

Imperial College London

**Conformation of cellulose-based
polyelectrolytes and development of
microflow scattering approaches.**

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Declaration of Originality

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Abstract

The work reported on this thesis is primarily a small angle neutron scattering (SANS) and rheology study of cellulose derivative polyelectrolyte Sodium Carboxymethyl Cellulose (NaCMC) in aqueous solutions. We measure, for the first time using SANS, the relevant structural length scales as a function of polymer (c_p) in aqueous salt free and NaCl solutions. The intrinsic persistence length is measured by SANS to be 55 Å, characteristic of a semiflexible polymer. In salt free solutions, the correlation length is found to scale as $c_p^{-1/2}$ across the entire semi-dilute and concentrated range. Both SANS and viscosity measurements are in general agreement with scaling theory predictions for flexible polyelectrolytes in salt free solution. The crossover between the semidilute and concentrated regimes cannot be explained as arising from the overlapping of correlation and electrostatic blobs, and appears to relate to the intrinsic persistence length of the polymer. As expected, the addition of salt leads to a decrease in viscosity and an increase in the correlation length. Flexible scaling theory cannot describe the variation of these two quantities accurately, as it neglects the intrinsic rigidity of the chains. The scaling picture put forward by Odijk appears to be correct in the high salt limit, although it suffers from several approximations, namely the use of a simplified expansion factor and an inaccurate expression for the excluded volume. Once these are corrected, theory and experiment show good agreement. We finally report the combination of SANS with microfluidics, which is a useful technique to probe the soft matter dynamics under flow, and illustrate it with well-known strongly scattering liquid crystal systems, quantifying alignment through a contraction-expansion flow field. Different microfabrication techniques and materials are discussed in terms of their compatibility with SANS. Finally, we outline a roadmap for microfluidic SANS, enabling the spatiotemporal investigation of conformational changes under flow, focusing on low scattering systems, including NaCMC in solution.

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List of publications

1. Huang, Y. Y., Marshall, J. E., Gonzalez-Lopez, C., and Terentjev, E. M. (2011). Variation in carbon nanotube polymer composite conductivity from the effects of processing, dispersion, aging and sample size. *Materials Express*, 1(4), 315-328.
2. Watanabe, T., G. Lopez, C., Douglas, J. F., Ono, T., and Cabral, J. T. (2014). Microfluidic Approach to the Formation of Internally Porous Polymer Particles by Solvent Extraction. *Langmuir*, 30(9), 2470-2479.
3. G. Lopez, C., Watanabe, T., Martel, A., Porcar, L., and Cabral, J. T. (2015) Microfluidic-SANS: flow processing of complex fluids. *In press*. Scientific reports
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Thesis outline

Chapter one provides a basic outline of the statics and dynamics of polymers, and the three techniques used in this thesis, namely small angle neutron scattering (SANS), rheology and microfluidics. Chapters two and three describe the conformation and dynamics of sodium carboxymethyl cellulose (NaCMC) in aqueous solutions. Chapter two focuses on salt free solutions, where it is found that NaCMC behaves similarly to other synthetic and considerably more flexible polyelectrolytes, and is reasonably well described by the de Gennes-Dobrynin model for flexible polyelectrolytes. Chapter 3 deals with the effect of salt (NaCl) in NaCMC solutions, and significant deviations from theoretical predictions for flexible polyelectrolytes are found. A semiflexible polyelectrolyte theory developed by Odijk provides a better description of the viscosity data in high salt conditions. The theory is expanded to calculate the dynamic properties of polyelectrolyte solutions and to correct for a deficiency arising from some simplifications used. Given the well known flow response of complex fluids including polyelectrolyte solutions we then evaluate the possible coupling of SANS with microfluidics. Microfluidic-SANS is illustrated in chapter 4 with two highly scattering surfactant liquid crystal mixtures, where different rotations of lamellae entering and exiting a constriction are measured. A road map for the future interrogation of low scattering (including polyelectrolyte) solutions is provided. In chapter 5, we review and evaluate materials and microfabrication techniques in terms of their suitability for microfluidic devices for SANS experiments. All chapters contain a separate introduction, where the previous work on the field and the basic theory is outlined, except when this has been addressed in a previous chapter.

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List of symbols

α - expansion factor

β - binary cluster integral, subscripts hc, el and a refer to hard core, electrostatic and attractive components respectively.

$\Delta\delta^2$ - scattering contrast term

ϵ_0 - vacuum permittivity

ϵ - relative permittivity

η - kinematic viscosity

η_0 - zero shear rate viscosity

η_{rel} - relative viscosity

η_s - solvent viscosity

η_{sp} - specific viscosity

$[\eta]$ - intrinsic viscosity

γ - strain

$\dot{\gamma}$ - strain rate

κ^{-1} inverse Debye screening length

λ wavelength

ϕ_C - critical conversion fraction

ϕ - volume fraction

Π - osmotic pressure

ρ - shear stress

τ_ξ correlation blob relaxation time

τ_{rep} - reptation time

τ_R - Rouse relaxation time

τ_Z - Zimm diffusion coefficient

τ - relaxation time of a chain

θ - theta temperature

ξ_T - electrostatic blob size

ξ - correlation length

ζ_m - monomer friction coefficient

ζ - polymer friction coefficient

a - tube diameter

A - number of monomers per effective charge

A_2 - second virial coefficient
 b_p - coherent scattering length of a monomer
 b_s - coherent scattering length of a solvent molecule
 b - monomer size
 B - solvent quality or stretching parameter
 B' - Excluded volume strength
 c_D - semidilute to concentrated crossover
 c_s - salt concentration
 c_p - polymer concentration
 c^* - overlap concentration
 d_c - chain diameter
 D - diffusion coefficient of a polymer chain
 D_Z - Zimm diffusion coefficient
 $dc/d\Pi$ - osmotic compressibility
 $d\sigma / d\Sigma$ - differential scattering cross section
 De - Deborah number
 G_e - reptation time of an entanglement strand
 g_L - number of segments in a correlation blob
 g_T - number of monomers in an electrostatic blob
 G - terminal modulus
 $H(q)$ - intermolecular structure factor
 h - depth of polymerising front
 $I(q)$ - scattered intensity in cm^{-1}
 I - ionic strength
 k_B - Boltzmann constant
 k_H - Huggins coefficient
 L_{tube} - contour length of a reptation tube
 L_0 - Intrinsic persistence length
 l_B - Bjerrum length
 L_e - electrostatic persistence length
 L_K - Kuhn length
 L_T - total persistence length
 L - contour length
 M_0 - monomer molecular weight
 M_n - number average molecular weight
 M_w - weight average molecular weight
 N_A - Avogadro's number
 N_e - number of Kuhn segments in an entanglement strand
 N_p - number of particles per unit volume

N - degree of polymerisation
 n - number of chain overlaps needed to form an entanglement strand
 P_{cs} - cross sectional form factor
 $P(q)$ - form factor
 P - pitch of a helix
 p - shear thinning parameter in carreau model
 Pe - Peclet number
 q^* - peak position in scattering curve [$\text{\AA}^{-1}$]
 q - scattering vector
 $R_{ee,0}$ - End-to-end distance in the absence of excluded volume
 R_{ee} - end to end distance of a chain
 R_F - Flory radius of a chain (expanded radius in dilute solution)
 R_g - radius of gyration
 r_p^H - cross sectional radius of helix
 r_p - cross sectional radius of a polymer chain, used in modelling of scattering data.
 R^H - radius of a Helix
 R - radius of a polymer chain
 Re - Reynolds number
 S_{ij} - total structure factor
 S_{inc} - total incoherent scattering in cm^{-1}
 $S(0)$ - structure factor at zero wavevector
 S_{inc}^{pol} - incoherent scattering due to polymer in cm^{-1}
 T - temperature
 T - transmission
 v_p - volume of a monomer
 V_p - volume of a scattering particle
 v_s - volume of a solvent molecule
 v - excluded volume
 V - sample volume
 z_i - valence of species i
 z - excluded volume parameter

1 Introduction

In this chapter, we introduce the techniques used in this thesis: rheology, small angle neutrons scattering and microfluidics. A brief description of neutral polymer statics and dynamics is provided along with a more detailed review of salt free polyelectrolyte scaling theory, this discussion is expanded in chapter 3. Scattering theory is described in more detail chapter 2.

1.1 Rheology

Rheology is the study of deformation and flow of matter under the influence of a force [1]. Soft matter systems are typically viscoelastic, that is they display both solid-like and liquid like properties. Two extremes are useful when considering the viscoelastic properties of soft matter:

A **Hookean solid** shows perfectly elastic behaviour when subjected to a shear stress. When a shear stress is applied, a constant shear strain results. The constant of proportionality between the shear stress and shear strain is called the shear modulus (G),

$$\sigma = G\gamma$$

where σ is the shear stress, G is the shear modulus and γ is the shear strain.

A **Newtonian liquid** on the other hand shows a purely viscous response: an applied stress produces a constant shear strain rate. The constant of proportionality between the two quantities is referred to as the kinematic viscosity:

$$\sigma = \eta\dot{\gamma}$$

Polymer solutions, and many other systems show intermediate behaviour between these two cases. Generally, if the system is deformed on timescales shorter than its characteristic relaxation time, the material is not able to relax and it responds like a solid. In the opposite limit, when the system is deformed over very long time scales, it is always able to fully relax and its behaviour

is liquid like. The instantaneous modulus (G_0) characterises the short time elastic response and τ , the crossover time to viscous behaviour. An important scaling relation for the viscosity may be derived [3,2]:

$$\eta \sim G_0 \tau$$

while the applicability of this equation is limited [3] (it is an approximation to $\eta = \int_0^\infty G(t)dt$), it serves as a useful conceptual relation to derive later scaling laws for polymer solutions.

Non-Newtonian liquids have a viscosity that varies as a function of shear rate. Two phenomena are commonly observed for polymer (and more specifically polysaccharide solutions) are:

Shear thinning or pseudo plasticity: A typical stress vs. shear rate curve for a shear thinning material is shown in figure 1.1. At low shear rates, the fluid is Newtonian, and the stress is directly proportional to the shear rate. At higher shear rates, the curve is seen to bend downwards, indicating a decrease in the slope, the viscosity obtained from this slope is often referred to as an 'apparent viscosity'.

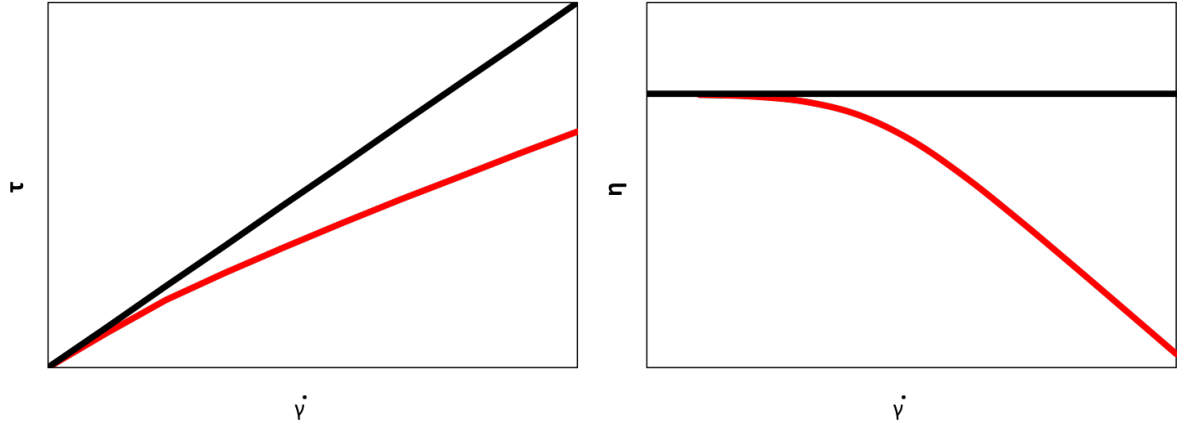


Figure 1.1: Schematic rheograms for a Newtonian (black line) and shear thinning (red line). Left: Stress vs. strain rate. Right: Viscosity vs. shear rate.

Thixotropy: Materials for which the viscosity is a function of time for a given shear rate are said to be *thixotropic*. When a thixotropic material is subjected to a constant shear, its viscosity will decrease as a function of time due to the breakdown of the fluid's structure, until it eventually reaches a constant value. Leaving the fluid to rest, as the structure rebuilds, the viscosity recovers its original value [1,4]. If the later condition is not met, and the structure

of the fluid has been changes permanently by shear, the fluids are referred to as degraded or time-dependent [1].

1.1.1 Definitions of viscosity

The kinematic viscosity (η) of a liquid has units of Pas. Several other quantities are often used in the literature. For a mixture of a polymer in a solvent, it is often assumed that the polymer contribution to the viscosity is given by $\eta - \eta_s$, where η is the viscosity of the solution and η_s is the viscosity of the solvent [2]. The relative viscosity is given by:

$$\eta_{rel} = \eta / \eta_s$$

and the specific viscosity is given by:

$$\eta_{sp} = \eta_{rel} - 1 = \frac{\eta - \eta_s}{\eta_s}$$

The intrinsic viscosity is defined as the ratio of the specific viscosity divided by the concentration (c_p) at infinite dilution. i.e.:

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c_p}$$

The relevance of the intrinsic viscosity is further discussed in chapter 3.

1.2 Introduction to polymers

1.2.1 Statics

Classes of polymers

Polymers are long chains of N monomers of length b , which in the nanometer length-scale can be defined without full consideration of their chemical structure. When dissolved, short range interactions between monomers and the configurational entropy of a chain determine its conformation. The forces between two monomers are characterised by the excluded volume, given by [2]:

$$v = \int (1 - e^{-U(\mathbf{r})/k_B T}) d^3 \mathbf{r}$$

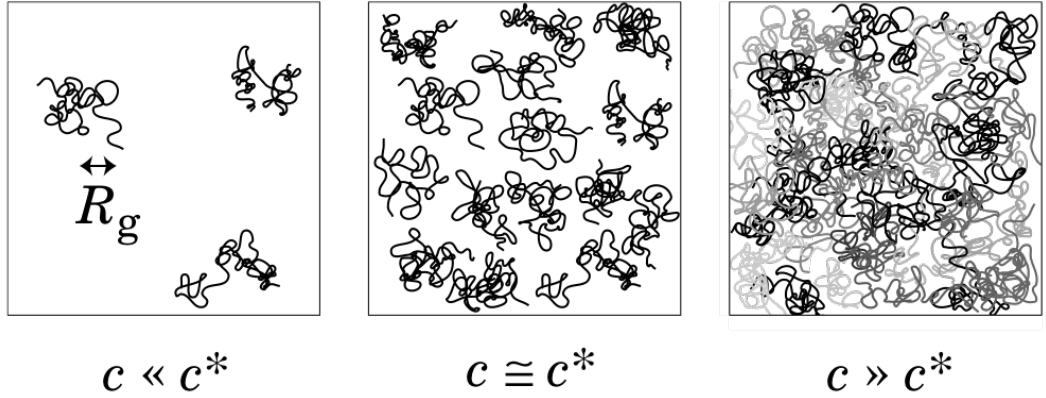


Figure 1.2: Left: dilute solution of non overlapping chains. Middle: transition regime, where chains begin to overlap. Right: semidilute solution of strongly overlapping chains. Image adapted from reference [5].

where $U(\mathbf{r})$ is the potential between two monomers. Depending on the value of v , polymers can be divided into three different classes: For polymers in good solvents, v is positive, signifying that interactions between monomers are repulsive. For poor solvents, v is negative and thus the forces between monomers are attractive. The intermediate case is that of theta solvents, where $v = 0$, thus attractive and repulsive interactions are exactly cancelled. Polymers in theta solvent are referred to as ideal. Ideal chains are characterised by random walk statistics which lead to the coil size dependence on N of $R \sim bN^{1/2}$, while expanded chains show a stronger dependence of $R \sim bN^{3/5}$.

Concentration regimes

Figure 1.2 shows a schematic of the different concentration regimes in polymer solutions. When polymer chains in solution do not overlap, the solution is referred to as dilute. Above $c^* \simeq N/R^3$, chains begin to overlap and a new length scale must be considered, the correlation length ξ . For length scales smaller than ξ dilute solution properties apply and for length scales larger, excluded volume interactions are screened by other chains leading the chains to adopt Gaussian statistics. This is illustrated in figure 1.3.

The variation of these parameters with concentration and molecular weight and other parameters are explained in more detail in the following chapters. A second crossover concentration, $c_D \simeq v/b^3$, where b is the monomer size, is observed when ξ becomes of the order of the thermal

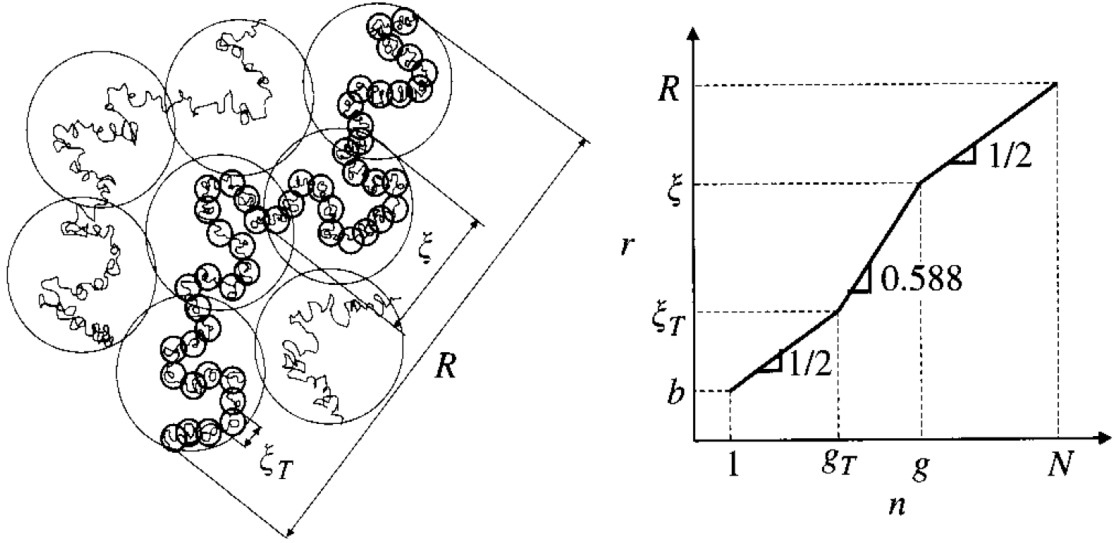


Figure 1.3: Left: Schematic of a semidilute polymer in good solvent. Right: variation of distance between two points on the chain as a function of contour length. Figure adapted from [2]. For distances smaller than the monomer size (or Kuhn length), the chain is rigid ($R \propto N$), for distances between the monomer size and the thermal blob (ξ_T , the chain is ideal as thermal energy dominates ($R \propto N^{1/2}$). For distance between the thermal blob and the correlation length, the chain shows dilute conformation, ($R \propto N^{3/5}$, in good solvent). For distances larger than the correlation length, excluded volume interactions are screened and the chain is again ideal.

blob size ξ_T , the latter being the length scale below which thermal energy dominates. Chains are then predicted to be ideal at all length scales above the monomer size. Experimentally, c^* and c_D may be measured from a change in the slope of the specific viscosity, osmotic pressure or diffusion coefficient. This is further discussed in chapters 2 and 3. Polymers with a semiflexible backbone, that is, where rigidity persists above the monomer size b , can be treated in an analogous manner by replacing the monomer size by the Kuhn length L_K , which is the lengthscale at which the chains become flexible. As the treatment is analogous, we will refer to the monomer size and the Kuhn length interchangeably throughout this chapter.

1.2.2 Dynamics

The dynamics of polymer systems are typically described by three models, which are briefly introduced here:

Rouse Model

The Rouse model treats the chain as a system of monomers linked by springs, which do not interact hydrodynamically with the solvent molecules. The monomer friction coefficient (ζ_m) is modelled by the Stokes law:

$$\zeta_m = 3\pi\eta_s d$$

where η_s is the solvent viscosity and d is the backbone chain diameter. The friction coefficient for the chain (ζ) is simply given by $N\zeta_m$. The diffusion coefficient (D) of the chain is calculated via the Stokes-Einstein equation:

$$D = \frac{k_B T}{N\zeta}$$

The longest relaxation time of a Rouse chain can be calculated as the time it takes for a chain to diffuse a distance equal to its size, for chain in θ solvent:

$$\tau_R \sim R^2/D \simeq \frac{\zeta(bN^{1/2})^2}{k_B T} N$$

A more rigorous calculation yields an extra factor of $1/(6\pi^2)$ [2,6]. When a chain is probed on timescales longer than τ_R , it is able to relax to its equilibrium conformation and it gives viscous behaviour, when probed on time scales shorter than τ_R , it exhibits viscoelastic behaviour. The above expression corresponds to the relaxation time of the full chain. In fact, different sections of the chain will relax at different characteristic times. Using the above expression to calculate the relaxation time of a single monomer ($N = 1$) yields:

$$\tau_1 \sim \frac{\zeta_m b^2}{k_B T}$$

The full relaxation time of the chain can be re-written as:

$$\tau_R = \tau_1 N^2$$

The chain can relax with $\tau_0 \dots \tau_N$ different modes with $\tau_1 = \frac{1^2}{2^2} \tau_2 \dots \tau_{N-1} = \frac{(N-1)^2}{N^2} \tau_N$, which are sometimes referred to as breathing modes and represent the relaxation of different segments of the chain. The polymer contribution to the solution viscosity estimated as the product of the relaxation time by the chain's modulus [2] ($\simeq k_B T$ per chain [2,7]):

$$\eta - \eta_s = \phi \frac{\zeta}{b} N$$

where ϕ is the volume fraction. A full calculation yields an additional factor of $1/36$ in the right hand side of the above equation. The Rouse model is appropriate to describe screened polymer dynamics, for example, polymers in the melt or in concentrated solutions. The dynamics of chains for length scales larger than the correlation length in semidilute solutions can also be computed in the framework of Rouse dynamics. The intrinsic viscosity calculated by the Rouse model is [2]:

$$[\eta] \simeq \frac{b^2 N_A}{M_0} N$$

where M_0 is the monomer molecular weight. This relation is not observed experimentally. The reason for this disagreement is that hydrodynamic interactions are neglected. An extension of the Rouse model, the Zimm model, includes hydrodynamic interactions.

