></td>
</tr>
<tr>
<td>$b_{before}$ (µm)</td>
<td>51.14</td>
<td>51.47</td>
<td>51.10</td>
</tr>
</tbody>
</table>
Table (A.5): The steady-state pressure drop (kPa) recorded during solvent flow after the flow of the 5000 ppm PEO in water solution through the glass capillaries at different solution flow rates. The temperature values at which these measurements have been conducted are listed.

<table>
<thead>
<tr>
<th>$Q_w$ (cm$^3$/h)</th>
<th>$Q_p = 0.15$ cm$^3$/h</th>
<th>$Q_p = 0.3$ cm$^3$/h</th>
<th>$Q_p = 0.6$ cm$^3$/h</th>
<th>$Q_p = 1.5$ cm$^3$/h</th>
<th>$Q_p = 3.0$ cm$^3$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta P$ (kPa)</td>
<td>$T$ ($^\circ$C)</td>
<td>$\Delta P$ (kPa)</td>
<td>$T$ ($^\circ$C)</td>
<td>$\Delta P$ (kPa)</td>
<td>$T$ ($^\circ$C)</td>
</tr>
<tr>
<td>0.15</td>
<td>0.414 22.1</td>
<td>0.501 21.4</td>
<td>0.526 21.4</td>
<td>0.509 20.9</td>
<td>0.502 21.0</td>
</tr>
<tr>
<td>0.6</td>
<td>1.729 21.6</td>
<td>1.855 21.6</td>
<td>1.857 21.7</td>
<td>1.937 21.2</td>
<td>1.925 21.2</td>
</tr>
<tr>
<td>$b_{\text{before}}$ ($\mu$m)</td>
<td>49.25</td>
<td>48.66</td>
<td>48.87</td>
<td>48.39</td>
<td>48.91</td>
</tr>
</tbody>
</table>

A.2 2D Model Flow Measurements

Table (A.6): The steady-state pressure drop (kPa) recorded before the 1000 ppm CPAM in water flow through the 2D model at different solvent flow rates. The steady-state pressure values are listed also after polymer flow through the 2D model at different solution flow rates. The average temperature values during the measurements are listed.

<table>
<thead>
<tr>
<th>$Q_w$ (cm$^3$/h)</th>
<th>Before</th>
<th>$Q_p$ (cm$^3$/h)</th>
<th>9.26</th>
<th>18.53</th>
<th>27.79</th>
<th>37.06</th>
<th>46.32</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta P$ (kPa)</td>
<td>$\Delta P$ (kPa)</td>
<td>$\Delta P$ (kPa)</td>
<td>$\Delta P$ (kPa)</td>
<td>$\Delta P$ (kPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.26</td>
<td>0.870</td>
<td>1.065</td>
<td>1.088</td>
<td>1.218</td>
<td>0.999</td>
<td>1.030</td>
<td></td>
</tr>
<tr>
<td>18.53</td>
<td>1.750</td>
<td>1.896</td>
<td>1.892</td>
<td>2.150</td>
<td>1.954</td>
<td>2.006</td>
<td></td>
</tr>
<tr>
<td>27.79</td>
<td>2.584</td>
<td>2.794</td>
<td>2.772</td>
<td>3.133</td>
<td>2.855</td>
<td>2.871</td>
<td></td>
</tr>
<tr>
<td>37.06</td>
<td>3.455</td>
<td>3.657</td>
<td>3.554</td>
<td>4.034</td>
<td>3.779</td>
<td>3.737</td>
<td></td>
</tr>
<tr>
<td>$T_{\text{average}}$ ($^\circ$C)</td>
<td>20.2</td>
<td>21.3</td>
<td>21.4</td>
<td>21.6</td>
<td>21.9</td>
<td>21.8</td>
<td></td>
</tr>
</tbody>
</table>
Table (A.7): The steady-state pressure drop (kPa) recorded before the **1000 ppm CPAM in 0.34 M NaCl** flow through the 2D model at different solvent flow rates. The steady-state pressure values are also listed after polymer flow through the 2D model at different solution flow rates. The average temperature values of the measurements are listed.