Zimm Model

When a polymer chain moves through a solvent, it drags solvent molecules along with it. In the Rouse model hydrodynamic forces are ignored and the chain is said to be free draining. The Zimm model treats a polymer chain in the opposite way, it assumes all solvent is dragged along with the chain and the chain can therefore be effectively treated as a hard object. The friction coefficient can then be calculated by Stokes law:

$$\zeta_Z \sim \eta_s R$$

For a Gaussian chain, the friction coefficient has a weaker dependence on N than the linear relationship predicted by the Rouse model. Following the same procedure as above, we can calculate the diffusion coefficient:

$$D \simeq \frac{k_B T}{\eta_s R} \simeq \frac{k_B T}{\eta_s b N^\nu}$$

where we have used a general relation for the chain size $R = bN^\nu$. The relaxation time of the chain is given by:

$$\tau_Z \simeq \frac{R^2}{D_Z} \simeq \frac{\eta_s R^3}{k_B T} \simeq \frac{\eta_s b^3 N^{3\nu}}{k_B T}$$

and thus the polymer contribution to the viscosity of a solution is:

$$\eta - \eta_s \sim \phi \eta_s N^{3\nu-1}$$

and the intrinsic viscosity is given by [2]:

$$[\eta] \simeq \frac{b^3 N_{AV} N^{3\nu-1}}{M_0}$$

The Zimm model is correct, up to a prefactor, for polymers in dilute solution where hydrodynamic forces are unscreened [2].

Semidilute unentangled dynamics, the Rouse-Zimm chain

In semidilute unentangled solutions, polymer statistics and dynamics are dilute-like for length scales smaller than the correlation length, and screened for distances larger than the correlation length. The relaxation time of a single chain up to the correlation length is thus described by the Zimm model:

$$\tau_\xi \simeq \frac{\eta_s \xi^3}{k_B T}$$

For larger length scales, the Rouse model applies since hydrodynamic interactions are screened. The total relaxation time of the chain is

$$\tau_R \simeq \tau_\xi (N/g)^2 \sim N^2 \xi^{0.31}$$

where g is the number of monomers in a correlation blob. This is equivalent to a Rouse chain of N/g monomers which relax with τ_Z . For the last step, pre-factors were dropped and good solvent conditions assumed ($\xi \sim c_p^{-0.76}$).

Entangled dynamics, the reptation model

As the polymer concentration in solution increases, chains begin to entangle. The motion of chains can now be described by reptation theory. A single chain is constrained by other chains

to tube (diameter $a \sim 5 - 10\xi$ [2,8]). As the chain 'reptates' out of this tube, other chains again constrain its motion, forming a new tube. An schematic of the reptation process is provided in figure 1.4. The chain is constrained by the 'tube' formed by other chains, starting and ending points A_0 and B_0 respectively. At a later time, the chain has reptated to its right, the new tube is now defined by the starting and ending points A and B . The section A_0 to A has now disappeared and has been replaced by other chains and a new tube B_0 to B has been generated.

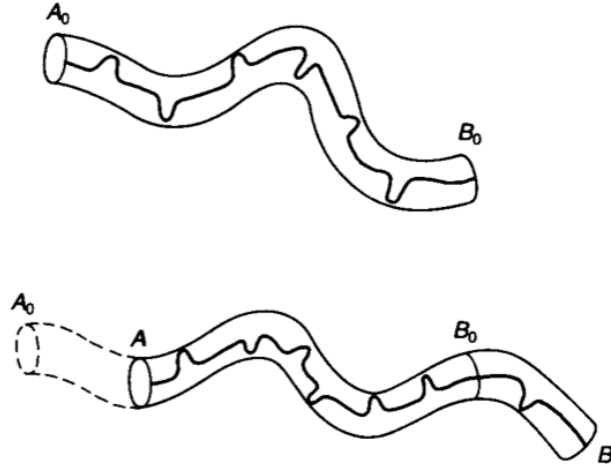


Figure 1.4: Schematic of the reptation process, adapted from reference [9]. Top: chain constrained in a tube, A_0 and B_0 mark the beginning and end of the tube. Bottom: a time t later, the chain has diffused along the tube. The new tube now is now defined by positions A and B . The segment A_0 to A has now disappeared.

Reptation mechanism

In a melt, excluded volume is screened and Gaussian statistics apply [10]. We can divide the chain into segments of N_e Kuhn monomers which form an entanglement of size equal to the tube diameter a . N_e is thus given by:

$$N_e \simeq (a/b)^2$$

The average contour length of a tube is then

$$L_{tube} = aN/N_e \simeq bNN_e^{-1/2}$$

The relaxation time of the chain is given by the time taken to diffuse or 'reptate' out of the orig-

inal tube. The diffusion coefficient along the tube can be calculated assuming Rouse dynamics:

$$\tau_{rep} = \frac{L_{tube}^2}{D} \simeq \frac{\zeta_m b^2 N^3}{N_e k_B T} = \frac{\zeta_m b^2 N_e^2}{k_B T} \left(\frac{N}{N_e} \right)^3$$

The prefactor to the term in brackets on the R.H.S. of the above equation can be recognised to be the Rouse time of the entanglement strand. Thus, once the tube diameter is known, the relaxation time can be calculated as $(N/N_e)^3$ times the relaxation time of the entanglement strand.

Reptation in solution

We now examine the dynamics of an entangled solution in good solvent. The tube diameter, proportional to and larger than the correlation length, $a = n\xi$, where n is the number of chain overlaps needed to form an entanglement is a function of concentration. The chain is a random walk of correlation blobs inside the tube. This is shown in figure 1.5.

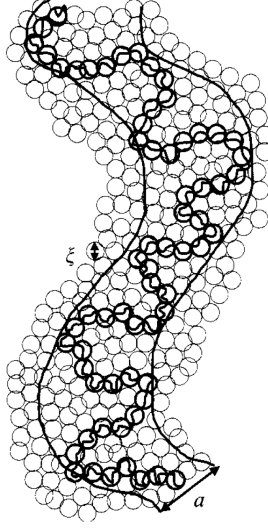


Figure 1.5: Schematic of a chain in an entangled solution. The correlation blobs of the chain are shown as dark circles, and those of other chains in grey. The entanglement tube is depicted by a black line.

The relaxation time of a correlation blob is assumed to be the same as in an unentangled solution $\tau_\xi \sim \frac{\eta_s \xi^3}{k_B T}$. The relaxation time of an entanglement strand τ_e is calculated by the Rouse model:

$$\tau_e = \tau_\xi \left(\frac{N_e}{g_e} \right)^2$$

where N_e is the number of monomers per entanglement strand and N_e/g_e is the number correlation blobs per entanglement strand. The relaxation time of the whole chain τ_{rep} , that is the time taken for a chain to diffuse out its tube, is given by the reptation model, as described above:

$$\tau_{rep} \simeq \tau_e \left(\frac{N}{N_e} \right)^3$$

The terminal modulus is given by $k_B T$ per entanglement strand:

$$G_e = \frac{k_B T}{\xi a^2}$$

The viscosity, obtained from the product of the two expressions above yields a molecular weight dependence of $\eta_{sp} \propto N^3$, which is close to the experimentally observed value of $\eta_{sp} \propto N^{3.4}$. In solution N_e is a function of concentration as the tube size decreases with concentration.

1.3 Polyelectrolytes

Polyelectrolytes are polymers with ionic groups attached to their backbones. When dissolved in a high dielectric constant medium, typically water, counterions dissociate leading to a charged backbone. In the following we give an introduction to scaling theory of salt free polyelectrolyte solutions. The case of added salt is considered in chapter 3.

COUNTERION CONDENSATION

The Bjerrum length $l_B = \frac{e^2}{4\pi\epsilon\epsilon_0 k_B T}$, where e is the unit of charge, ϵ_0 is the vacuum permittivity, ϵ is the relative dielectric constant and k_B is the Boltzmann constant, is defined as the distance at which the electrostatic energy between two charges is equal to the thermal energy (7.1 Å for water at 25°C). In the Manning model, counter ions can either be bound to the chain (i.e. condensed) or free. Manning's theory is derived for dilute solutions and predicts that if the distance between two charged groups along the chain is less than the l_B counter ions will condense. A model that accounts for counterion condensation in semidilute solutions was later developed by Colby and co-workers [11]. To the best of our knowledge no model exists for counterion condensation in the concentrated regime. Bordi et al [11,12] studied the low frequency dielectric properties of NaCMC solutions, D.S. quoted as $\simeq 0.7$, of two molecular weights. The charge density along the polyion was found to be approximately 1 charge per two monomers ($\simeq 10$ Å) in the semidilute regime and a decrease ($\simeq 15$ -30%) in the fraction of free counter ions occurs when the solutions cross over to the concentrated regime. Such a decrease could indicate more aggregation at higher concentrations which would bring carboxymethyl groups closer together hence forcing more counter ions to condense. This decrease has also been observed for other systems such as sodium polyacrylate (NaPAA) or sodium poly(4-styrenesulfonic acid-co-maleic acid) (Na-PSS-Mal) [12].

SCALING THEORY

Salt free solutions of flexible polyelectrolytes can be classified into dilute, semidilute (non entangled and entangled) and concentrated, as in the case of neutral polymer solutions. In dilute solutions, that is for $c_p < c^*$, where c^* is the overlap concentration, polyelectrolytes adopt an extended conformation and can be represented by a directed random walk of electrostatic blobs of diameter ξ_T . For good and theta solvents, the electrostatic blob is calculated as the

length at which the electrostatic energy between the monomer charges is equal to the thermal energy. For poor solvents it is determined by the balance of the electrostatic energy and the interfacial tension of a polymer blob and the solvent:

$$\xi_T = \begin{cases} b(A^2b/l_B)^{1/3} & T \leq \theta \\ b(A^2b/l_B)^{3/7} & T \gg \theta \end{cases} \quad (1.1)$$

where A is the number of monomers per charged group and b is the monomer length. For distances below ξ_T , thermal energy dominates and the chain conformation depends on the solvent quality. In poor solvents $\xi \simeq l_B$ is found and each electrostatic blob has ~ 1 charge, while in the good solvent case the electrostatic blobs can be much larger with more effective charges [14]. The solvent quality parameter B is defined as the ratio between the polymer contour length Nb , where N is the degree of polymerisation, and the end to end length in dilute solution $R_{ee} = N\xi_T/g_T$, where g_T is the number of monomers per electrostatic blob. The scaling prediction for the specific viscosity ($\eta_{sp} \equiv \frac{\eta - \eta_s}{\eta_s}$) in this regime is $\eta_{sp} \approx c_p/c^*$.

At the c^* , given by:

$$c^* \simeq \frac{N}{R_{ee}^3} = B^3 b^{-3} N^{-2} \quad (1.2)$$

chains begin to overlap. In the semidilute regime, the most relevant length scale is now the correlation length ξ . At length scales smaller than ξ , chains do not interact and the conformation is like that of a dilute solution. At length scales larger than ξ , the electrostatic energy is screened and chains follow random coil statistics. A peak in the structure factor, $S(q)$, is predicted and observed in flexible semidilute salt free polyelectrolytes, the position of which scales as $q^* \propto c_p^{1/2}$, in agreement with the scaling prediction $\xi = (B/c_p b)^{1/2}$. q^* is the wavenumber related to a characteristic distance r by $q^* = 2\pi/r$. The origin of this peak has been assigned to the inability of correlation blobs to overlap due to the strong repulsion generated by the counterion clouds surrounding the polyions, thereby resulting in the suppression of long range fluctuations [15,16]. This is also manifested in the unusually low compressibility of polyelectrolyte solutions [17]. Scaling theory assumes that the osmotic pressure arises from the free counter ions as well as the polyions, the former contribution usually being much greater since each correlation volume has many free counter ions:

$$\Pi/k_B T = 1/\xi^3 + c_p/A \quad (1.3)$$

The first term takes into account the contribution of the polyions ($k_B T$ per correlation blob) and the second term is $k_B T$ per free counterion. The second term typically dominates. The osmotic compressibility is given by $dc/d\Pi = (\frac{1}{A} + (\frac{bc}{B})^{3/2})^{-1}$ which is related to the scattering at zero wavevector as $S(0) = k_B T dc/d\Pi$.

In the semidilute unentangled regime, the relaxation time of a chain is given by the Rouse time of a chain of correlation blobs: $\tau_R = (N/g_\xi)^2 \tau_0$, where $\tau_0 = \eta_s \xi^3 / k_B T$ is the relaxation time of a single correlation blob, modelled by a Zimm chain and g_ξ is the number of monomers in a correlation blob. The specific viscosity is then the product of the terminal modulus ($k_B T$ per chain) and the relaxation time:

$$\eta_{sp} = N(c_p b^3)^{1/2} B^{-3/2} \quad (1.4)$$

This power law dependence is usually referred to as the Fuoss law [18], which has been observed for a number of polyelectrolyte systems, although its validity has been questioned [19,20]. Equation 1.4 predicts the viscosity to depend linearly on N while, experimentally, it has been found that $\eta_{sp} \propto N^{2-2.4}$ for NaPSS, thus suggesting the scaling argument might not be valid. However, the concentration dependence of both the viscosity and longest relaxation time, [14,21] have been found experimentally and via simulations [22] to agree with those expected from the Rouse model, as has the experimentally measured relaxation time distribution [23]. At sufficiently high concentrations ($\phi \geq 0.3$) however, an increase in the monomeric friction coefficient need to be considered within the Rouse model, as shown by both simulations [22] and experiments [23]. Further, we note that the Fuoss law has been observed for very short polyelectrolyte chains [24], for which the above derivation should not hold. Thus there is something missing from our understanding of the Fuoss law. We conclude that the Rouse model provides a useful framework for the description of unentangled hydrodynamically screened polyelectrolyte dynamics.

Chains start to entangle at $c_e = n^4 c^*$, where n is the number chains required to form an entanglement. The tube diameter can be calculated to be $a = n\xi$ and the reptation time and viscosity in semidilute entangled solutions are given by:

$$\tau_{rep} = (\eta_s b^3 / k_B T) n^{-2} N^3 B^{-3} \quad (1.5)$$

$$\eta_{sp} = n^{-4} N^3 (c_p b^3)^{3/2} B^{-9/2} \quad (1.6)$$

The crossover concentration to the concentrated regime (c_D) is expected when the correlation blob reaches the electrostatic blob, that is $\xi_T = \xi$. The chains are then predicted to behave similarly to neutral polymers and the viscosity varies as $\eta_{sp} \propto c_p^{3.75}$ in good solvent and $\eta_{sp} \propto c_p^{14/3}$ in θ solvents. These high exponents for the concentration dependence of the specific viscosity have been experimentally observed [14,25]. For polyelectrolytes in poor solvent, there is no predicted exponent but it may be an even stronger concentration dependence, since counter ions condense to form ion pairs that attract each other. The terminal modulus is expected to scale as $c_p^{2.3}$ for neutral polymers in good or theta solvent. This scaling is not observed for concentrated polyelectrolyte solutions. Dou et al [14] observed a dependence of the terminal modulus with concentration of $c_p^{3/2}$ for poly(2-vinyl pyrridine-co-N-methyl-2-vinyl pyridinium chloride) in ethylene glycol in the semidilute entangled and concentrated regimes. Liberatore et al [25] measured the viscosity and relaxation times of Xanthan in salt free aqueous solutions and obtained a power law of 3.75 for the viscosity and of 4 for the relaxation time, indicating that the terminal modulus is approximately independent of concentration in the concentrated regime. Concentrated polyelectrolyte solutions are therefore rheologically distinct from neutral polymers. Scaling theory does not give a prediction for the existence of a peak in the scattering function in this regime. Experimentally, it has been observed that for sodium polystyrene sulfonate, the scaling of the peak position with concentration changes from 0.5 to 0.25, coinciding with a change in the scaling of osmotic pressure with concentration, approaching a value similar to that of neutral polymers [27]. A crossover to the 0.25 exponent has also been reported for less flexible polyelectrolytes poly(α -methylstyrene sulfonate), poly(diallyl dimethylammonium chloride) and hyaluronic acid at intermediate concentrations, followed by a steeper power law of c_p^1 at higher concentrations for the latter two [26,27]. SANS experiments in the concentrated regime for sodium polystyrene sulfonate (NaPSS) in D₂O indicate that the radius of gyration is approximately independent of concentration above c_D [28], in contrast with the semidilute regime, where it scales as $c_p^{-1/4}$ in agreement with scaling theory. Different exponents at high polymer concentrations have been reported for hydrophobic polyelectrolytes by Waigh et al [29].

1.4 Microfluidics

Microfluidics refers to the study of fluids confined to dimensions on the order of 100 μm [30]. Microfluidics allows unprecedented precision in the design of flow types and magnitude. Current

micro fabrication techniques allow micro devices to be made in under an hour from initial design. In this section, we give a brief introduction to microfluidic flow, micro fabrication techniques and its relevance to the study of soft matter.

1.4.1 Dimensionless numbers

Figure 1.6 shows a schematic of a microfluidic channel. Several dimensionless parameters are useful in describing the flow in a microfluidic system. The Reynolds number:

$$Re = \rho U L_0 / \eta$$

expresses the ratio of inertial to viscous forces. Flows can be described as turbulent ($Re > 4000$), transient ($4000 < Re < 2300$) or laminar ($Re < 2300$) [31]. For virtually all microfluidics systems, the flow is laminar [30], meaning that the inertial forces are negligible. It is possible however, for fluids with a high elastic component, that elastic turbulence may develop if the timescales of applied shear are commiserate with the relaxation times of the system.

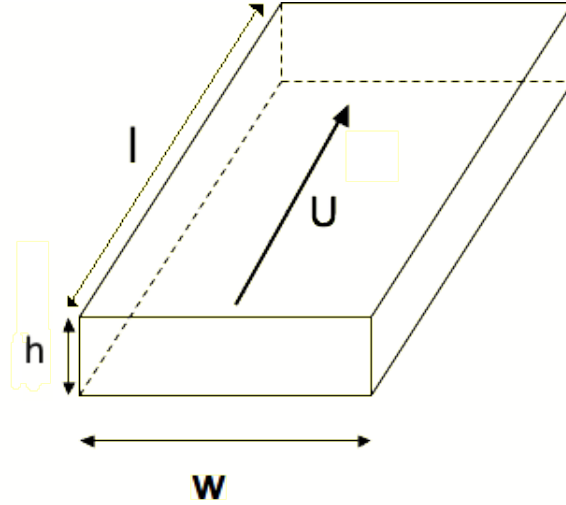


Figure 1.6: Schematic of a rectangular microfluidics channel, width w , height h and length l , the normal velocity through it is denoted by U .

The Péclet number $Pe = UL_0/D$ expresses the ratio of convection to diffusion. While at high Reynolds numbers random currents cause turbulent mixing, in laminar flow, all mixing between fluids occurs by diffusion. Figure 1.7 shows a T sensor [32]. As the two fluids going through the side channels flow into the central channel they diffuse and mixing occurs. The time taken

for the two fluids to diffuse across the whole channels (full mixing) can be estimated as $t \simeq \frac{w^2}{D}$ where D is the diffusion coefficient of the fluids. The distance travelled by the liquid along the channel in this time is $z \simeq \frac{Uw^2}{D}$. The number of widths along the channel required for full mixing to occur is then $z/w \simeq Uw/D$, this is known as the Peclet number [30]. The Deborah number is given by the ratio of the characteristic relaxation time (τ) of the system and the time on which the system is probed τ_{exp} , $De = \frac{\tau}{\tau_{exp}}$.

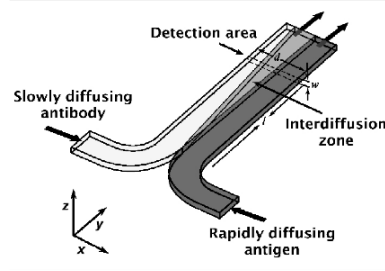


Figure 1.7: Schematic of a T-sensor geometry: two fluids go in through the side channels and meet along the central channel, where the streams diffuse laterally and mixing occurs, indicated by the yellow region. Image from [33]

1.4.2 Microfluidic flow

Microfluidics offers unprecedented precision and flexibility to generate precise flow fields, and to confine fluids within length scales of a few microns, commensurate with those of many soft matter structures such as vesicles or aggregates. The time scales on which shear can be applied and/or released are also commensurate with the relaxation times of many systems, such as polymer or surfactant solutions. As an example, dilute high molecular weight polyethylene oxide solutions entering and exiting through small constrictions have been the subject of a number of studies with optical microscopy [34]. Interesting phenomena such as the formation of viscoelastic instabilities when the crossover time through a constriction becomes similar to the polymer relaxation times are observed. Figure 1.8 shows dilute solutions of polyacrylic acid entering through a hyperbolic constriction, as the flow rates are increased and the crossing time becomes similar to the relaxation time of the polymers, instabilities develop as seen by particle tracking. Flows of this type, where large Deborah and small Reynolds numbers occur simultaneously are an example of a new area in fluid mechanics, which is best studied with microdevices.

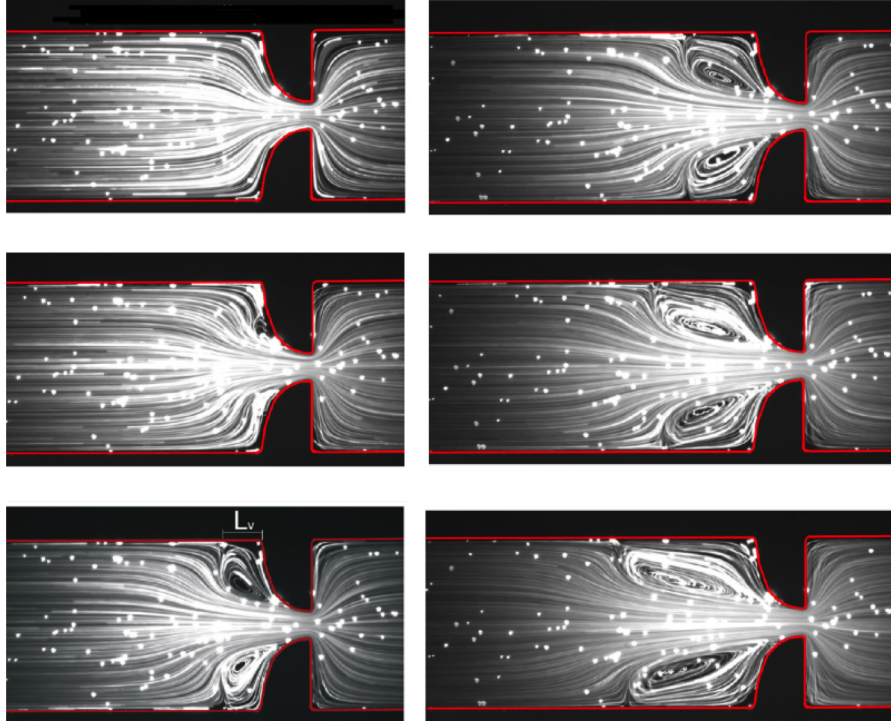


Figure 1.8: Dilute PAA in 1 wt% NaCl aqueous solutions exiting through a constriction at different velocities. Flow direction is from left to right. The flow rate is lowest (0.25mL/hr) in the top left and highest (0.75mL/hr) in the bottom right image. At a critical velocity, corresponding to $De \simeq 4$ instabilities occur. Adapted from reference [34].

Flow fields can be divided into active and passive flows, in the former case, external forces (e.g. electric or mechanical) are present while in the later they are not. Following Astarita's convention [35,36], flow types (Ξ) can be purely extensional ($\Xi = 1$), purely rotational ($\Xi = -1$) or a combination of the two. For incompressible fluids, Ξ can be expressed as:

$$\Xi = \frac{D_1 - W_1}{D_1 + W_1} \quad (1.7)$$

where W_1 and D_1 are the principal eigenvalues of the rotational and stretching tensorial rates respectively. Figure 1.9 shows the microfluidic analogue of a four roll mill, designed by Muller and co-workers [37] based on the work of Hudson et al [36], and the flow type (Ξ) it generates as a function of Q_1/Q_2 .

Flow in microfluidics is almost always laminar, meaning that mixing happens only by diffusion and is therefore intrinsically slow. A number of approaches have been developed for achieving

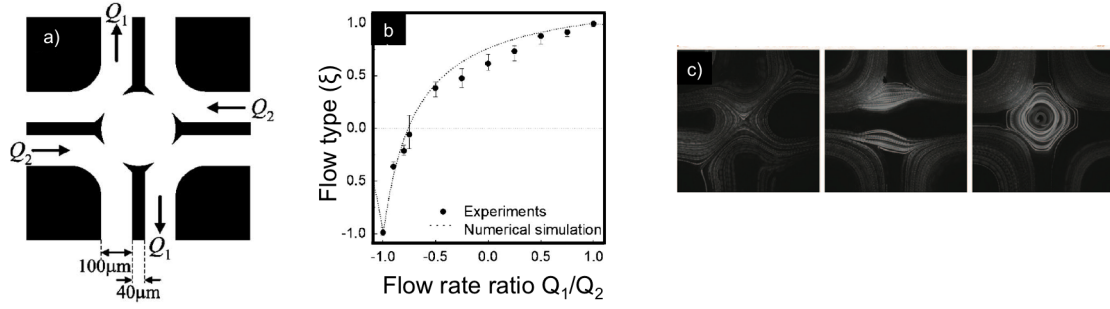


Figure 1.9: a) Schematic of microfluidic analogue of the four roll mill, b) flow type generated as a function of flow rate ratio, c) particle tracking images for different flow rates, corresponding extension, shear and rotation.

fast mixing, either in continuous [38,39] or multiphase flow [38,39,40]. Mixing of two or more components can often be achieved in less than a millisecond [40,41]. Figure 1.10a-c shows schematics of different approaches to mixing including both continuous and multiphase mixers. For a review of mixing in microfluidic devices see references [38,39]. Figure 1.10d-e shows schematics of geometries that may be used to impose specific flow fields, d) contraction/expansion device, extensional shear ($\Xi = 0$), and e) a cross slot or opposing jet device which generates purely elongation shear ($\Xi = 1$) (neglecting wall shear effects).

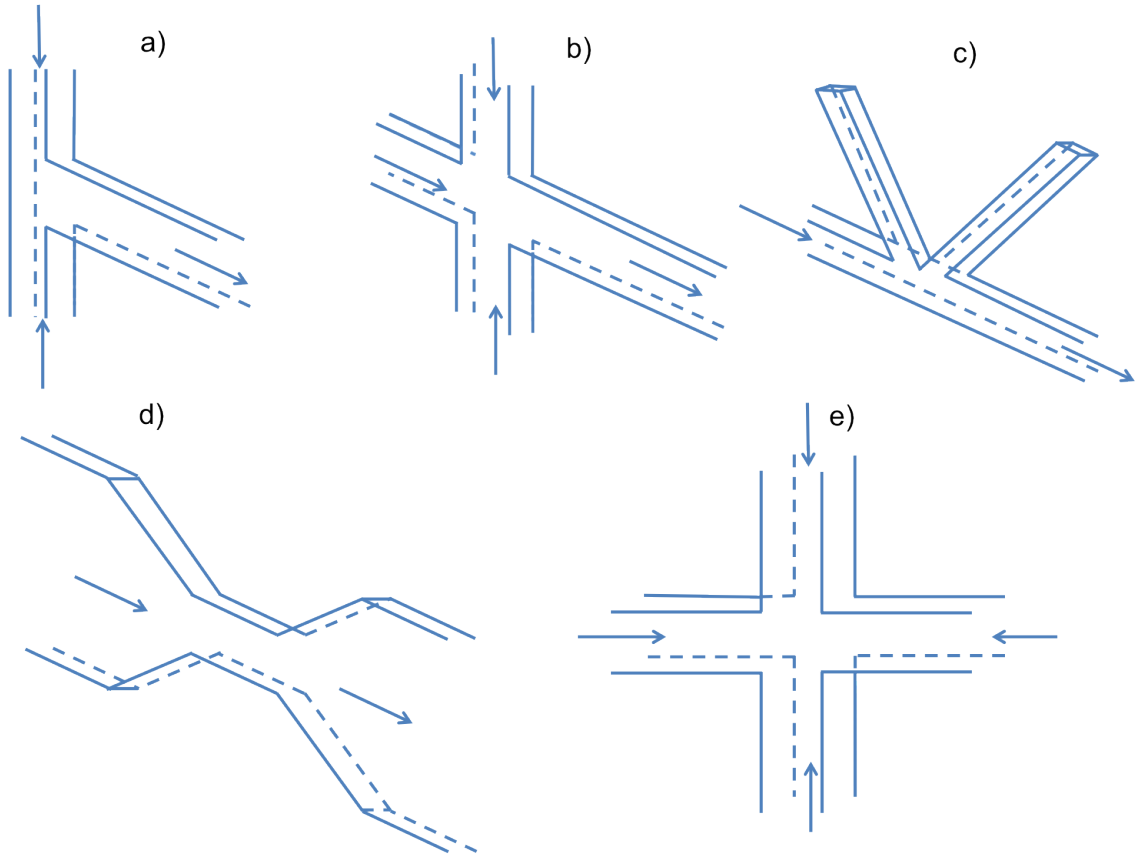


Figure 1.10: Schematics of different chips: a) T mixer, b) flow focusing mixer c) droplet generator, d) constriction expansion, e) cross slot.

1.4.3 Microfabrication

A variety of methods are available to produce microfluidics devices, these include mould replication and a number of lithographic techniques [42]. Cabral et al. [43] have developed a method for microfluidic device fabrication based on frontal photopolymerisation of a commercial thiol-ene based copolymer, used as a negative photoresist. Figure 1.11 shows a schematic of the process. In the places where the mask is clear, the photoresist is exposed to UV light and it polymerises, where it is dark, the photoresist remains liquid and can be flushed out, this leaves the empty space that are the channels. The the polymerising front h varies with time t as:

$$h = \frac{\ln(t/\psi)}{\mu} \quad (1.8)$$

where μ is the optical attenuation coefficient of the polymer and

$$\psi = \frac{\ln[1/(1 - \phi_C)]}{KI_0}$$

where ϕ_C is a critical conversion fraction (ϕ varies between 0 and 1 and represents the extent of polymerisation) below which the polymer is a liquid and above is a solid, K is the reaction conversion rate and I_0 is the intensity of the UV light.

This method provides a fast and cheap way to manufacture microfluidics devices with widths down to $50 \mu\text{m}$ (dependent on the resolution of the mask) and thicknesses between a few μm and several hundreds μm . The method is explained in more detail in chapter 5.

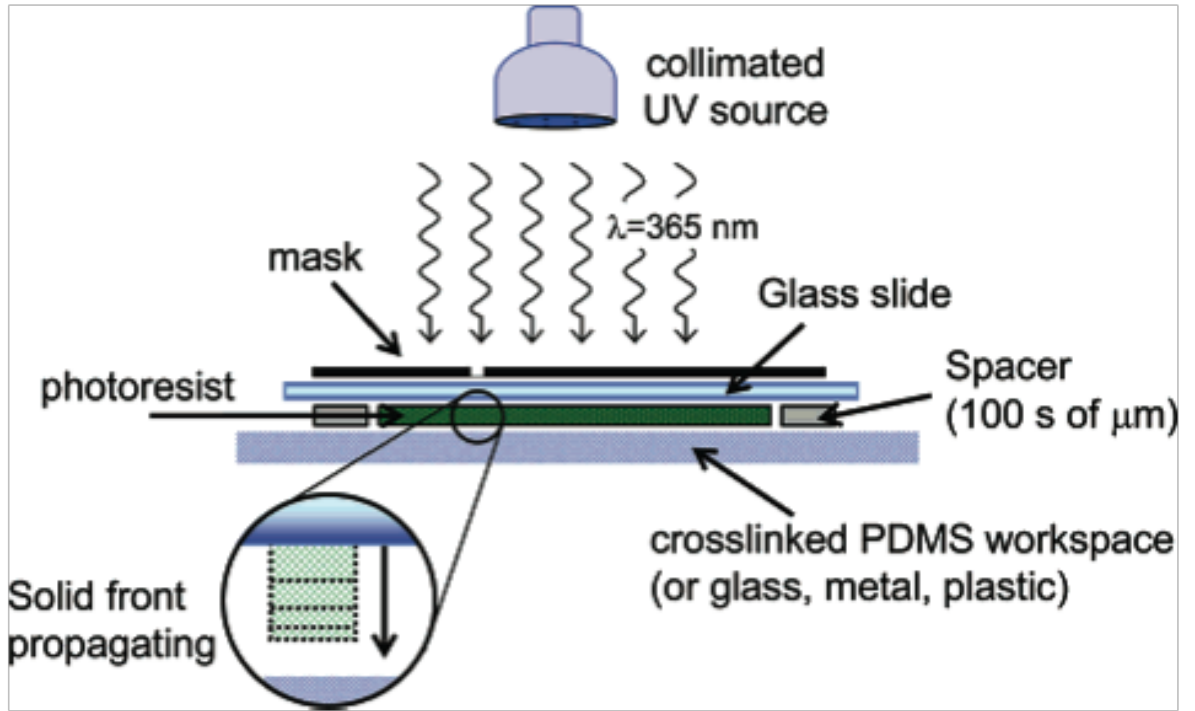


Figure 1.11: Schematic of Frontal Photopolymerisation process applied to microfluidics chip fabrication [41].

1.5 Small angle scattering

Techniques such as optical and electron microscopy give real space information about the structure of matter. Optical microscopy has limited resolution ($\approx 1 \mu\text{m}$) while techniques like scanning electron microscopy (SEM) or transmission electron microscopy (TEM) need to be carried out

under vacuum. Solutions therefore need to be frozen and thus the observed conformation may not be representative of the solution properties under ambient conditions. This also leaves out the possibility of carrying out experiments under flow. Other real space techniques include magnetic resonance imaging (MRI) or infra red spectroscopic imaging suffer from relatively low spatial resolution, of the order of microns in both cases. Fluorescence microscopy is a powerful technique to probe the dynamics of single molecules, which has been used in combination with microfluidics to measure, for example, the dynamics of wormlike micelles in elongational flows [44].

Scattering is a well established technique that measures structural and dynamic correlations of matter. Three different types of radiation are commonly used for studying soft matter: neutrons, X-rays and light in the UV and visible range. These techniques have been reviewed extensively in a number of texts [45-50]. Here we give a very brief introduction to small angle scattering for different types of radiation. Further details of SANS theory can be found in chapters 2 and 3, implementation of SANS/SAXS with microfluidics is considered in chapters 4-5.

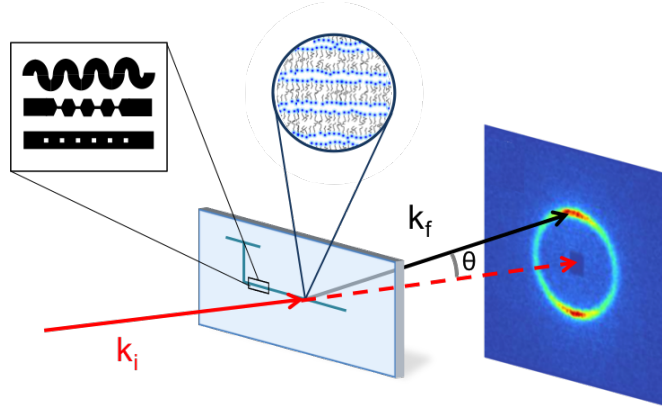


Figure 1.12: The incident radiation is scattered by the sample, indicated by the red slab, and the diffraction pattern is recorded at the detector.

Scattering arises from differences in the interaction of radiation with matter within a sample. Figure 1.12 shows an incoming beam of radiation before and after being scattered by a sample. The change in momentum $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$ is given by:

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

where λ is the wavelength of the neutrons or light, and n is the refractive index.

The intensity measured in an elastic scattering experiment after correcting for transmission and detector efficiency is given by:

$$I(q) = I_0 V \frac{\partial \sigma_s}{\partial \Omega}$$

where I_0 is the flux at sample, V is the sample volume (that is, the cross sectional area of the beam times sample thickness), and $\frac{\partial \sigma_s}{\partial \Omega}$, referred to as the differential cross section is given by:

$$\frac{\partial \sigma_s}{\partial \Omega} = N_p V_p^2 (\Delta \delta)^2 P(q) H(q) + S_{inc}$$

for spherically symmetric objects assuming single scattering, that is, neutrons or photons are scattered only once before hitting the detector. N_p is the number density of particles, V_p is the volume of a single particle (a scattering unit), $P(q)$ is the form factor, which describes the scattering from a single particle and $H(q)$ is the intermolecular structure factor which describes the correlations between individual particles. $(\Delta \delta)^2$ is contrast term. The source of contrast depends on the type of radiation used. Table 1.1 summarises the contrast factors for three different types of radiation. Neutrons are sensitive to the scattering length density (SLD), which does not show a trend with atomic number and can vary significantly for different isotopes. An important example of this is that of hydrogen and deuterium (SLD = -0.3741 and 0.6674 $\times 10^{-12}$ cm⁻² respectively). While chemically very similar, they interact very differently with neutrons. As hydrogen is one of the main components of soft matter [45], specific components of a system may be labelled by deuterium substitution. Figure 1.13 shows an example of how contrast variation by selective deuteration can be used to decompose the signal of different components of a system. In the case of X-rays, the contrast arises from the electron density, and labelling is generally not an option, all images in figure 1.13 would 'look' the same to X-rays. However, by tuning the energy of X rays, one can make use of an absorption edge for a given element which allows deconvolution of the signal from the whole sample and that arising from a particular element [51]. Contrast matching is also not an option for light scattering (LS) where the source of contrast is the refractive index of the material. Additionally, owing to the larger wavelength of radiation, LS probes larger length scales ($\sim \mu\text{m}$). Given the availability of in-house LS setups, it is a useful technique for determining parameters such as the radius of gyration, R_g , the molecular weight, M_w , or the second virial coefficient A_2 which are best determined in the Guinier regime, that is, $q \leq 1/R_g$. Table 1.1 summarises the typical beam size, contrast source, q-range and typical acquisition times for different scattering techniques. Light scattering is divided into two

techniques: small angle light scattering (SALS) which is analogous to SAXS or SANS except for the differences outlined above, and static light scattering (SLS), which is not a small angle technique and typically offers much higher sensitivity than SALS setups.

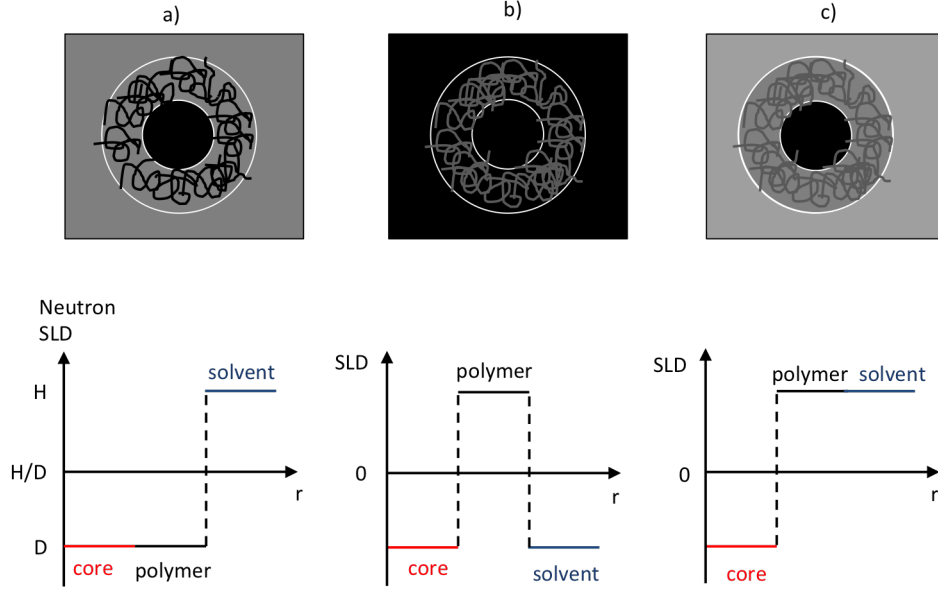


Figure 1.13: Silica particle grafted with polystyrene. The schematics illustrate how information about the different components can be achieved by contrast variation with neutrons. Top row: schematics of particles and solvent, bottom row, SLD's of different components. a) the polystyrene is contrasted matched with silica but not with the solvent. b) the solvent is contrast matched with the silica particle but not with the polystyrene. c) polystyrene and solvent contrast matched.

After reviewing the fundamental theory and main experimental techniques, we next study carboxymethyl cellulose in aqueous salt free and salt containing solutions in chapters 2 and 3. We then demonstrate the coupling of microfluidics with SANS which is shown to be a useful technique for probing the non-equilibrium dynamics of soft matter in chapters 4-5.

Technique	Beamsize	Contrast	q range	wavelength / nm	typical acquisition time
SANS	1-0.05cm ² *	SLD	0.001 - 0.5 Å ⁻¹	0.1-3	strongly dependent on sample (~ 30 min)
USANS	1cm ² *	SLD	0.00005 - 0.03 Å ⁻¹	0.2 - 1	strongly dependent on sample
SAXS	0.01mm ²	e ⁻ density	0.001 - 0.5 Å ⁻¹	0.02 - 1	~ few seconds
microSAXS	0.25 < 100 μm ²	e ⁻ density	0.02 - 0.5 Å ⁻¹	0.02-1	~ minutes
SLS	1mm ²	R.I.	0.2 - 2 μm ⁻¹	400-650	~ one minute
SALS	100 μm ² -1mm ²	R.I.	0.1 - 1 μm ⁻¹	400-650	~ few seconds

Table 1.1: Comparison of different scattering techniques *the beam size can be collimated at the expense of flux.

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2 Structure and rheology of hydrophilic NaCMC in aqueous solution

Abstract

We report a small angle neutron scattering (SANS) and rheology study of cellulose derivative polyelectrolyte Sodium Carboxymethyl Cellulose (NaCMC) with a degree of substitution of 1.2. Using SANS, we determine the cross sectional radius of the chain ($r_p \simeq 3.4 \text{ \AA}$), the correlation length and the characteristic low wavenumber upturn intensity in the semidilute and concentrated regimes. The scaling of the correlation length with concentration ($\xi = 296 c_p^{-1/2} \text{ \AA}$ for c_p in g/L) is found to remain unchanged from the semidilute to concentrated crossover as identified by rheology. Viscosity measurements are found to be in qualitative agreement with scaling theory predictions. In the semidilute unentangled regime, we observe a power of the specific viscosity with concentration of 2/3 instead of the Fuoss exponent of 1/2. The crossover between the semidilute and concentrated regimes cannot be explained as arising from the overlapping of correlation and electrostatic blobs, and appears to happen when the correlation length becomes of the order of the intrinsic Kuhn length.

2.1 Introduction

2.1.1 Cellulose and cellulose derivatives

Cellulose is the most abundant polymer on Earth with annual cellulose synthesis by plants approaching 10^{12} tons [1]. Cellulose derivatives are commonly used in the food, pharmaceutical, cosmetic, textile and paper industries, with applications such as thickening agents, emulsifiers or stabilisers [2]. While cellulose is insoluble in water and most common organic solvents [3], cellulose derivatives are soluble in a wide range of solvents [4], depending on their monomer substitution; for example, cellulose acetate is soluble in acetone, tetrahydrofuran and other organic solvents while MethylCellulose (MC), Ethyl Hydroxyethyl cellulose (HEC), methyl hydroxypropyl cellulose (MHPC) and NaCMC are water soluble [2, 3].

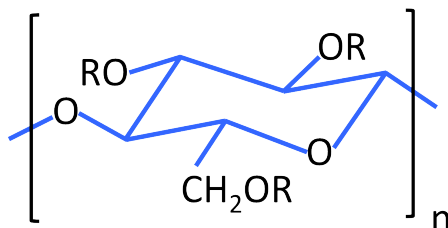


Figure 2.1: Monomer structure of NaCMC. R can be H or CH_2COONa . The degree of substitution (D.S.) is defined as the average number of CH_2COONa groups per monomer out of a maximum of 3.

Solutions of cellulose derivatives are typically highly viscous, as a result of the rigidity of the cellulose backbone and the intermolecular forces arising from hydrogen bonding, and often display pseudoplasticity and thixotropy, which depends on molecular structure, concentration, temperature, salt and surfactant content [2, 5]. Some cellulose derivatives such as MC are known to gel upon heating [6, 7], with the gelation temperature depending on degree of substitution (D.S.), M_w and solvent composition. Cellulose derivatives can form supramolecular structures in both aqueous and non aqueous solutions [3, 4, 8]. These structures are complex and it is often difficult to determine them unambiguously. A characteristic form of supramolecular aggregation observed for a number of cellulose derivatives is the formation of star-like aggregates; these have been experimentally studied by light scattering [9] and SANS [10], and described by a fringed micelle model [9].