<table>
<thead>
<tr>
<th>$Q_w$ (cm$^3$/h)</th>
<th>Before</th>
<th>$Q_p$ (cm$^3$/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9.26</td>
<td>18.53</td>
</tr>
<tr>
<td>$\Delta P$ (kPa)</td>
<td>0.936</td>
<td>0.885</td>
</tr>
<tr>
<td>$\Delta P$ (kPa)</td>
<td>1.775</td>
<td>1.759</td>
</tr>
<tr>
<td>$\Delta P$ (kPa)</td>
<td>2.569</td>
<td>2.633</td>
</tr>
<tr>
<td>$\Delta P$ (kPa)</td>
<td>3.425</td>
<td>3.333</td>
</tr>
<tr>
<td>$\Delta P$ (kPa)</td>
<td>4.255</td>
<td>4.190</td>
</tr>
<tr>
<td>$T_{average}$ (°C)</td>
<td>20.3</td>
<td>20.9</td>
</tr>
</tbody>
</table>

Table (A.8): The steady-state pressure drop (kPa) recorded before the **500 ppm PAM in water** flow through the 2D model at different solvent flow rates. The steady-state pressure values are also listed after polymer flow through the 2D model at different solution flow rates. The average temperature values of the measurements are listed.

<table>
<thead>
<tr>
<th>$Q_w$ (cm$^3$/h)</th>
<th>Before</th>
<th>$Q_p$ (cm$^3$/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9.26</td>
<td>18.53</td>
</tr>
<tr>
<td>$\Delta P$ (kPa)</td>
<td>0.870</td>
<td>0.787</td>
</tr>
<tr>
<td>$\Delta P$ (kPa)</td>
<td>1.750</td>
<td>1.662</td>
</tr>
<tr>
<td>$\Delta P$ (kPa)</td>
<td>2.584</td>
<td>2.553</td>
</tr>
<tr>
<td>$\Delta P$ (kPa)</td>
<td>3.469</td>
<td>3.383</td>
</tr>
<tr>
<td>$\Delta P$ (kPa)</td>
<td>4.207</td>
<td>4.170</td>
</tr>
<tr>
<td>$T_{average}$ (°C)</td>
<td>22.3</td>
<td>22.4</td>
</tr>
</tbody>
</table>
### A.3 3D Model Flow Measurements

Table (A.9): The steady-state pressure drop (kPa) recorded at different solvent flow rates before the flow of the 1000 ppm CPAM in water through the 3D model. The steady-state pressure values are also listed after polymer flow through the 2D model at different solution flow rates. The average temperature of the measurements was 20°C.

<table>
<thead>
<tr>
<th>$Q_w$ (cm$^3$/h)</th>
<th>Before</th>
<th>$Q_p$ (cm$^3$/h)</th>
<th>$\Delta P$ (kPa)</th>
<th>$\Delta P$ (kPa)</th>
<th>$\Delta P$ (kPa)</th>
<th>$\Delta P$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>120</td>
<td>240</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.169</td>
<td>0.255</td>
<td>0.375</td>
<td>0.576</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>0.326</td>
<td>0.510</td>
<td>0.757</td>
<td>0.899</td>
<td></td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>0.659</td>
<td>1.098</td>
<td>1.041</td>
<td>1.767</td>
<td></td>
<td></td>
</tr>
<tr>
<td>360</td>
<td>0.992</td>
<td>1.686</td>
<td>1.517</td>
<td>2.658</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table (A.10): The steady-state pressure drop (kPa) recorded at different solvent flow rates before the flow of the 500 ppm PAM in water through the 3D model. The steady-state pressure values are also listed after polymer flow through the 2D model at different solution flow rates. The average temperature of the measurements was 20°C.

<table>
<thead>
<tr>
<th>$Q_w$ (cm$^3$/h)</th>
<th>Before</th>
<th>$Q_p$ (cm$^3$/h)</th>
<th>$\Delta P$ (kPa)</th>
<th>$\Delta P$ (kPa)</th>
<th>$\Delta P$ (kPa)</th>
<th>$\Delta P$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>120</td>
<td>240</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Initial</td>
<td>After 15 h</td>
<td>120</td>
<td>Initial</td>
<td>After 15 h</td>
</tr>
<tr>
<td>60</td>
<td>0.070</td>
<td>0.284</td>
<td>0.189</td>
<td>0.323</td>
<td>0.539</td>
<td>0.127</td>
</tr>
<tr>
<td>120</td>
<td>0.119</td>
<td>0.549</td>
<td>0.316</td>
<td>0.657</td>
<td>0.578</td>
<td>0.314</td>
</tr>
<tr>
<td>240</td>
<td>0.241</td>
<td>1.176</td>
<td>0.630</td>
<td>1.401</td>
<td>1.152</td>
<td>0.588</td>
</tr>
<tr>
<td>360</td>
<td>0.378</td>
<td>1.686</td>
<td>1.012</td>
<td>1.980</td>
<td>1.882</td>
<td>0.833</td>
</tr>
</tbody>
</table>
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