Carboxymethylcellulose (CMC), generally used as sodium salt NaCMC, is one of the most

widely used polyelectrolyte cellulose derivatives [15]. NaCMC is an anionic, water-soluble, polyelectrolyte with vast applications in the food, pharmaceutical, personal care/cosmetic, paper and other industries. For instance, NaCMC is widely used as a rheology modifier in foods and personal care products such as toothpastes and shampoos [16], as a film-former in textile treatments [17] and to prevent the redeposition of soil removed by detergents during the fabric washing process [18]. Its monomer structure is shown in 2.1, where R stands for -H or -CH₂CO₂Na. The degree of substitution (D.S.) is the average number of carboxymethyl groups substituted per monomer unit, ranging from 0 to 3 with the remaining R = H. A range of intrinsic persistence lengths (L_0) for NaCMC have been reported, varying from 5 to 15 nm [32,33,35] characteristic of a semiflexible polymer and typical of many polysaccharides [14,33] .

2.1.2 Previous work on NaCMC

Aqueous solutions of NaCMC are generally complex. The degree of solubility of NaCMC in water remains an open question, with some studies suggesting that only a fraction is fully dissolved [19, 20] and others reporting full solubility in dilute solution [35]. The degree of solubility is accepted to be a function of the degree of substitution, with less substituted (more hydrophobic) NaCMC showing a larger fraction of aggregates [20]. Xiquan et al. [21] reported the presence of aggregated crystalline domains in aqueous solutions of NaCMC by X-ray diffraction. The degree of crystallinity was also found to be a function of the degree of substitution, with less substituted samples showing higher crystallinity; no crystallinity was observed for samples with a D.S. above 1.06. Additionally, low substitution grades often exhibit thixotropy [20,22] which is thought to result from the formation of networks or soft aggregates [20]. Elliot and co-workers concluded from their studies of the rheology of NaCMC aqueous solutions that the main factor controlling the rheological properties is not the average D.S. but the regularity of substitution [20]. NaCMC of low D.S. but uniform substitution, i.e. lacking blocks of unsubstituted monomers, yields similar properties to highly substituted grades. Typically, samples with D.S. $\gtrsim 1$, do not exhibit thixotropy, as with increasing D.S., substitution becomes more random. For this study, we have selected a sample of D.S. = 1.2 and therefore we expect no significant blocks of unsubstituted cellulose; our results indeed indicate that no thixotropy or gelling occurs at high concentrations. The cellulose backbone is known to be amphiphilic [23]. According to a model by Reuben et al. [24,25], for an average D.S. = 1.2, 10-20% of the monomers will not be substituted hence, even in the absence of large unsubstituted blocks, there will still be both hydrophilic and hydrophobic

interactions from unsubstituted monomers. Cellulose derivatives are known to form both intra and intermolecular hydrogen bonds in solution, and it is thought that water 'clusters' form around the backbone [3].

Simulations by Somasundaran and co-workers [26] found that NaCMC adopts a helical conformation in bulk and in solution, while Biermann et al [27] found that, depending on the substitution pattern, the chain may be locally collapsed or highly extended. The helical conformation of the NaCMC chain is supported by some experimental data [28–30], although light scattering, intrinsic viscosity, potentiometric titration and dielectric spectroscopy data have been successfully interpreted assuming a rigid conformation [32, 32, 33, 35, 41].

While there is a significant amount of literature on the rheology of NaCMC, much of it is inconclusive. For example, many studies do not give the precise M_w or D.S. used ([15, 22, 34, 35]), study only narrow concentration ranges [15, 35] or report qualitatively different results. In terms of rheology, for instance Ref [36] reports shear thickening followed by shear thinning of NaCMC, not observed in any other study, (and likely the result of non steady state measurements), [37] claims the intrinsic viscosity increases with temperature while ref [25] shows a decrease, additionally, a number of studies report 'zero shear rate viscosity' values that are clearly in the shear thinning regime. The reported intrinsic viscosities as a function of M_w at 0.01M NaCl vary by more than an order of magnitude between different articles [25, 54, 55]. Often, either raw data is not presented or a good sample characterisation is not available, making it difficult to distinguish which data is correct. A Fuoss or near Fuoss dependence of the specific viscosity has been reported in the semidilute unentangled regime [5, 34, 35, 41]. Concentrated solutions are reported to have a strong dependence of the specific viscosity (η_{sp}) with polymer concentration ($\eta_{sp} \sim c_p^{3.75-5.5}$) [5, 41].

Questions regarding the local conformation and solubility of NaCMC in water remain unresolved. In this chapter we will use Small Angle Neutron Scattering (SANS) to probe the solubility and conformation of NaCMC in aqueous solution. We complement SANS results with careful steady shear rheological measurements across a wide concentration range, which allows us to deduce the different concentration regimes and give further insights into the conformation and dynamics of NaCMC in water.

2.2 Background Theory

SCATTERING

The differential cross section of scattered intensity per unit volume in a small angle experiment for an n-component system may be written as:

$$I(q) = N_p \sum_{i=1}^n k_i k_j S_{ij}(q)$$

where N_p is the concentration in number of species per unit volume and $k_i = b_p - b_s v_p / v_s$; b is the coherent scattering length and v is the partial molar volume. The subscript p refers to a solute species and s refers to the solvent. Salt free polyelectrolyte solutions comprise three components: solvent, polymer and counter ions. $S(q)$ is often divided into an intramolecular part $P(q)$, the form factor and an intermolecular part, $H(q)$ where q is the scattering wavevector, $S(q) \equiv P(q)H(q)$. While the form factor of polyelectrolytes in solution can be modelled by a semiflexible chain, the intermolecular structure factor $H(q)$ is significantly more complex to model. PRISM theory has been used to successfully model data in selected systems and q ranges. It does not predict the so-called low q upturn, thought to be caused by multi chain domains, and is computationally demanding.

We follow a systematic approach to data fitting, building up from small length scales (high q) toward the forward scattering signal.

High q : chain diameter

At high q , we assume that no intermolecular effects are present and the single chain signal dominates [44, 50]. The form factor of a stiff chain for $qL_T > 1$ is given by the product of an infinitely long, thin wormlike chain $P_0 = \frac{\pi}{bq}$ and a term that accounts for its finite cross section P_{cs} yielding:

$$P_0 P_{cs}(q) = \frac{\pi}{bq} \mathfrak{H}_0(\rho(r)) = \frac{\pi}{bq} \left(\int 2\pi r J_0(qr) \rho(r) dr \right)^2$$

The term inside the brackets is the zeroth order Hankel transform ($\mathfrak{H}_0$) of the radial density profile $\rho(r)$, J_0 is a zeroth order Bessel function of the first kind. This expression is only valid for objects with radial symmetry [43]. Modeling $\rho(r)$ as step function, corresponding to a cylinder of uniform density $\rho(r) = \rho_0$ for $r < r_p$ and $\rho(r) = 0$ for $r > r_p$, gives $\mathfrak{H}_0(\rho(r)) = \frac{2J_1(qr_p)}{qr_p}$, where J_1 is a first order Bessel function of the first kind and r_p thus defines the radius of the chain.

The high q data is therefore fitted with:

$$I(q)_{highq} = I_0 \left(\frac{2J_1(qr_p)}{qr_p} \right)^2 + S_{inc} \quad (2.1)$$

with I_0 , r_p and S_{inc} left as free parameters. The constant I_0 is a function of the contrast factor, the polymer concentration and the monomer length ($b = 5.15 \text{ \AA}$) for a glucose unit. S_{inc} accounts for the q -independent scattering.

Intermediate q: correlation peak

At lower q values, inter molecular correlations become important and $H(q)$ is no longer negligible. Hammouda et al. [44] proposed a Lorentzian function to fit polyelectrolyte peaks and related the peak intensity to the solvation quality, by analogy with neutral polymers, where the random phase approximation establishes a direct link between the high q intensity and the solvent quality. We find that, while a Lorentzian function can describe our data, it does so by forcing a constant slope at high q by background fitting. If we use the value of S_{inc} obtained by fitting a worm like chain to the high q region of our data, the Lorentzian fit becomes poor. We therefore opt to use an empirical function which correctly describes the peak profiles and is compatible with eq (2.1):

$$H(q) = \frac{1}{1 - \exp(-(qd)^m - kq)} \quad (2.2)$$

which yields a descriptive fit to the data from which the q^* , $I(q^*)$, the peak position and intensity, and a sharpness parameter can be extracted. We assign no physical meaning to the fitting parameters m , d and k . We allow I_0 to vary in the peak fitting.

Low q upturn and fluctuations

Polyelectrolyte solutions exhibit a scattering upturn at low q values, which is not expected from scaling theory or PRISM, and is thought to be related to the slow mode observed in Dynamic Light Scattering (DLS). Its origin is not well understood but has been associated with clusters or aggregates of chains [45–47], which however appears incompatible with the suppression of long range concentration fluctuations by the large osmotic pressure created by counterions, which serves as a definition of the correlation length in scaling theory. Osmotic pressure measurements, confirm the validity of eq (1.3), from which the scattering intensity at

$q = 0$ is predicted to be much lower than that at the peak. Assuming the low q upturn is caused by supramolecular structures, a tentative power law fit $I(q) = Dq^{-n}$ may provide insight into its nature. Typically, exponents between 2 and 3 correspond to mass fractals while $3 \leq n \leq 4$ correspond to surface fractals or a combination of mass and surface fractals; $n = 4$ would indicate sharply interfaces. D is a constant proportional to the concentration of aggregates and their surface to volume ratio. The power law of the upturn in polyelectrolytes varies from system to system. For example Sodium Polystyrene Sulfonate (NaPSS) in D_2O shows a power law dependence of 3.8 ± 0.2 [45], which decreases with filtering [11] (this decrease is also seen for alginate solutions [49]), while quaternized Poly(2-vinylpyridine) (Q2PVP) in D_2O shows a lower n value of 2.2 ± 0.2 [45, 50]. Other systems show intermediate values: poly(3-thiophene sodium acetate), P3TNaA, in D_2O gives $n = 3$ [51], hyaluronic acid, P3TNaA, in 0.05M NaCl aqueous solution $n \simeq 3.2$ [52], sodium alginate in H_2O gives 2.7, [53] and chondroitin sulfate in D_2O $n \gtrsim 3$ [54]. For comparison, polyethylene oxide, a neutral polymer which forms clusters in water shows an upturn with a power law dependence of $\simeq 3.2$ [29]. The upturn intensity was found to increase linearly with concentration for P3TNaA in the 0.08-1M concentration range.

2.3 Methods

NaCMC of average degree of substitution (D.S.) 1.15 - 1.45 and nominal $M_w \simeq 250$ kg/mol was purchased from Sigma Aldrich. Aqueous GPC with elution solvent 0.3M $NaNO_3$ /0.002 NaOH gave $M_w = 280$ kg/mol and $M_w/M_n = 3.4$. The degree of substitution was measured by converting the polymer into its acid form in a nitric acid ethanol mixture, adding a known amount NaOH and titrating the excess NaOH with HCl using phenolphthalein as an indicator, giving D.S. = 1.17 ± 0.10 . The residual salt in the polymer was calculated by dialysing a solution against DI water (using a 10kDa Spectrapor membrane) and measuring the conductivity increase of the water. Using a totally dissolved solids conversion factor of $0.6 \mu S/pmm$, the salt content in the polymer is estimated to be $\simeq 0.4$ wt%, in good agreement with the typical purity of NaCMC samples (purity ≥ 99.5 wt %). Water was obtained from a MiliQ source and with resistivity of $18 M\Omega/cm$. D_2O 99.8% D content was purchased from Cambridge Isotopes. Rheological measurements were carried out on a stress controlled TA hybrid rheometer using a cone and plate geometry of diameter 40 or 60 mm and angle of 1° or 2° , as well as an Anton Paar Physica MCR 301 using a double gap geometry, with internal and external gaps of 0.5 mm.

SANS experiments were carried out on three diffractometers: time-of-flight SANS2D (ISIS, STFC, HSIC, Didcot, U.K.) with q-range of 0.0045-0.8 Å⁻¹; D11 (ILL, Grenoble, France) with incident $\lambda = 6$ Å and sample-detector distances of 1.2 m, 8 m, 39 m, yielding q-range 0.0013-0.5 Å⁻¹; and D22 (ILL, Grenoble, France) with $\lambda = 6$ Å and sample-detector distances of 1.5 m, 5.6 m, 17.6 m yielding 0.003-0.6 Å⁻¹. Quartz Hellma cells of path length 5 or 2 mm were employed, depending on polymer concentration.

2.4 Results

Rheology

Figure 2.2 summarises representative results of NaCMC solutions. We first obtain the zero shear rate viscosity (η_0) from the Newtonian region of the profile and then fit the viscosity dependence of the shear rate with the Carreau model $\eta = \eta_0 / (1 + (\tau\dot{\gamma})^2)^p$, where τ is a constant with units of time, which may be identified with the inverse of the shear rate at which shear thinning starts, p is an exponent which determines the power law of the viscosity with shear rate in the shear thinning regime and $\dot{\gamma}$ is the shear rate. We also estimated the relaxation time from the inverse shear rate at which the viscosity reached 90% of its zero shear rate value. Fits to the Cross and Carreau-Yusuda models yielded significantly different results, a comparison with these two models is included at the end of this chapter. For samples with $\eta_{sp} \leq 10$, inertial effects become important at high shear rates which lead to an apparent increase in the viscosity. We therefore consider only the Newtonian region below 100 s⁻¹, corresponding to the onset of inertial instabilities in water, and extract its Newtonian viscosity value.

Figure 2.2b shows the specific viscosities (η_{sp}) of NaCMC solutions as a function of concentration. The lines are the scaling predictions for the slopes of η_{sp} for the semidilute unentangled (0.5), entangled (1.5) and concentrated regimes (3.75). These compare well to the best fit slopes 0.68 ± 0.02 , 1.7 ± 0.2 and 3.4 ± 0.3 respectively, and we identify c_e to be $\simeq 2.9$ g/L and $c_D \simeq 14.4$ g/L using the scaling theory power laws and $c_e = 4$ g/L and $c_D = 14.3$ g/L using the best fit power laws. Although our measurements do not extend to low enough concentrations to measure the overlap concentration c^* , we can obtain an estimate by extrapolating the unentangled data to $\eta_{sp} = 1$; this gives $c^* \simeq 0.07$ g/L. The relaxation times in the 3-10 g/L range, within the semidilute entangled region as identified from viscosity, remain constant within experimental error in agreement with Eq. 4. The relaxation times for concentrations above $\simeq 10$ g/L vary as

$c_p^{2\pm0.3}$, which falls between the scaling prediction for entangled neutral polymers in good (1.6) and theta (2.3) solvent. If we only fit the concentrated region as identified from viscosity, we obtain $\tau \propto c_p^{3\pm1}$.

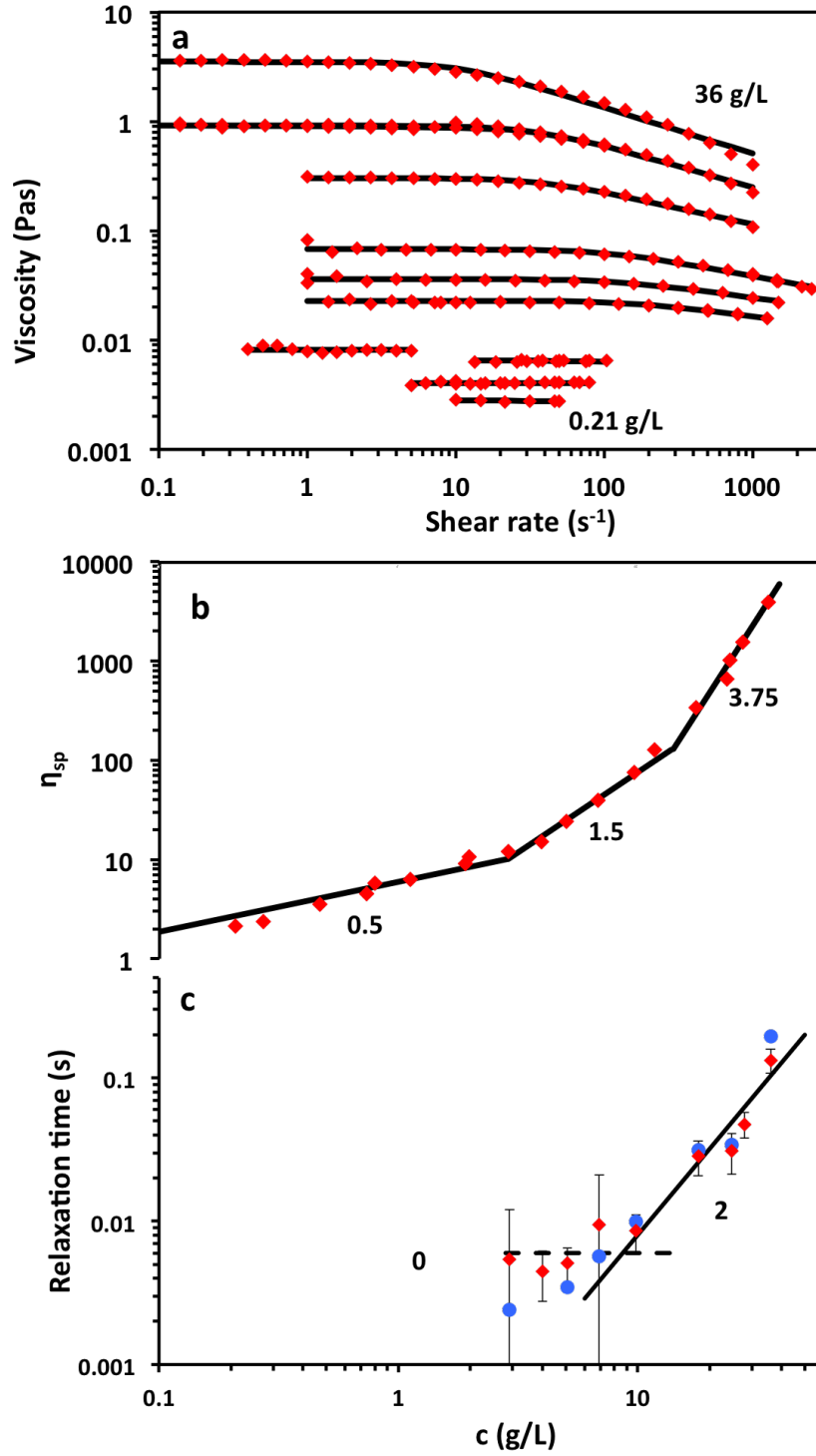


Figure 2.2: Rheology of NaCMC aqueous solutions. a) Representative rheograms for $c_p = 0.21$ to 36 g/L, b) specific viscosity as a function of concentration. The lines indicate the scaling predictions for the semidilute unentangled, semidilute entangled and concentrated power laws. c) Relaxation times (τ) as a function of concentration, red diamonds from Carreau model and blue circles from shear rate at which viscosity is equal to 90% of its zero shear value. Lines indicate power laws of 0 and 2.

SANS

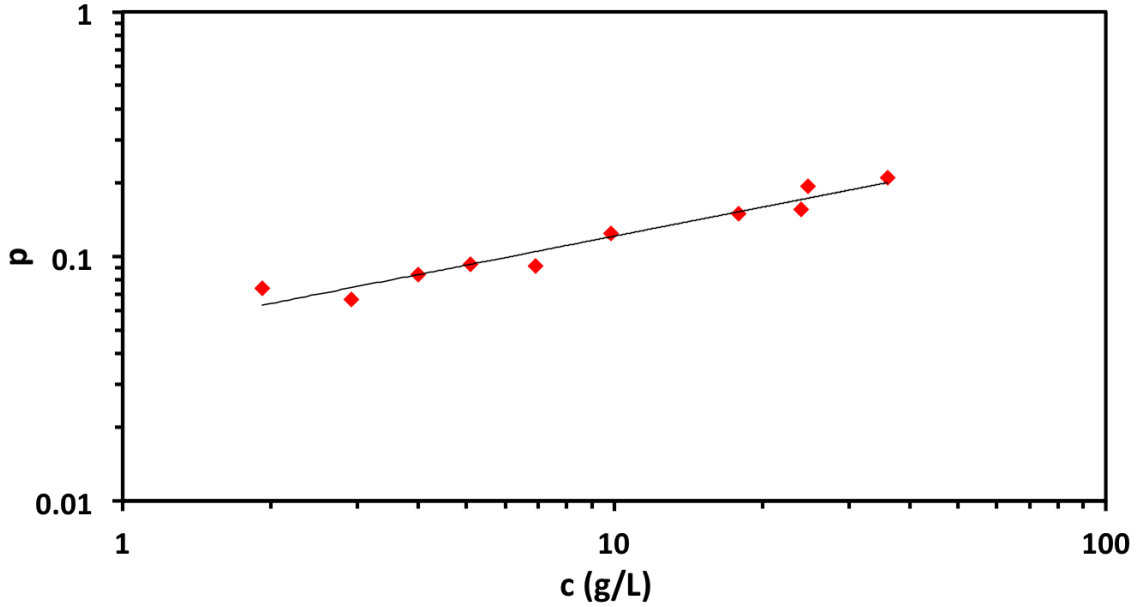


Figure 2.3: Shear thinning exponent p as a function of concentration.

Figure 2.3 shows the value of p as a function of concentration. The increase of p with concentration is common for polymer solutions [56]. A limiting value of $p = 0.25$ is predicted for unentangled solutions on the basis of the Rouse model which is observed experimentally for NaPAMS and NaPSS. The lowest two concentrations on the graph correspond to the semidilute unentangled regime, we see that the value of $p \simeq 0.06$ is significantly smaller than the predicted value. In fact, even for high concentrations, p never exceeds a value of 0.2.

We tested a high concentration ($c = 40$ g/L) sample for thixotropy by measuring its viscosity in the shear rate range of 1 to 800 s^{-1} before and after shearing for 2 minutes at 800 s^{-1} . No time dependence of the viscosity was observed.

SANS

Figure 2.4 shows the scattering profiles for NaCMC solutions with concentrations from 4 to 40 g/L. Typical polyelectrolyte features are observed, namely the presence of a correlation peak, whose position increases with concentration, and the characteristic low q upturn discussed earlier.

High q : chain diameter

The profiles obtained from the D11 and D22 instruments were fitted with eq (2.1). We find that more consistent results are obtained when fitting the range $q > 1.5q^*$, and representative fits to such data are shown in 2.5a. A Gaussian instead of step density profile gives similar values of r_p . The model describes the higher concentrations well but becomes poorer for $c_p \leq 10$ g/L, when an additional feature, a weak broad shoulder appears at high q . This feature has been observed in dilute solutions of NaPSS [57] and semidilute solutions of tobacco mosaic virus [58], as well as in the small angle x-ray scattering of sodium alginate (in the concentration range of $\simeq 2$ -6g/L, although not discussed). [49]

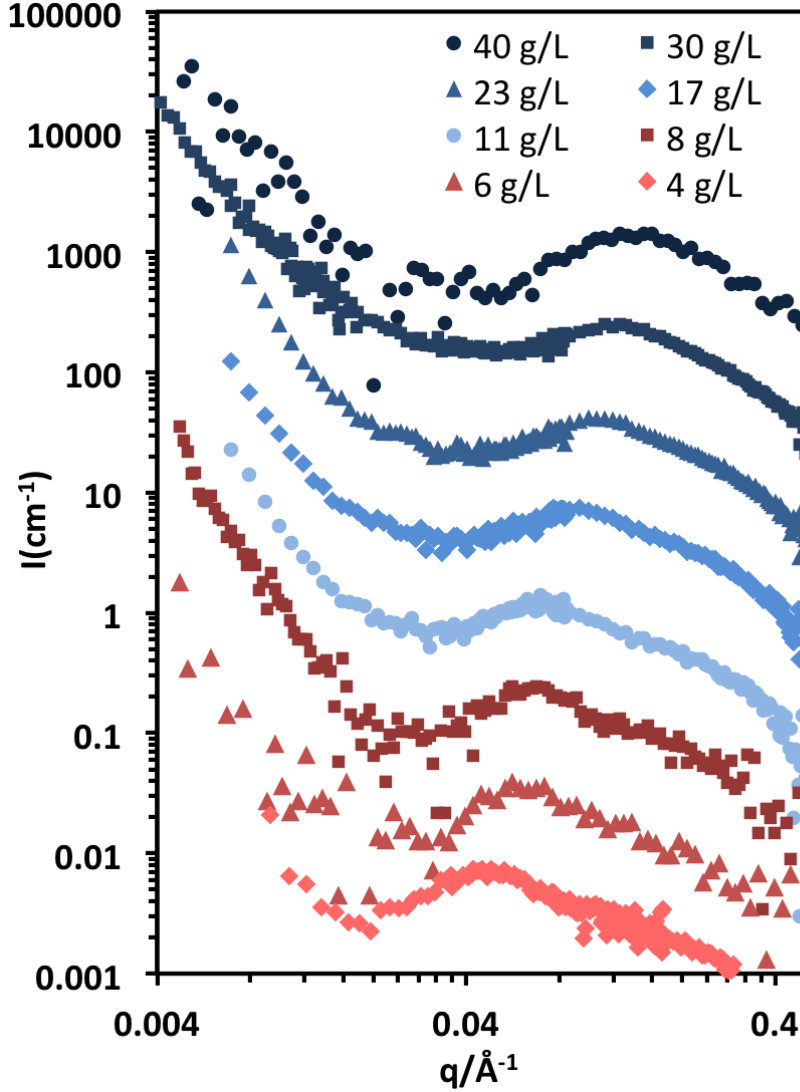


Figure 2.4: SANS profiles for aqueous solutions of NaCMC for different concentrations ranging from 4 to 40 g/L, curves shifted in $5\times$ increments for clarity.

More complex form factors, including the pearl-necklace, elliptical cross section cylinder and single helix (pitch with an upper bound of $180 \text{ \AA}$) form factors also do not yield significantly better agreement than a single cylinder. A core-shell cylinder form factor, leaving the SLDs of the core and shell as free parameters gives a good fit but its not clear to us if the SLD values obtained are valid. Finally, two cylinders of different cross sections, the fraction and radii of which were left as free parameters, did not improve the agreement. Inclusion of the contribution of the counter ions, as calculated by the Katchalsky cell model [44, 59, 60] also did not improve the fit. This feature will be considered in more detail in the discussion section.

r_p values obtained from fitting the data with eq (2.1) are plotted in figure 2.5b. The slight increase at low concentrations is possibly an artefact due to the scattering shoulder at lower concentrations. The values are approximately constant for concentrations higher than 15 g/L.

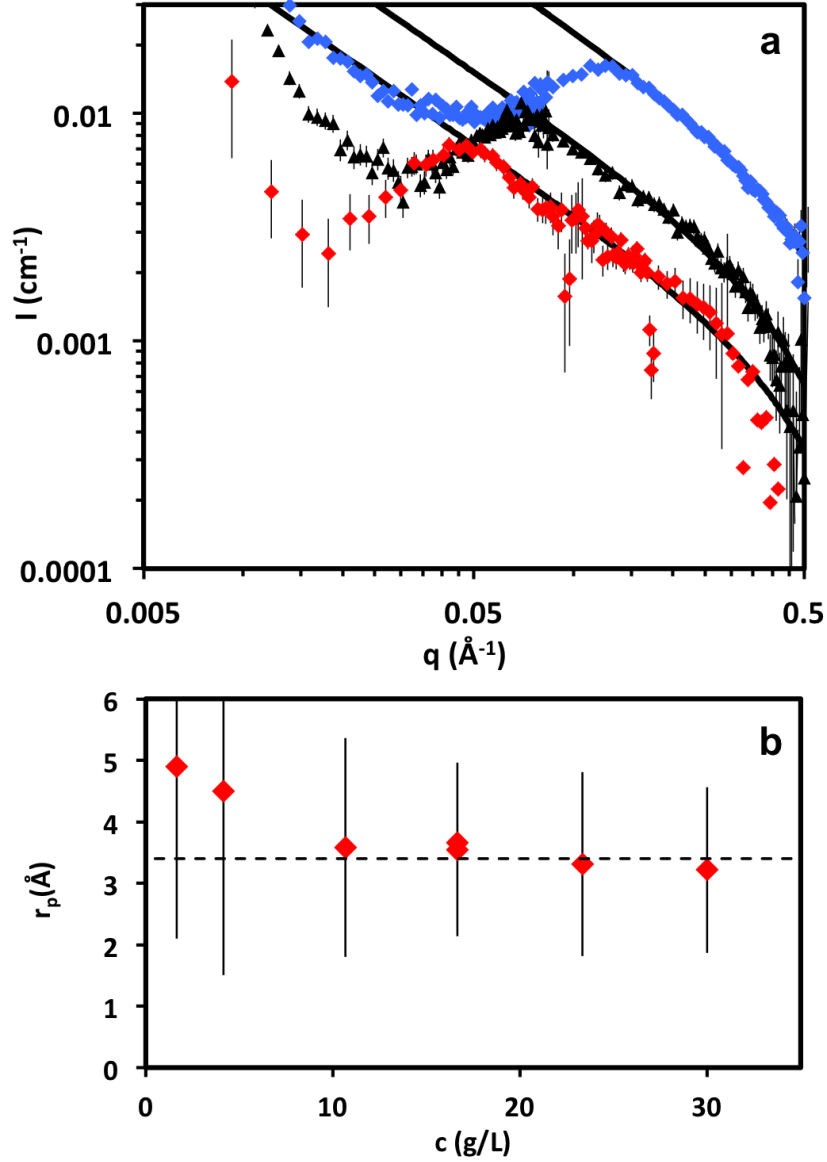


Figure 2.5: a) Coherent scattering data for NaCMC solutions with concentrations: Blue diamonds $c_p = 30\text{g/L}$, Black triangles $c_p = 11\text{g/L}$ and red diamonds $c_p = 4\text{g/L}$. Black line: fit to $q > 1.5q^*$ data using eq (2.1). b) Cylindrical chain radius as a function of concentration. Dashed line indicates $r_p = 3.4 \text{ \AA}$.

A value of $r_p = 3.4 \pm 1 \text{ \AA}$, indicated by the dashed line in figure 2.5b is selected and imposed on subsequent data fits for all the samples with I_0 and S_{inc} now being the only free parameters.

The model agreement with the data does not change significantly compared to leaving r_p as a free parameter. In order to ensure consistency, we evaluate the dependence of I_0 and S_{inc} with concentration, as we expect S_{inc} to be proportional to ϕ , the volume fraction, and I_0 to be proportional to $\phi(1-\phi) \simeq \phi$ both with an intercept at the origin. This is confirmed with a linear regression correlation coefficient (R^2) in the range of 0.99 to 0.93 for all datasets. The I_0 and S_{inc} values for the SANS2D datasets are shown in figure 2.6. Comparing the value of I_0 with the calculated one from the SLDs and partial molar volume of CMC [61], we estimate the water content in the samples to be $\simeq 16$ wt% for SANS 2D and $\simeq 21$ wt% for the D11 and D22 samples, the difference arising possibly due to slightly different drying conditions and small errors in the absolute calibration of the instruments. All the concentrations in this paper are reported using the corrected concentration (assuming the water content to be 18 wt% for the rheology samples). The incoherent scattering of the polymer can be obtained from the value of S_{inc} , after the contributions from water and D₂O have been subtracted, and is found to be $0.4 \pm 0.1 \text{ cm}^{-1}$.

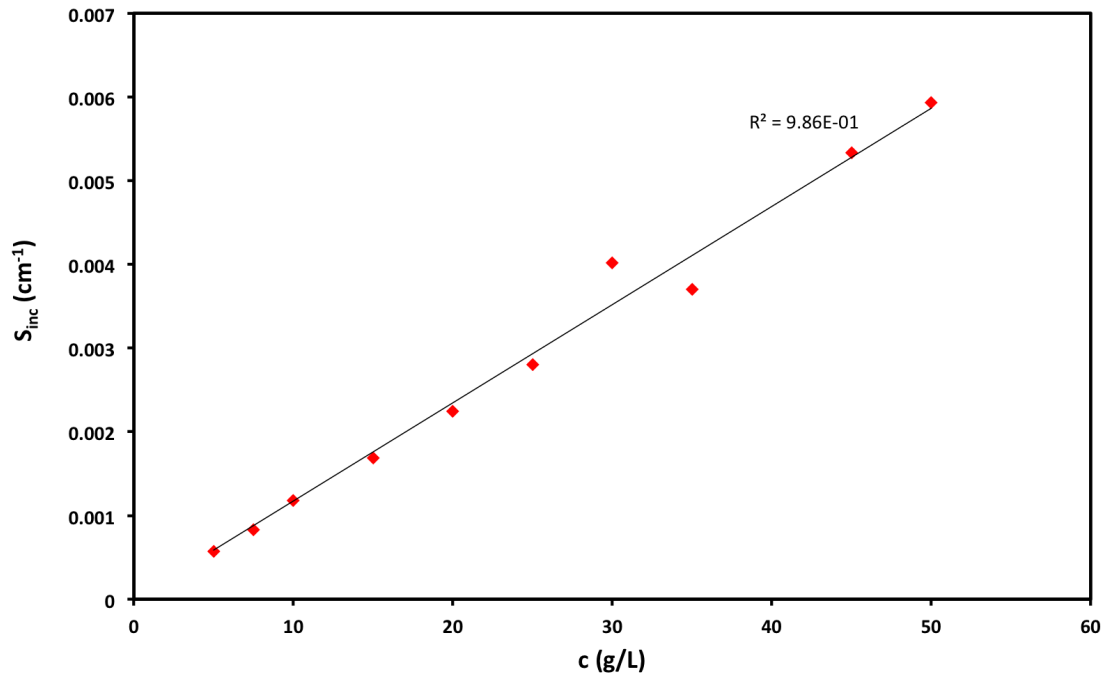
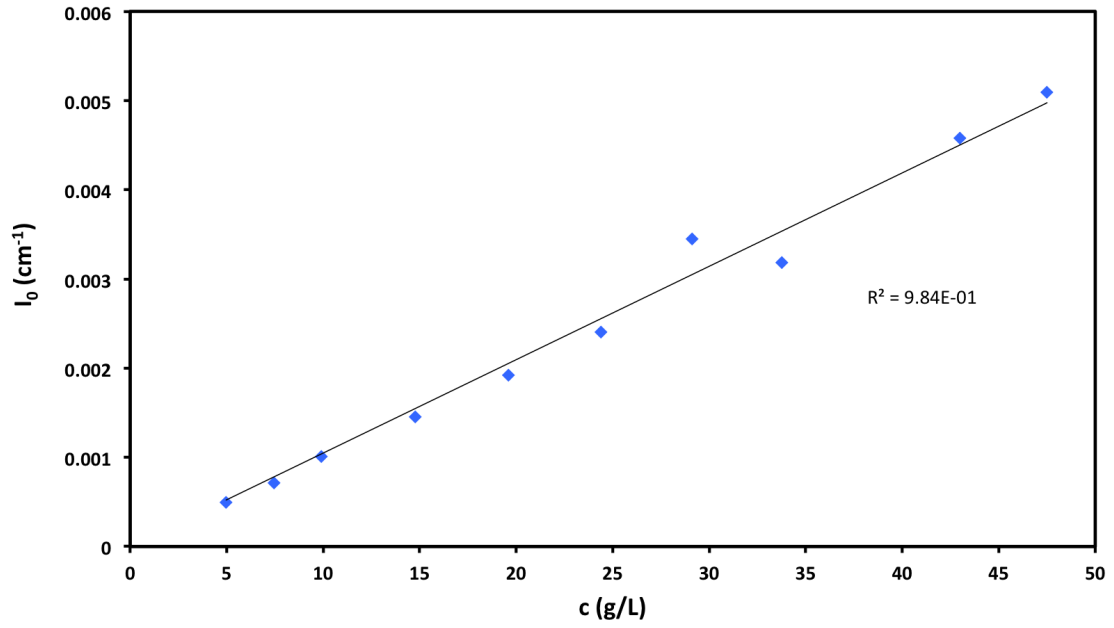


Figure 2.6: I_0 and S_{inc} as a function of concentration for the samples run at SANS2D. The concentration is calculated assuming no water content in the powder.

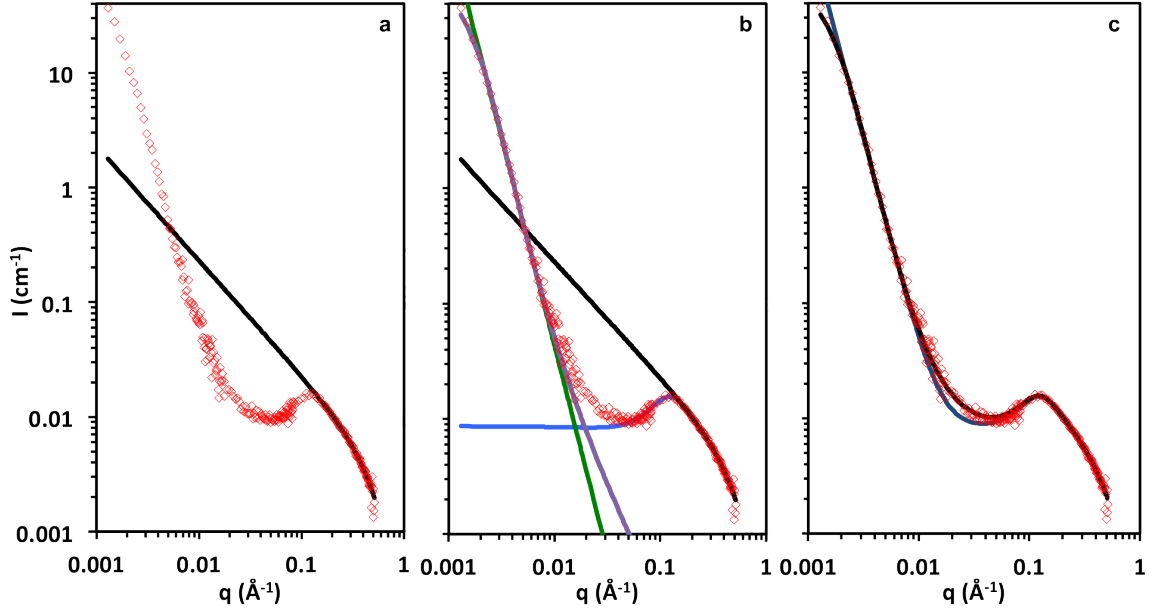


Figure 2.7: Sequence of fitting stages for 30g/L aqueous solution of NaCMC. a) worm-like chain fit to high q data. b) peak function and upturn, the green line is a power law fit to the upturn and purple line is a star form factor. c) total fit: the blue line corresponds to power law fit at low q , while black line corresponds to a Gaussian star fit.

Intermediate and low q ranges: correlation peak and upturn

Figure 2.7a shows the sequential stages of data fitting. First, a worm-like chain form factor with finite cross section, determined previously is fitted to the high q data. Then we use eq (2.2) to fit the correlation peak and finally we add an upturn term D/q^n indicated by the green line. We find that $n = 3.6 \pm 0.2$ is close to the best fit slope for all samples and is thus fixed. Alternatively, a Gaussian star form factor is used [62]. This was only used for this 30g/L sample as the q range extended down to low enough values where a 'flattening' of the upturn is observed.

The peak position q^* and the intensity at the peak $I(q^*)$ are plotted as functions of concentration in 2.8. The best fit imposing a 0.5 power law is found for $q^* = (0.021 \pm 0.003)c_p^{1/2}\text{\AA}^{-1}$. No change in the trend of peak position with concentration is observed across c_D , the concentrated crossover. The $I(q^*)$ data, albeit more scattered, do not exhibit a crossover either. The best fit power law for all samples is $I(q^*) \propto c_p^{0.4 \pm 1}$, similar to what has been observed for other systems [53] in the semidilute and in reasonable agreement with the scaling prediction of $I(q^*) \propto c_p^{0.5}$. A 12 g/L sample was run at 5, 25, 45 and 65°C, and the peak position was found to be insensitive to temperature within experimental error $\simeq 10\%$.

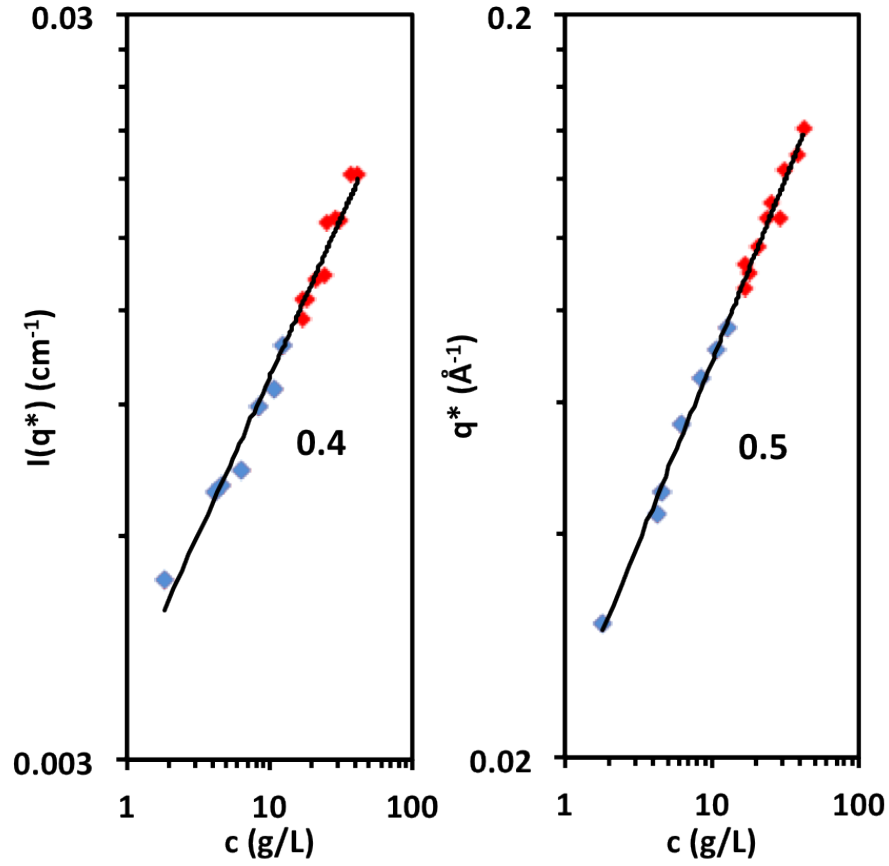


Figure 2.8: Correlation peak position q^* and corresponding intensity at peak $I(q^*)$ as a function of concentration; blue symbols for samples in the semidilute regime and red for those in the concentrated. Numbers indicate the slopes for the best fit single power law.

Determining the peak width (e.g. a FWHM parameter) is somewhat complex as this requires extrapolation into the region where the low q upturn dominates. We therefore compute the full width at 75% of its maximum value (i.e. $3I(q^*)/4$) ($FW75M$) as a measure of peak sharpness which yields more consistent results. The peak sharpness, defined as $I(q^*)/FW75M$ shows no trend with concentration and remains approximately constant at a value of $(9.6 \pm 0.5)10^8$ (dimensionless). The data from SANS2D shows slightly sharper peaks than those from D11 and D22, which could be due to data reduction and/or a small presence of salt in our samples.

Low q upturn intensity

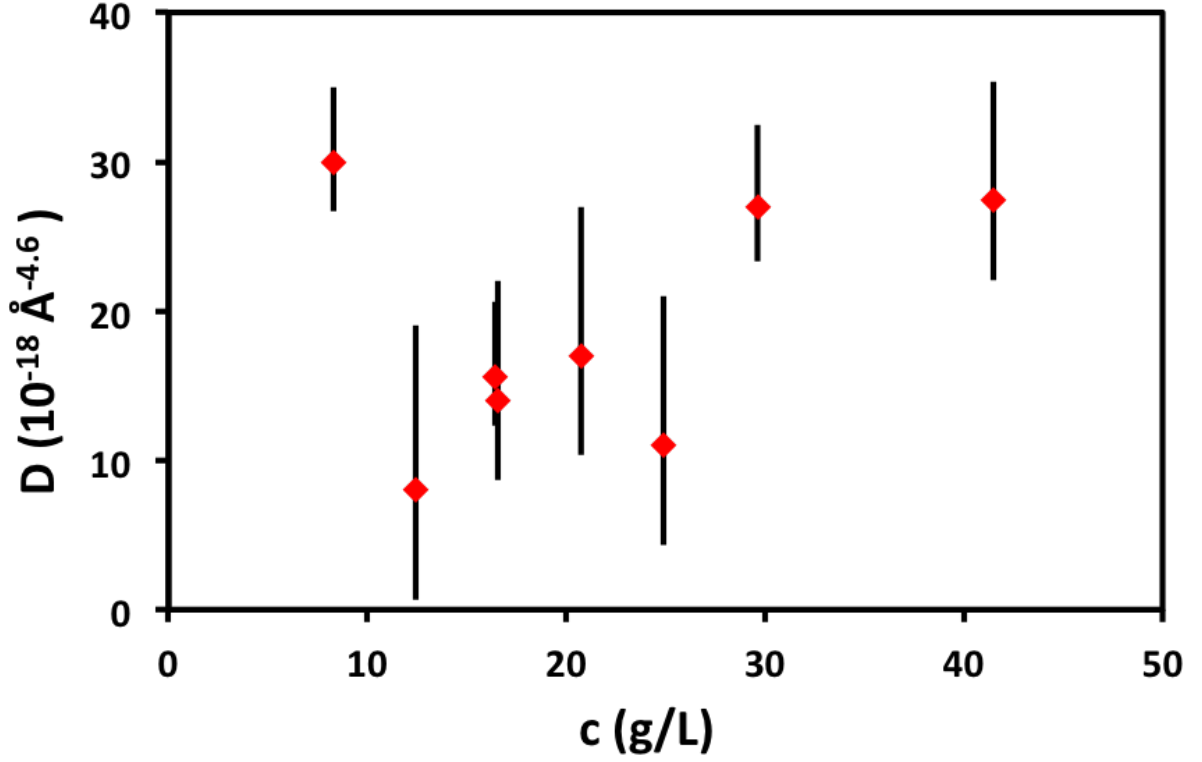


Figure 2.9: Low- q upturn intensity D from power law fits $I(q) = D/q^{3.6}$ at low q as a function of concentration.

The upturn parameter D is plotted as a function of concentration in figure 2.9. We lack the q range or statistics in the low q region for a number of samples to estimate D , and therefore only plot D for concentrations at which it can be obtained with reasonable accuracy. It is not possible from our data to deduce a clear functional dependence for the upturn intensity. We note that all measurements are in the concentrated regime except for the 10 g/L sample which is in the semidilute region. Following the alternative fitting procedure shown in 2.7b (purple line), the star form factor fitted to the 30 g/L sample gives a radius of 1200 Å and $\simeq 110$ arms. Using the approximate M_z value obtained from GPC, the average contour of a NaCMC chain is approximately 12000 Å, the radius of gyration for such chain if it adopts a Gaussian conformation with step length 50 Å ($\simeq L_0$) is $R_g^{Gauss} \simeq 320$ Å and using step length of 150 Å gives $R_g^{Gauss} \simeq 570$ Å. Hence, chains may be stretched, or each 'arm' could correspond to a number of chains.

2.5 Discussion

Structure

Chain diameter/Electrostatic blob size

Cellulose is known to have a reasonably stiff backbone [33] with estimates for the persistence length varying between 50 and 150 Å. The local conformation of a semiflexible polyelectrolyte is expected to be rigid, and therefore, our fit to a cylindrical form factor should give the cross sectional radius of the chain. The fitted radius of $r_p = 3.4 \pm 1$ Å is slightly lower than the one calculated from bond lengths 5 Å [32] but higher than that found for sodium alginate [63], another polysaccharide, from X-ray scattering. A finite cross section helical form factor did improve the fit to the data. The shoulder appearing in the lower concentration samples ($c \lesssim 10$ g/L) could not be fitted to any of the models we attempted. It has been predicted by theory [64] and verified by experiment [11, 58], that the intermolecular structure factor is not exactly equal to one at high q but shows small, damped oscillations, which become less prominent with increasing concentration. It is thus possible that it arises from an intermolecular effect. We note, however, that the local conformation of cellulose derivatives is still unclear: cellulose tricarbanilate (CTC) is known to adopt an irregular helix in tetrahydrofuran, with different helical conformations arising as a function of temperature [65]. Simulations have also suggested a collapsed or stiff conformation of NaCMC depending on D.S. and therefore the assumption of complete rigidity at small length scales may not be entirely correct.

We now compare our results with the predictions of scaling theory for flexible polyelectrolytes, where the local conformation is expected to be that of a collapsed chain for poor solvents or swollen for good solvents. The thermal blob size predicted by scaling theory for flexible polyelectrolytes is given by eq (1.1). If we assume the same charge density as for the less substituted samples studied by Bordi et al [41], we obtain one charge per 2.4 monomers. Using this value for A , $\xi_T = 8.4$ Å assuming poor solvent conditions and 9.4 Å for good solvent conditions. In the poor solvent, if the chain tended to collapse in these length scales, we would have expected the fitted radius to be somewhat larger than 3.4 Å. In the good solvent case where the chain remains flexible but expanded, we can include this flexibility in the fit by adding a term to account for it though the persistence length. However, as the chain would again become rigid for distances greater than ξ_T , this can only be fitted in a very narrow range, and it is thus not possible to test with our data. Working with the assumption that the chain does not bend on small length-

scales, viz the size of a disaccharide unit ($10.4 \text{ \AA}$), then the chain remains rodlike up to ξ_T due to intrinsic rigidity, and rod like for distances above ξ_T due to electrostatic repulsion up to the correlation length. This is equivalent to a solvent quality parameter of $B = 1$.

Correlation length

Assuming the solvent quality parameter B to be 1, the correlation length is predicted by scaling theory to be $\xi = 286c_p^{-1/2}$, which is close to the measured value of $\xi = 296 c_p^{-1/2} \text{ \AA}$ with c_p in g/L, which corresponds to $B = 1.06 \pm 0.1$. Scaling theory also predicts $I(q^*)$ to vary as $c_p^{1/2}$ in the semidilute regime, close to the observed dependence $c_p^{0.42 \pm 0.1}$. Alternatively, $I(q^*)$ can be fitted with a 0.5 power law for $c_p \geq 8 \text{ g/L}$ and a 0.3 slope for $c_p \leq 8 \text{ g/L}$. It is interesting that no change in the correlation length scaling with concentration is observed from the semidilute to concentrated regimes, contrary to that observed by Nishida et al. [66] for NaPSS, where the power law exponent changed from 0.5 to 0.25 and the $I(q^*)$ power law with concentration decreased at the crossover (specific values were not reported). This difference could arise due to the hydrophobic nature of NaPSS. Assuming the chain is stiff for dimensions up to the correlation length ($B = 1$), is also compatible with the temperature insensitivity of the correlation length, as increasing the thermal energy is not sufficient to render the cellulose chain flexible at small lengthcales and hence the conformation remains unchanged. On larger length scales, electrostatic forces, much larger than $k_B T$, dominate. We note that this behaviour is analogous to flexible polymers far from the θ condition, i.e. deep into the good or poor solvent regime.

The crossover between the semidilute and concentrated regimes is predicted to happen by scaling theory when the correlation length decreases to the electrostatic blob size, but that should not apply to a more rigid polyelectrolyte. From the value of the peak position at c_D , as measured by rheology, we estimate $\xi(c_D) \simeq 80 \text{ \AA}$. This is much larger than the estimated values of the thermal blob length for the good or poor solvent cases. It is however similar to the intrinsic Kuhn length reported in the literature for NaCMC [32,33]. Scaling theory assumes that polyelectrolytes are flexible above the monomer size and hence are collapsed or extended rather than rod-like at distances smaller than ξ_T . With respect to the intrinsic persistence length $L_0 = L_{K0}/2$, it is often the case that $\xi_T \leq L_0$, and in this situation we could expect polyelectrolytes to remain rigid at small length scales, if the covalent bonds or steric hinderance that give rise to intrinsic rigidity involve energies much greater than $k_B T$. A crossover may

then be expected at $\xi = L_0$, rather than $\xi = \xi_T$. Below, we compile literature data on other polyelectrolyte systems to assess whether this conjecture is consistent for polyelectrolytes of different persistence lengths.

Table 1 shows the intrinsic persistence length, c_D in molar units and the correlation length at c_D for a number of polyelectrolyte systems, along with the method used to estimate the crossover to the concentrated regime. For the majority of these systems, the crossover is identified from rheological methods, while for the first three it is identified from scattering measurements of the correlation length, where a change of the scaling of ξ with concentration from 0.5 to 0.25 is observed. For NaPSS, the crossover has been identified by scattering techniques (SANS and SAXS) and osmometry, all agreeing within experimental error. $\xi(c_D)$ is obtained by extrapolating scattering measurements from the semidilute regime to c_D in the case of QP2VP-55 and NaPA, and from the concentrated back to c_D for xanthan and alginate. c_D and $\xi(c_D)$ for HA are obtained from the results of Lorchat [67] et al. who observed a power law change in the scaling of ξ from $1/2$ to $1/4$. Using SAXS Salamon et al. [68] however see no crossover in the scaling of the correlation length with concentration up to 0.2M for NaHA. The case of xanthan is somewhat complicated [69] as it adopts a double helix conformation in solution. The power law in the concentrated regime is $\simeq 0.5$ at high concentrations and $\simeq 0.3$ at lower concentrations (but still in the concentrated regime as identified by rheology). For systems where no data exists for the intrinsic persistence length (QP2VP, NaP α MSS, PDADMAC), the persistence length of the neutral polymer has been used.

Polyelectrolyte	L_0 Å	c_D /M	$\xi(c_D)$ /Å	Method	ref
NaPαMSS	22	0.5	52	SANS	[70]
PDADMAC	26	0.15	79	SANS	[67, 70].
NaPSS	9.5	1	35	SANS, SAXS, Osmometry	[2, 11, 66, 70, 71]
NaCMC	50	0.054	84	Rheology	This work [32, 33]
QP2VP-55	15	1	43	Rheology	[17, 50, 74–76]
NaPa	15	1.3	32	Rheology	[77–79]
Alginate	103	0.07	139	Rheology	[53, 80–84]
HA	65	0.08	71	SAXS	[1, 12, 67, 86, 88]
Xanthan	930	0.002	314	Rheology	[60, 69, 90–92]

Table 2.1: Polyelectrolyte, intrinsic persistence length, correlation length at $c_p = c_D$ and method(s) for estimating c_D . All refer to aqueous systems except QP2VP-55 for which the solvent is ethylene glycol. The reference column includes the source for c_D , ξ and L_0 . For the latter quantity, a range of values can be found, the spread in the values is used for the error bars in the two figures below.

The figures below show c_D and $\xi(c_D)$ as a function of L_0 . The former shows a clear correlation, with intrinsically stiffer polyelectrolytes having a lower c_D . The opposite trend is observed between L_0 and $\xi(c_D)$. We may expect no correlation for the more flexible systems where the concept of a thermal blob applies. The dashed line indicates $\xi(c_D) = 10.5L_0^{1/2}$ while the full line indicates $\xi(c_D) = L_0$. The former shows a better agreement suggesting that, while there is a correlation between L_0 and $\xi(c_D)$ it is not linear, and therefore the crossover to the concentrated is unlikely to correspond to a crossover between the two quantities.

Power law dependence of the correlation length with concentration, flexible vs. stiff polyelectrolytes

NaPSS, NaPαMSS and PDADMAC show a change in the scaling of the correlation length with concentration from 0.5 to 0.25 at $\xi(c_D)$ while NaCMC and HA do not. Additionally, ξ for DNA and chitosan scales as $c_p^{1/2}$ even when $\xi \leq L_0$. It would appear therefore that the scaling of the correlation length remains unchanged for stiff polyelectrolytes but not for flexible ones. One exception to this is HA and NaHA, where, despite having the same intrinsic flexibility, the former does not show a change in the scaling while the latter does, hence, there must be other parameters affecting whether this change in scaling happens or not.

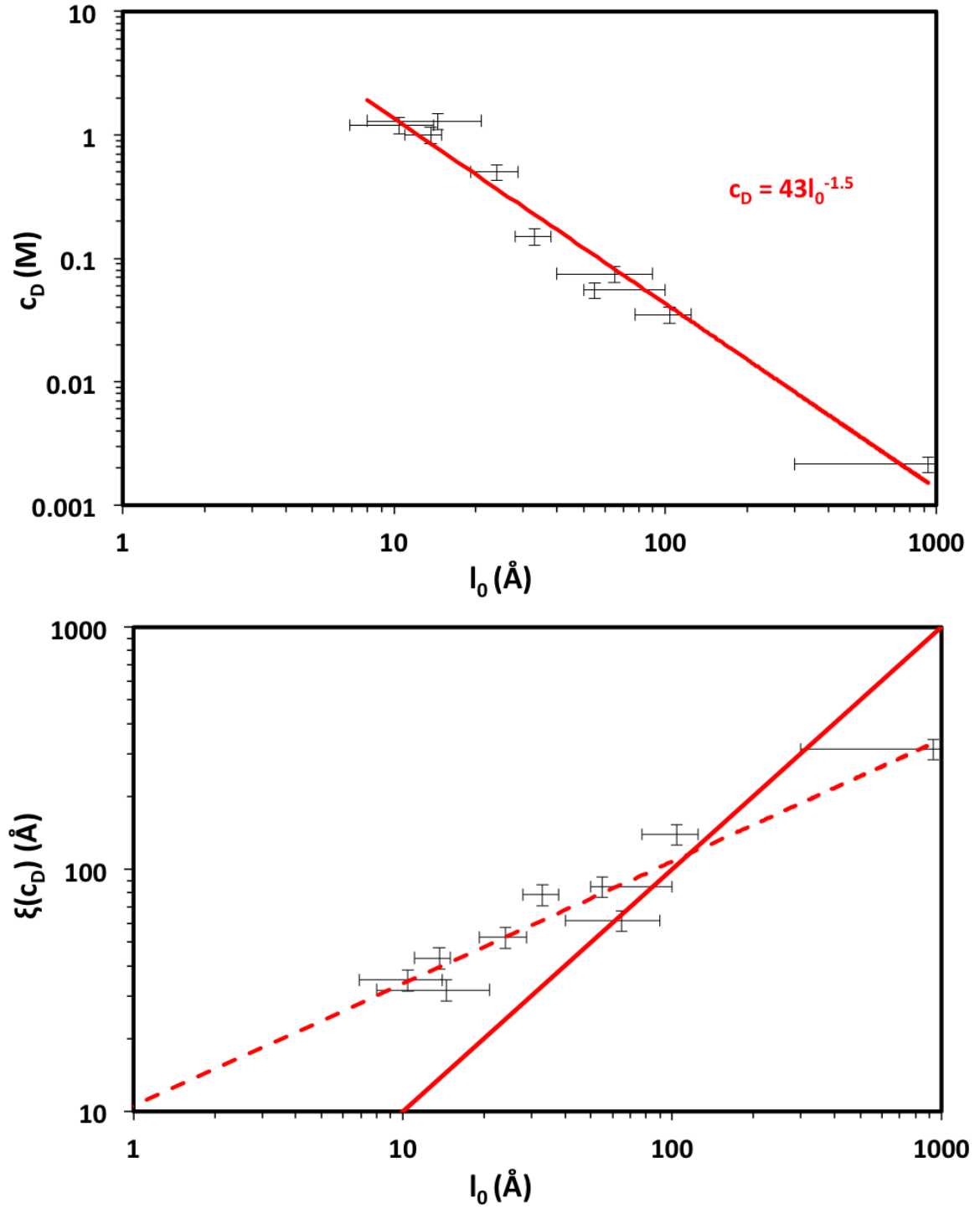


Figure 2.10: (Left): c_D vs. L_0 for the systems listed in Table 1, line is a power law best fit $c_D = 43L_0^{-3/2}$. (Right): Correlation length at the crossover to the concentrated ($\xi(c_D)$) as identified by scattering or rheology (see text) vs. intrinsic persistence length L_0 . Dashed line indicates is a power law best fit $\xi(c_D) = \sqrt{110L_0}$, full line indicates $\xi(c_D) = 2.5L_0$.

Comment on clustering and solubility

The origin of the scattering upturn in polyelectrolyte solutions remains controversial as solutions simultaneously exhibit low osmotic compressibilities but pronounced low wavenumber 'fluctuation' scattering. We find that our data is reasonably well modelled by a fractal law of power 3.6, which we find to be concentration *independent*, and a pre factor D that broadly increases with concentration. Such power laws can be interpreted as arising from fractal surfaces [51] or globular clusters [45], however, other structures, including branched systems yield similar results for $q \gg 1/R_g$.

In order to discuss the low q upturn in more detail, we make the following assumptions: 1) the upturn at low q is caused by clusters of polyelectrolyte chains and 2) We can model the solution as consisting of two 'phases': Phase 1, the dispersed chains, which behaves as that expected from scaling theory, and would show a scattering function that monotonically decays for $q \leq q^*$, and phase 2, the clustered chains. Such a model was proposed by Amis et al [45]. We note that the first assumption is somewhat incompatible with our understanding of polyelectrolytes in that we expect osmotic pressure to suppress concentration fluctuations for length scales greater than the correlation length.

Assuming that each branch in the star fit corresponds to one chain (110 chains per star), we can work out the fraction of clustered chains from the $I(0)$ ($\propto \phi V_p$) value. This gives a relatively low amount of chains clustered ($\simeq 3\%$) for the 30g/L sample. The volume fraction occupied by the stars, calculated by assuming each star occupies a volume of $2R_{ee}^3$, where $R_{ee} = 6^{1/2} R_g^{Gauss}$ is the end to end distance of a Gaussian branch is $\phi_{Stars} = 0.09$. From this, the mean concentration inside a star is approximately 0.33g/L, over two orders of magnitude lower than the mean concentration of the solution. Requiring that the concentration inside the stars is the same as the overall concentration, the number of chains inside a star is then $\simeq 15000$ (i.e., each branch corresponds to $\simeq 140$ chains). The volume fraction of the stars is now $\phi_{Stars} \sim 7 \times 10^{-4}$, and the fraction of clustered chains is $\simeq 0.02\%$. This suggests the stars are not interpenetrating. We may then approximate their contribution to the viscosity of the solution by treating them as hard spheres. With this assumption $\eta \simeq \eta_s (1 + 2.5\phi_{Stars})$ [93]. Where η_s is the viscosity of the medium, in this case, the viscosity of the polyelectrolyte solutions if no stars were present. We expect the total clusters therefore to contribute to an increase of $\sim 0.1\%$.

We note here, that while we expect these clusters to be non penetrating, it is possible that

they could act as entanglement points as they are penetrated by phase 1 chains resulting in a much larger contribution to the viscosity than in the above estimate. However, the average distance between clusters is of the order of microns, which is too great a distance for them to act as entanglement points. Given these considerations, and noting the very coarse nature of the approximations involved here, we expect the clusters to not affect the rheology of NaCMC solutions significantly.

While our data is insufficient to resolve the structure of possible clusters, the high and intermediate q data allow us to effectively determine the solubility of NaCMC in water: The linear variation of I_0 with $\phi(1-\phi)$ suggests no concentration dependent aggregation. Further, the values for the correlation length, in excellent agreement with the expected values for locally stiff chains, again suggest that no significant aggregation occurs: if a fraction of chains were aggregated, the number of effective chains contributing to the polyion mesh would decrease, leading to a higher ξ . Our results unambiguously establish the full solubility of NaCMC (D.S. = 1.2) in water at a molecular level.

Overlap and entanglement concentrations

Estimating c^* from $\eta_{sp}(c^*) = 1$ is commonly used [94], but the definition is somewhat arbitrary. We obtain $c^* = 0.07$ g/L from this method as mentioned above. We may also estimate it by equating the experimentally measured correlation length to the end-to-end distance of chains at overlap and requiring that the chains occupy the whole volume of the solution, that is $c^* = N/\xi^3(c^*)$. This last method gives us $c^* = 0.003$ g/L. If we calculate the volume fraction occupied by the chains at $c_p = 0.07$ g/L assuming the end to end distance of the chains to be $\xi(0.07)$, we obtain 0.2, as opposed to the expected $\phi(c^*) \simeq 1$. This appears to be a large difference.

We check whether the disparity between the overlap concentration calculated from $\eta_{sp}(c^*) = 1$ method, denoted c_v^* , and from the use of eq 1.2, denoted c_s^* is common for other systems. The table below shows the values for c^* obtained a number of systems using these two methods. The calculated volume fraction occupied by the chains at c_v^* (ϕ_{pol}^*) assuming the end to end distance of the chains is given by $R_{ee} = \xi(c_v^*)$ and $\phi^* = c_v^* R_{ee}^3$ where c^* is in units of number of chains per unit volume.

Generally, we may expect that the calculation of the overlap from scattering would under predict c^* as it assumes chains to be rigid above ξ_T in dilute solution when, in fact, chains in

Polyelectrolyte	M_w (kg/mol)	c_s^* (g/L)	c_v^* (g/L)	ϕ_{pol}^*	ref
NaPAMS N = 300	70	3.37	3.22	1.02	[95]
poly(diisobutylene-alt-maleate)	82	0.39	0.51	0.88	[96]
NaPSS ^a	200	0.11	0.34	0.56	[26]
NaCMC	280	0.003	0.07	0.2	This work
poly(styrene-alt-maleate)	350	0.031	0.128	0.5	[96]
PMVP-Cl-55	454	0.032	0.23	0.36	[17, 50]
NaPAMS N = 2200	500	0.066	0.069	0.98	[95]
HA	1260	0.00046	0.016	0.17	[57, 67]

Table 2.2: Polyelectrolyte, M_w , c_v^* , c_s^* and ϕ^* all refer to aqueous systems except PMVP-Cl-55 for which the solvent is ethylene glycol. The reference column includes the source for $\eta_{sp}(c^*) = 1$ and $\xi(c_p)$. ^a Taken from line of best fit to a wide range of M_w in ref [26].

dilute solution are best described by a directed random walk of electrostatic blobs, and hence partially coiled.

Rheology

Semidilute unentangled

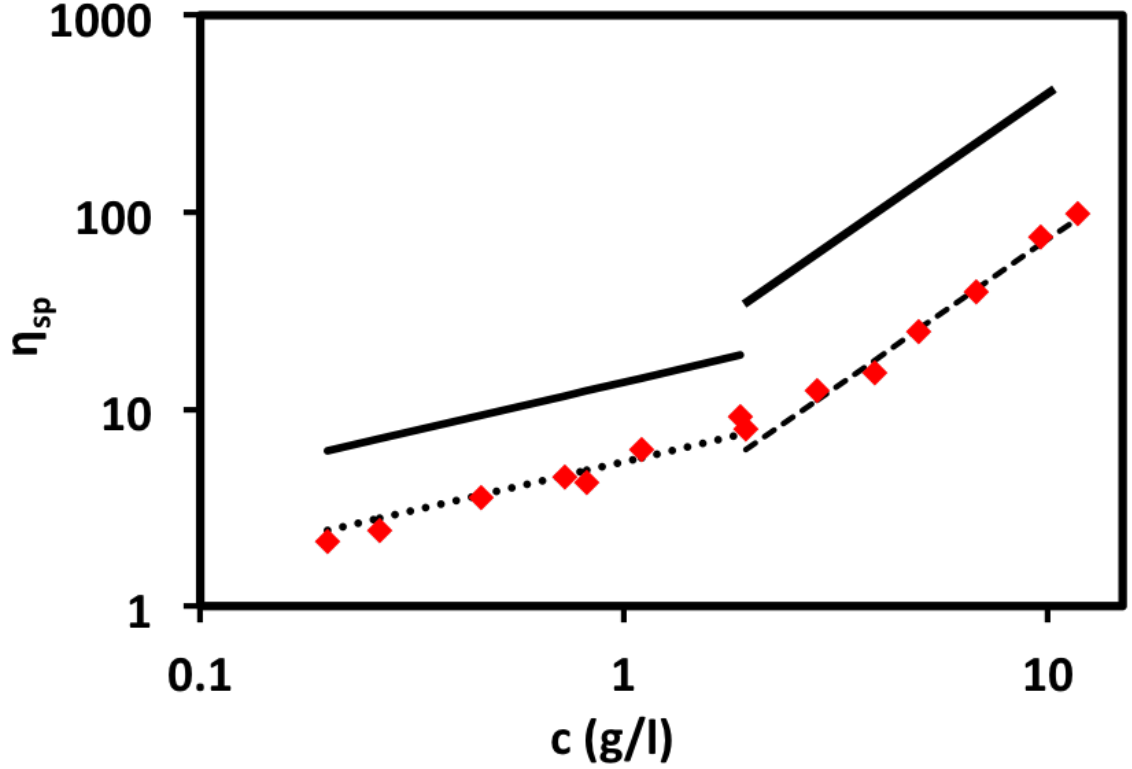


Figure 2.11: Viscosity in the semidilute unentangled and entangled regimes. Unentangled: The full line is computed from equation (1.4) with $B = 1$ and N calculated using M_w . The dotted line is a best fit line with exponent of 0.5, corresponding to $B = 2.3$. Entangled: full line is computed from equation (1.4) with $B = 1$ and $n = 5.5$. Dashed line corresponds to $n = 8$.

The viscosity results for the unentangled region indicate a power law of 0.68 ± 0.02 with concentration, higher than the predicted slope from scaling theory of 0.5. A power of 0.55 is observed for the absolute or relative viscosities in this regime, in agreement with previous data on NaCMC solutions of similar degree of substitution [35]. This exponent does not appear to be universal for polyelectrolytes: NaPSS has been shown to scale as 0.35 [26], poly(2-vinylpyrrolidone) (P2VP) quaternized with different ionic groups and to different extents shows a exponent of 0.5 [17, 95]. Other polymers show greater exponents [99, 100], these arise, at least in some cases due to shear thinning or residual salt [26]. The higher 0.68 exponent may arise from intrinsic rigidity of the chain; scaling theory assumes that the persistence length of chains is purely electrostatic and equal to the correlation length, i.e. $L_T = L_e = \xi$, resulting in the end-to-end

distance of the chain varying as $R \sim c_p^{-1/4}$. Considering the intrinsic rigidity of the chain (L_0) results in a weaker variation of R with concentration, and should thus lead to a higher exponent in the viscosity. We now try to quantify this exponent:

The specific viscosity of polyelectrolytes in the semidilute unentangled regime can be described as:

$$\eta_{sp} = K c_p^\beta \quad (2.3)$$

The best fit to our data is found for $K = 6 \pm 0.1$ and $\beta = 0.68 \pm 0.02$. Eq (1.4), commonly used to calculate B from viscosity data [17,101], which predicts $\beta = 0.5$ uses two simplifications. Firstly, it does not include pre factors in the calculation of the Rouse time and Zimm times. Secondly, it assumes $L_T = \xi$.

Including the pre factors in the Rouse and Zimm times affects K , but does not change the exponent β . We expect the agreement of K with the data to be qualitative, as it involves a number of parameters such as the friction factor, for which we do not have a precise form. We may however expect the scaling prediction for β to be more accurate, given the close match between theory and experiment for neutral polymer solutions and some flexible polyelectrolyte systems [94].

In contrast with the scaling assumption $L_T = \xi$, for semiflexible polyelectrolytes, we should take into account the intrinsic rigidity of the chain. It is also important to note that neutron scattering experiments on NaPSS show that the electrostatic persistence length is approximately proportional but not equal to the correlation length. Spiteri [11] finds $L_e \simeq 0.6\xi$, in agreement with theoretical predictions that $L_e \propto \kappa^{-1}$. It is of course possible for L_e to have a more complex concentration dependence. For simplicity here we write:

$$L_T = L_0 + \gamma\xi \quad (2.4)$$

Davis [32] calculated the electrostatic persistence length of NaCMC using non linear electrostatic wormlike theory [24] for dilute solutions of different ionic strengths in the range 0.01-0.2M. Assuming the persistence length is just a function of the total ionic strength and extrapolating his values to our concentration range, we obtain $\gamma = 0.54$. We may expect this to be slightly lower given the assumption of Manning condensation and for our semidilute solutions, the charge density is lower than this estimate. We now revise the resulting exponent taking into account

the intrinsic rigidity.

Free draining ideal chain

Assuming the chain to be free draining, the Rouse model applies, and the viscosity is then given by:

$$\eta_{sp} = \frac{\pi}{36} c N_l \zeta R^2 \quad (2.5)$$

where R is the end-to-end distance of the chain given by $R^2 = N_l L_T^2$, L_T is the step length and ζ is the friction coefficient of a segment, which can be modelled by that of a sphere: $\zeta = 6\pi\eta_s L_T$. Combining Eqs (2.4) and (2.5), we obtain $\beta = 0.61$, which compares more favourably with the experimentally measured $\beta = 0.68$ obtained for $\gamma = 0.26$.

The departure from the Fuoss exponent might be due to the intrinsic rigidity of the chain, which results in a power law dependence of the step length smaller than 0.5, and in turn in a variation of the end to end distance of $R \sim c_p^{-1/5}$, instead of the $-1/4$ dependence for flexible polyelectrolytes.

Rouse-Zimm chain

If we assume the chain is non-draining up to the segment length and free draining above it, we can calculate the Zimm time of a segment ($\tau_Z \sim L_T^3$) and estimate the total relaxation time of the chain to be $\tau = \tau_Z (\frac{Nb}{L_T})^2$. The viscosity is then estimated by multiplying the relaxation time by the modulus ($k_B T$ per chain). This gives an exponent of $\beta = 0.61$, identical to the free draining case. The same chain conformation but assuming chains to be non draining up to the correlation length (instead of L_T), yields $\beta = 0.72$.

For all the previous calculations, if the intrinsic persistence length is set to zero, we trivially recover the Fuoss scaling of 0.5. We do not know the exact length scale of hydrodynamic screening, which is required for an accurate calculation of the viscosity. However, we find that for chains with some intrinsic rigidity, we can expect the power law in the unentangled regime to be higher than those of flexible polyelectrolytes. Taking $L_0 = 54 \text{ \AA}$ and $\gamma = 0.54$, depending on the model used, the exponent is expected to be between 0.61 and 0.72, in reasonable agreement with the observed 0.68 ± 0.02 .

Figure 2.11 shows the specific viscosity of semidilute unentangled solutions as a function of concentration. The solid line is the scaling prediction using eq (1.4) with N calculated from M_w and $B = 1$. Eq (1.4) over predicts the viscosity values by a factor of 3.5. The best fit to the data

corresponds to $B = 2.3$, shown by the dashed line. Differences in B from SANS and rheology have been reported previously [17, 95, 96]. It is also important to note, that for some systems, such as NaPSS or NaPAMS in water, the viscosity in the semidilute unentangled regime varies as $N^{2-2.4}$, or may even show an exponential dependence [26, 95] as opposed to the linear scaling predicted by eq (1.4). This means that the B value obtained from rheology is N dependent, contrary to what is observed by SANS measurements of the correlation length. It has also been suggested that B varies with concentration [103]. We have analysed data published by Kastner et al. [5] and found $\eta_{sp} \propto N^{1.2 \pm 0.1}$ for unentangled salt free solutions of NaCMC in water of varying D.S. (0.75-1.47), in better agreement with the scaling prediction for flexible polyelectrolytes. We still expect the agreement between our data and eq. (1.4) to be only qualitative as pre factors are ignored in its derivation.

Semidilute entangled and concentrated

The scaling prediction for the slope in the entangled regime ($3/2$) is in good agreement with our best fit slope of 1.7 ± 0.2 . Using $c_e = 2.9$ g/L and our estimates of c^* we calculate the number of entanglements per chain n , to be 5.5 using the scattering derived c^* or $n = 2.6$ using c^* derived from viscosity. The scaling prediction for the viscosity in the entangled regime for $B = 1$ and $n = 5.5$ using eq (1.5) is shown in figure 2.11 (full line). This over predicts the viscosity by a factor of ~ 4 , and gives a best fit to the data for $n = 8$, or, if we use $B = 2.3$ for a value of $n = 3.2$, both indicated by the dotted line. Finally, we estimate n from the relaxation times in the entangled regime, which are approximately constant within experimental error. Assuming $B = 1$, eq. 1.6 gives $n = 3.1$ and assuming $B = 2.3$ $n = 0.9$. This last estimate is clearly incorrect as it predicts the tube length to be smaller than the correlation length.

The power law in the concentrated regime of 3.4 ± 0.2 is in good agreement with the scaling prediction that concentrated polyelectrolyte solutions should behave similarly to concentrated neutral polymer solutions. It is important to note that the change in slope from $3/2$ to $15/4$ is not a neutral polymer behaviour (concentrated solution), since the correlation length is rather large ($80\text{\AA}$) at c_D .

While we have not measured the terminal modulus as a function of concentration, we may estimate as $G \simeq (\eta - \eta_s)/\tau$. The error in the unentangled regime is too large to determine a power law, but for concentrations above $\simeq 2$ g/L, we find $G \sim c_p^{1 \pm 0.2}$ with concentration and about $k_B T/10$ per chain, in disagreement with the scaling prediction of $k_B T$ per chain for unentangled

solutions and of $G \sim c_p^{1.5}$ for semidilute entangled solutions. A linear scaling of the terminal modulus with concentration in entangled solutions has been reported previously for NaPAMS in water and PMVPI-60 in NMF [95,101], a scaling of $G \sim c_p^{0.2}$ was reported for entangled solutions of NaPSS in water [26]. For all these cases, the measured modulus was significantly closer to $k_B T$ per chain. The reason for the difference could be due to the fact that our sample is polydisperse. We estimate the relaxation time (which has a strong dependence on molecular weight $\tau \sim N^3$) from the onset of shear thinning. The onset of shear thinning is likely to correspond to the high molecular weight fraction of our sample, while the viscosity corresponds to the weight average of the whole sample. Overestimating τ will result in underestimating G . It is therefore possible that the modulus may be closer to $k_B T$ per chain.

2.6 Conclusions

We have studied aqueous solutions of carboxymethyl cellulose of average degree of substitution 1.2 in the semidilute and concentrated regimes by rheology and small angle neutron scattering. Rheologically, NaCMC shows similar behaviour to other polyelectrolyte systems, with a near Fuoss law in the semidilute unentangled regime and in good agreement with scaling predictions in the entangled and concentrated regimes. Using SANS, we measure the cross sectional radius of the chain to be $\simeq 3.4 \text{ \AA}$. At low concentrations, below $\simeq 10 \text{ g/L}$, a shoulder appears in the scattering function at high q , the origin of which could not be resolved but may be associated to an intermolecular effect.

We measure the correlation length from the position of the peak in the scattering function, which is in good agreement with scaling predictions. Interestingly, there is no change in the scaling of the peak position or intensity at the crossover to the concentrated regime, contrary to that observed in other systems. This contrasts with a sharp change in the viscosity scaling with concentration. The crossover happens when $\xi \simeq L_{k0}$ and cannot be accounted in terms of the overlap of electrostatic blobs and correlation blobs, as predicted by scaling theory for flexible polyelectrolytes.

The low q upturn in the scattering function shows a power law of $\simeq 3.6$, whose intensity increases with concentration in the concentrated region. The upturn could also be fitted to a star like form factor, which is common of cellulose derivatives in solution. Both our SANS and rheology results indicate that NaCMC is molecularly dispersed in water and, while fluctuations

or clusters are present as for other polyelectrolyte systems, it does not seem to be in a highly aggregated result as often reported in the literature.

We find that while NaCMC is a semiflexible polyelectrolyte with a relatively large persistence length, it behaves largely like more flexible systems, although it differs in the viscosity scaling and existence of a ξ crossover at c_D as also found for stiffer systems.

2.7 Annex: Time dependence of samples and fitting routines

2.7.1 Solution preparation and time dependent effects

Figure 2.12 shows the peak position q^* of NaCMC (D.S.=1.2) in D₂O, measured by SANS, as a function of concentration. Different symbols correspond to approximate times after sample preparation. No trend with time can be observed, indicating that the same polymer fraction is dissolved at all measurement timescales. In addition, we have found that $c_p^{1/2}$ dependence applies across the whole concentration range and that the solvent quality parameter $B = 1$, indicating that q^* corresponds to a mesh of isotropic, locally stiff polymer segments. These observations collectively establish that NaCMC D.S. = 1.2 is molecularly soluble in water within this concentration range.

The viscosity measurements were carried out between 1 and 4 days after sample preparation. We evaluated a possible time dependence in the viscosity by measuring one sample $c_p \simeq 25\text{g/L}$ using a DVI-Prime Brookfield viscometer with a Couette geometry. We found that the viscosity decreases by about 2% from day one to day 2 and by a further 2% by day 4. Approximately 10 months after sample preparation, the viscosity decreased between 20 and 30% for several samples tested. The time dependence of the viscosity may be described by $\eta_{sp} \simeq -12.39\ln(t) + 358.8$, where t is the time in days, for this time window. This slow dependence is likely due to small changes in the molecular weight caused by polymer degradation over time. The results are plotted in Fig 2.13.

The pH of solutions in the 5-35g/L concentration range was $\simeq 7.5$ -8 on fresh samples and showed no measurable time evolution on the 10 month samples.

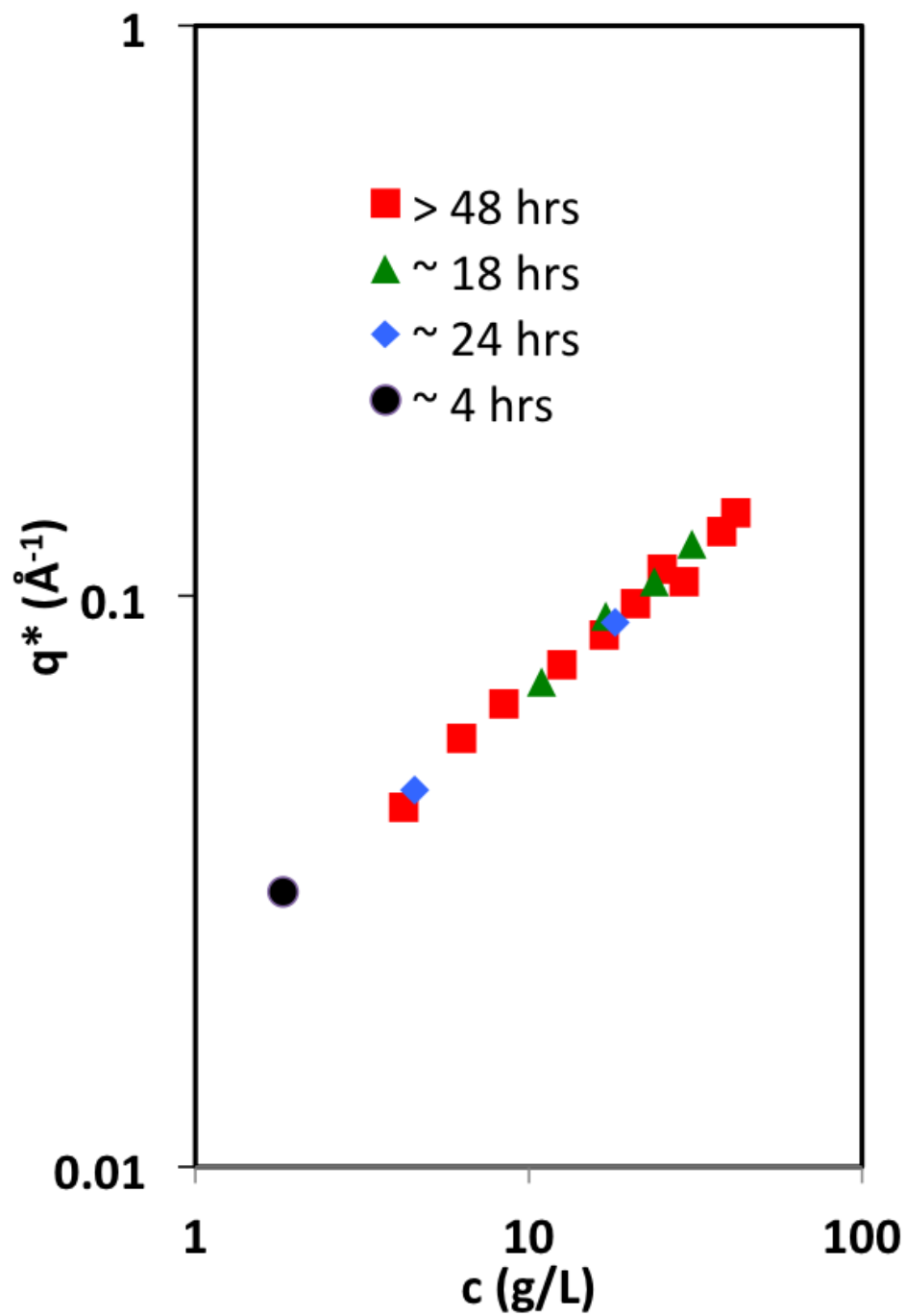


Figure 2.12: Correlation peak position q^* ($=2\pi/\xi$, where ξ is correlation length) as a function of NaCMC (D.S.=1.2) in D_2O concentration measured at different times after sample preparation. No time dependent effects are observed, as shown by the well defined $c_p^{1/2}$ behaviour obeyed by all samples.

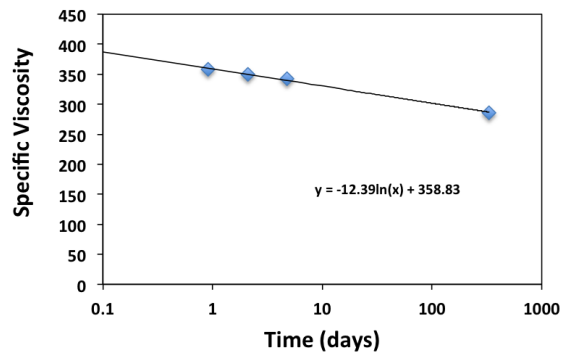


Figure 2.13: Specific viscosity as a function of time from sample preparation for samples $c=25$ g/L NaCMC in water. The last point was estimated as 75% of the viscosity at day 1. Logarithmic line serves as a guide to the eye.

2.7.2 Fitting of flow curves

Two common models that can be used to describe the viscosity vs. shear rate of polymer solutions are the Cross model:

$$\eta = \frac{\eta_0}{1 + (\tau\gamma)^m}$$

and the Carreau-Yusuda (CY) model

$$\eta = \frac{\eta_0}{(1 + (\tau\gamma)^a)^t}$$

which reduces to the Carreau model when $a = 1$, with $t = p$ and to the Cross model when $t = 1$, with $a = m$.

Figure 2.14 shows the flow curves for two NaCMC samples $c_p = 5$ g/L and $c_p = 36$ g/L along with the fits to the Carreau, Cross and Carreau-Yusuda models. For the lower concentration, the Carreau and CY ($a \simeq 1.4, t = 0.15$) models give nearly identical, good fits to the data. The Cross model yields a poorer description to the data. For the high concentration sample, the situation is different. Here, the CY ($a \simeq 0.7, t = 0.91$) gives a nearly identical description to the Cross model, while the Carreau model provides a significantly poorer description.

The zero shear rate viscosity obtained by the three different methods is always similar, but the relaxation times differ significantly. Figure 2.15 shows the relaxation time (τ) as a function of concentration obtained from the different fits. Qualitatively, the data shows the same trends, i.e. the relaxation time is concentration independent at low concentrations and increases with a power law of $\simeq 2$ at high concentrations. The power law in the concentrated region is approximately model independent, the CY model yields $\tau \propto c_p^{1.8}$, the Carreau model $\tau \propto c_p^2$ and the Cross model gives $\tau \propto c_p^{2.3}$. The crossover between the two regimes is also model independent: $c \simeq 5 - 7$ g/L for the Cross values, $c \simeq 10$ g/L for the CY model and $c \simeq 8$ g/L for the Carreau model. The main difference is in the absolute values obtained for the different models. The relaxation times in the low concentration region are similar for the Carreau and CY model but an order of magnitude lower for the Cross model. The values in the concentrated region for the Cross model are also an order of magnitude lower than for the Carreau model, while the CY values lie between the previous two. We conclude that values for the relaxation times obtained by different fitting methods may not be directly comparable. We selected the Carreau model to

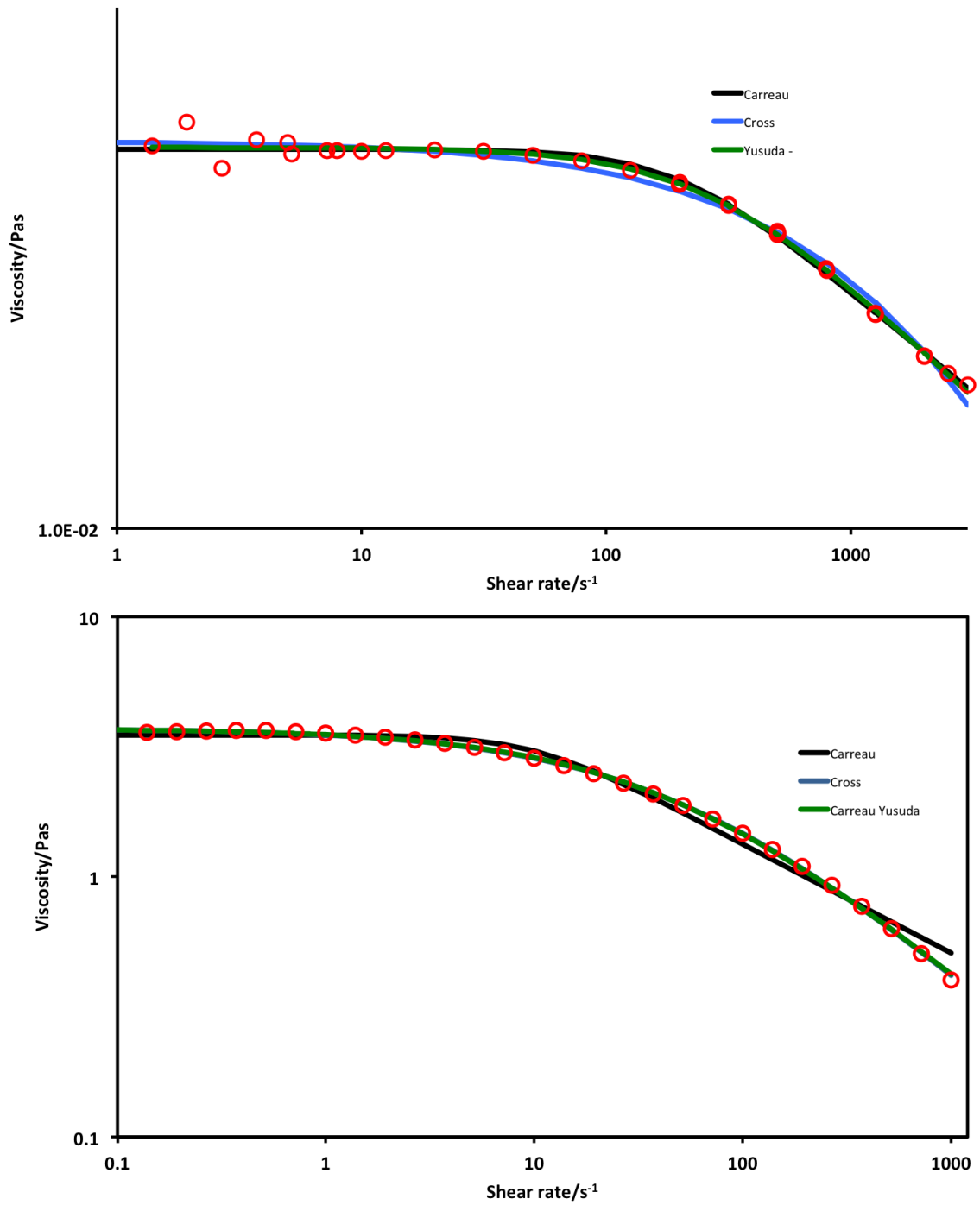


Figure 2.14: Samples with $c_p = 5$ g/L and $c_p = 36$ g/L along with the fits to the Carreau, Cross and Carreau-Yusuda models.

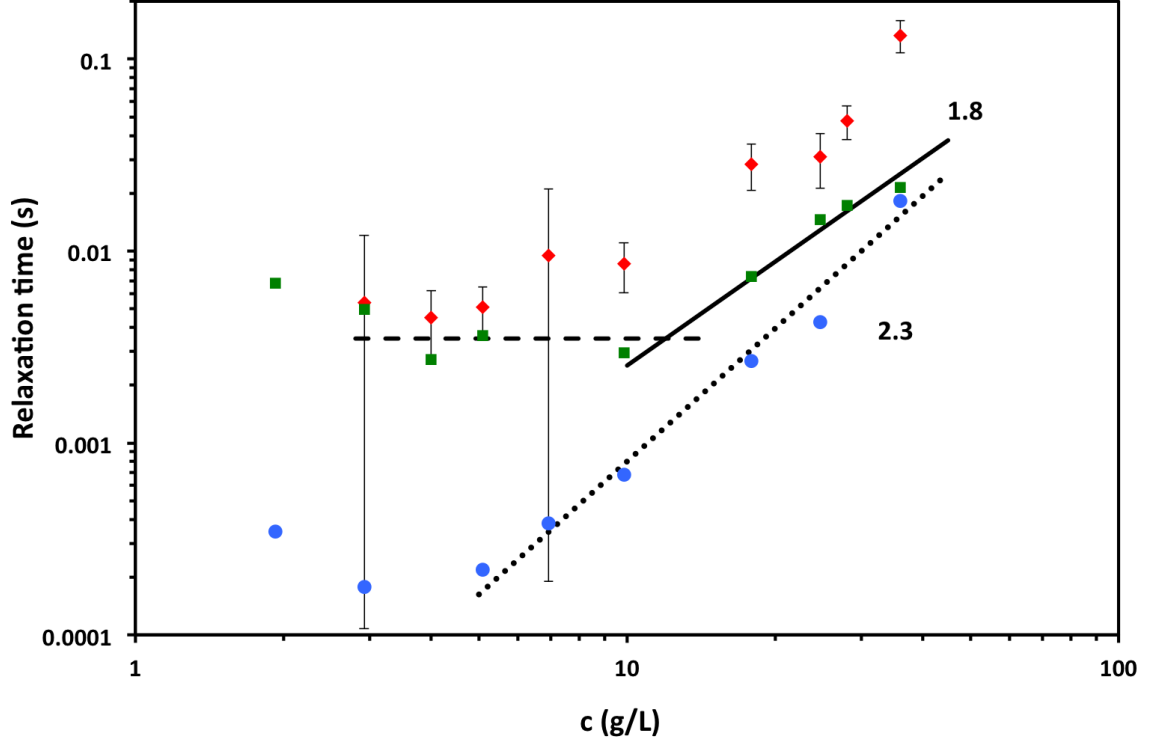


Figure 2.15: Samples with $c_p = 5$ g/L and $c_p = 36$ g/L along with the fits to the Carreau, Cross and Carreau-Yusuda models.

analyse the data in this chapter as it has been previously employed for similar systems [17, 95], thus making our results comparable to literature data.

2.7.3 Fitting of scattering data

Fitting procedure

Data fitting was carried out by least squares minimisation using the error values estimated by Grasp or Mantid (the data reduction software for the D11/D22 and SANS2D beamlines respectively). Due to the high number of parameters in equations 1-3, the fitting is carried out sequentially. Equation 2.1 is fitted to the high q part of the data leaving I_0 , r_p and S_{inc} as free parameters. Fitting different q ranges, always for $q \geq q^*$ we find greater consistency when fitting the data for $q \geq 1.5q^*$. The parameters I_0 and S_{inc} vary linearly with ϕ and $(1-\phi)$ respectively, where ϕ is the volume fraction occupied by the monomers. As explained in the main paper, a value of $r_p = 3.4\text{\AA}$ was selected and the data was refitted with this new value and I_0 and S_{inc} left as free parameters. The new values of I_0 and S_{inc} did not change significantly. The water

content and S_{inc}^{pol} were calculated using this last set of values. Next we fit the data around the peak position with equations 2.1 and 2.2 simultaneously allowing I_0 to vary (the value never deviates from the original by more $\simeq 5\%$). The term for the upturn is finally added and the full set of data is fitted leaving D , n , d , m , k and I_0 free. The value of n is found to be close to 3.6 for all samples and the previous step is repeated with n fixed at 3.6.

Fitting of high q data using a helical form factor

We employ the 'Series of Coaxial Shifted Infinitely Long Thick Helices with a Uniform Electron Density' form factor from ref [104], set to $k = 1$, corresponding to the case of a single helix. A cylindrical helix is defined by $x = R^H \cos(t)$, $y = R^H \sin(t)$, $z = P/(2\pi)t$, where R^H is the radius and P is the pitch of the helix. Additionally, r_p^H , is the cross sectional radius of the helical chain. It is unclear to us the meaning of the pre-factor in ref [104] expression as it is defined differently in two sections of the paper. In order to obtain the helical form factor in absolute units, we take the contour length of the helix to be Nb , and calculate the z-projected contour distance using $\text{arclength} = ((R^H)^2 + (P/2\pi)^2)^{1/2}t$, and require that the low q limit matches the form factor of a rod of equal mass per unit length, which is readily available in absolute units.

In the q -range studied, a number of combinations of r_p^H , R^H and P yield a form factor identical to that of a cylinder. Of course, a helix will reduce to a cylinder when r_p^H or P tend to infinity. We first consider the case of a thin helix, setting $r_p^H = 0$ and allowing P to vary between 5 and 250Å, we obtain $R^H \simeq 2.5\text{Å}$ and $P \geq 40\text{Å}$ as valid fits. Setting $r_p^H = 2$, a more realistic value, and varying P to vary over the same interval, we get $R \simeq 1 - 2\text{Å}$. While our data is insufficient to discriminate between a linear conformation and a helical one, we can state that our data is compatible with a linear conformation or a conformation with small helicity. The lateral fluctuations ($\approx R_H + r_p^H \simeq 3.5 \pm 1.0$) are within the cylindrical fit value of $r_p \simeq 3.4 \pm 1.0\text{Å}$. The mass per unit length being $\simeq 5\%$ higher than the straight conformation case. The water content calculated from the helical form factor is $\simeq 4\%$ lower than for the straight chain.

Fitting of the polyelectrolyte peak to a Lorentzian function The peak in $S(q)$ seen in polyelectrolyte solutions can be interpreted in terms of scaling theory in a straightforward manner as explained earlier in the chapter. Obtaining a physically meaningful expression to fit the scattering data on the other hand is problematic. The random phase approximation (RPA), successful in the description of $S(q)$ for neutral polymers in solution and in bulk, is known to fail for salt free polyelectrolyte solutions [11]. PRISM gives a reasonable prediction for the scattering function (except for the upturn) of polyelectrolytes, but is computationally demanding. For this

reasons, empirical models are often used to fit polyelectrolyte peaks. The most common model is that of a Lorentzian peak [44], to which a term is added to account for the upturn:

$$I(q) = \frac{D}{q^n} + \frac{A}{1 + (|q - q^*|B)^m} + S_{inc}$$

The exponent m gives the high q power law of the coherent scattering intensity, $A \simeq I(q^*)$ and B is a measure of the peak's width, which has been interpreted as a correlation length [44]. Fits to a 16 g/L NaCMC solutions are shown in figure (2.16) and (2.17), using both our fit and the Lorentzian fit. Our fit is seen to provide an excellent description to the data for the full q - range (figure 2.16), while the Lorentzian gives a poor description of the data in the $q < q^*$ region. The quality of the fit is to some extent artificial, if we use our estimate for the background (shown in figure 2.16), which is likely more accurate as it uses a more correct expression at high q , the Lorentzian fit become even worse. Other functions, such as a Gaussian peak do not yield a good fit to our data either.

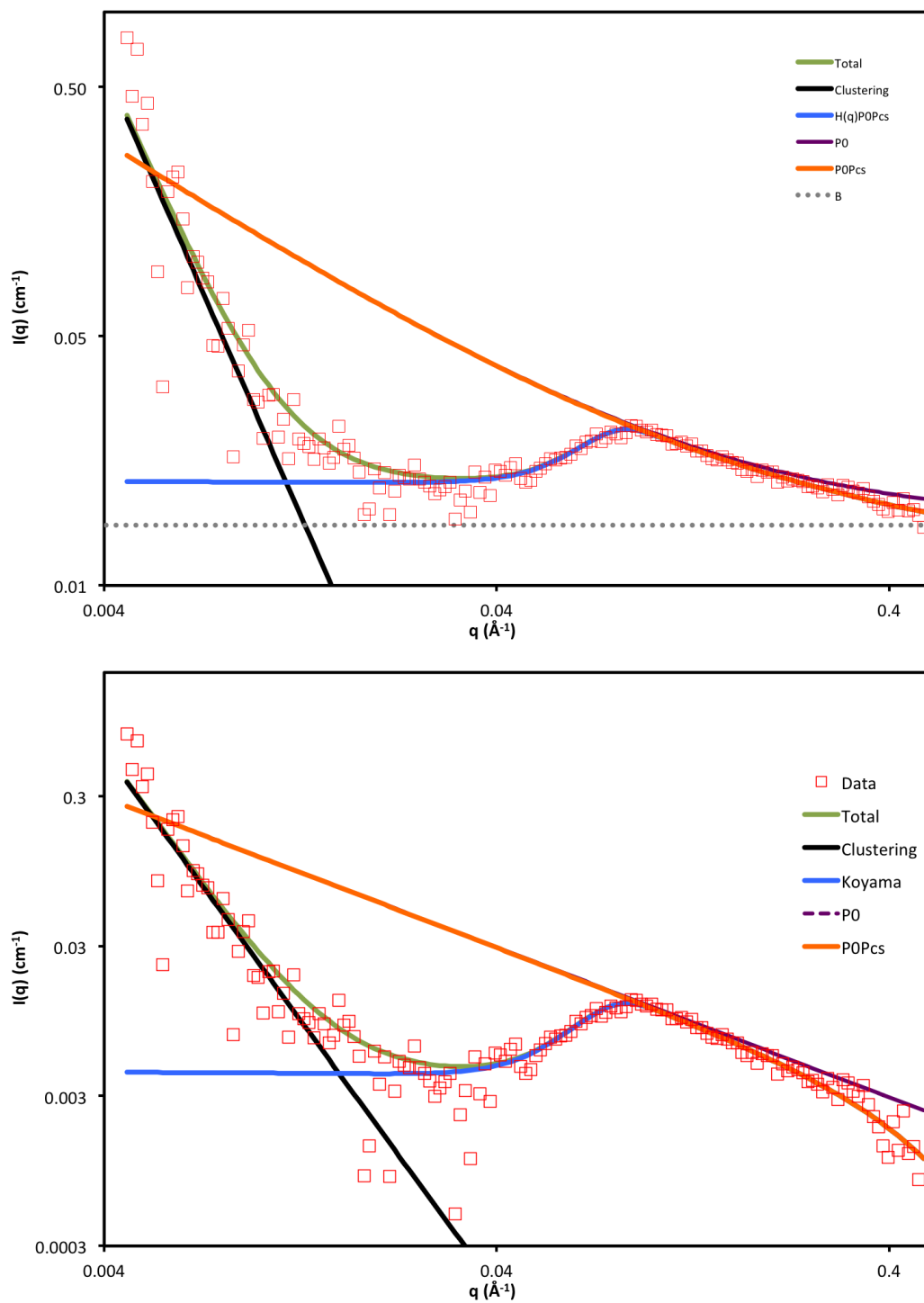


Figure 2.16: Sequential fit to 16g/L sample. Top graph: data without the incoherent scattering from the polymer or water subtracted. Bottom graph: coherent scattering intensity, after background incoherent subtraction as shown in the top graph. Red squares: data. The meaning of the different lines are stated on the caption.

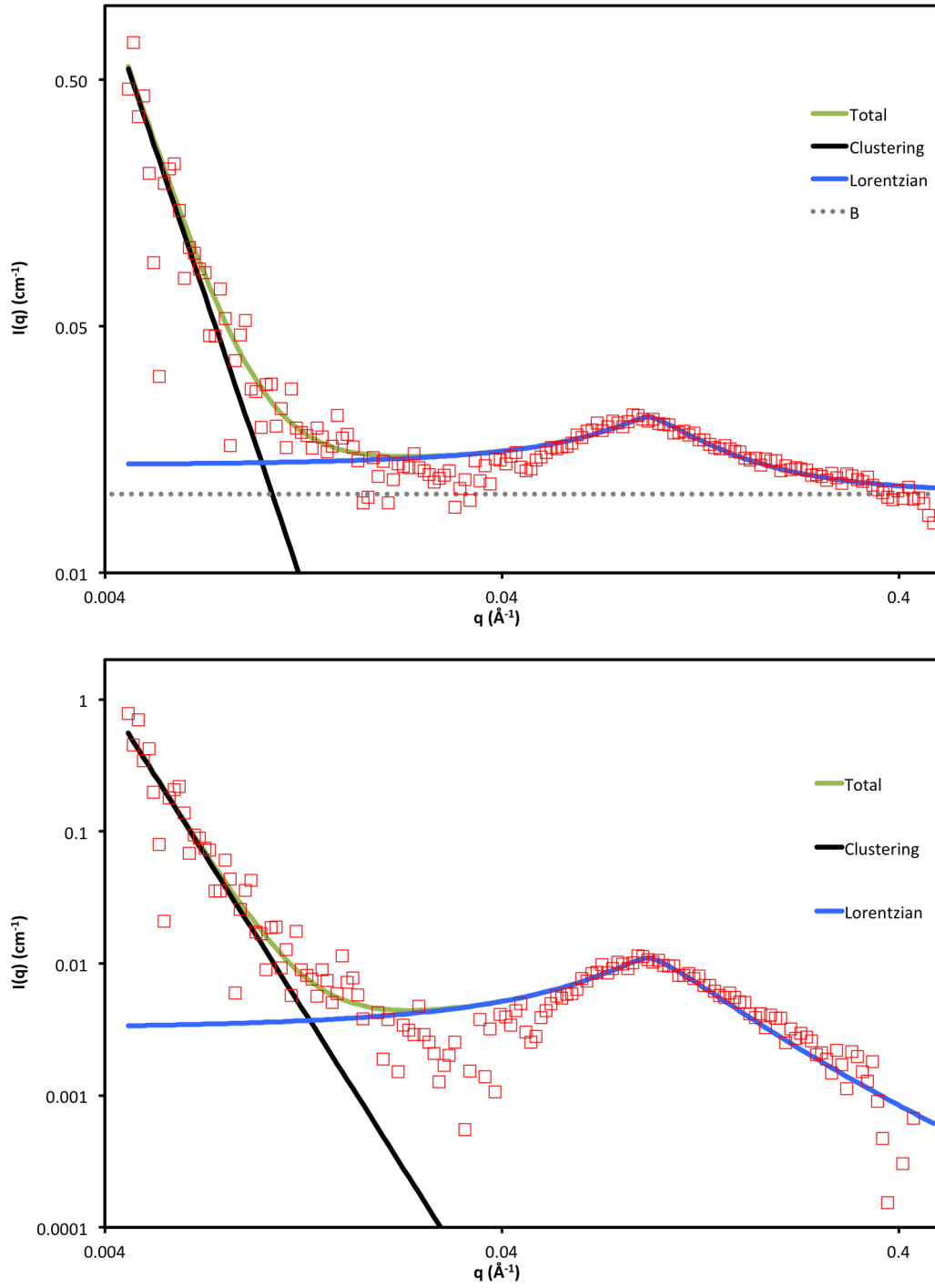


Figure 2.17: Sequential fit to 16g/L sample. Top graph: data without the incoherent scattering from the polymer or water subtracted. Bottom graph: coherent scattering intensity, after background incoherent subtraction as shown in the top graph. Red squares: data. The meaning of the different lines are stated on the caption.

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3 Conformation and viscosity of NaCMC in aqueous solution in the presence of salt

Abstract

We study solutions of sodium carboxymethyl cellulose in high ionic strength media by SANS and viscosimetry. We measure the persistence length, correlation length and zero shear rate viscosity as a function of added salt. The intrinsic persistence length is determined to be $L_0 \simeq 50 \text{ \AA}$ from SANS measurements in semidilute solutions. We first present an analysis of the data using the scaling model of de Gennes-Pfeuty-Dobrynin (GPD) and find strong disagreement between theory and experiment. Next, we compare the data with the theory of Odijk for semiflexible polyelectrolytes. While the theory fails to correctly describe the data, the disagreement is less significant. We revise and extend the theory of Odijk, incorporating more accurate expressions for the excluded volume and chain expansion. These modifications yield a good description of the data.

3.1 Introduction

Having studied the properties of NaCMC in salt free aqueous solutions in the previous chapter, we now move to the case of added salt. The addition of salt to polyelectrolyte solutions leads to increased electrostatic screening, which causes chain contraction and leads to lower solution viscosities. While these phenomena are well understood qualitatively, modelling the electrostatic persistence length and excluded volume as a function of ionic strength is known to be difficult [1], and the validity of current theories is questionable. On the experimental side, a large number of studies have dealt with the dilute solution properties of polyelectrolytes as a function of added salt [1–3]. Systematic studies on the semidilute properties of polyelectrolytes as a function of added salt are however rare.

In this chapter, we will study the effect of added salt on the solution viscosity of NaCMC as a function of added salt and polymer concentration. The structure of the chapter is as follows: we first give a brief review of the basic results for the electrostatic persistence length of polyelectrolytes and an introduction to the worm like chain model, which will be used throughout the chapter. We next consider scaling theories, first, the model of de Gennes, Pfeuty and Dobrynin (GPD) [4, 5], introduced in the two previous chapters, is reviewed for the case of salt containing solutions. We then move on to a model by Odijk [6], which is carefully reviewed. Odijk’s model is extended to calculate the dynamic properties of semiflexible polyelectrolytes (viscosities and relaxation times). Both theories are shown to fail to describe experimental data on solution viscosity, the failure of GPD theory being more significant. We propose two modifications of Odijk’s theory: first, we use an empirical relation for the excluded volume as a function of ionic strength, second, we use an accurate expression for the expansion factor. Once these are implemented, a good agreement between theory and experiment results.

The first annex (section 3.5) presents a compilation and analysis of literature data on the persistence length and electrostatic excluded volume of polyelectrolytes. The first aim is to determine whether any theory correctly describes the electrostatic persistence length and excluded volume as a function of ionic strength. We find that the Odijk, Schoknik and Fixman (OSF) prediction is qualitatively correct for semiflexible polyelectrolytes. While the excluded volume is not well modelled by current theories, we find an empirical relationship, which appears to hold for a range of systems. Sections 3.6–3.7 present further experimental details as well as an evaluation of the effect of salt on solution viscosity for a number of polyelectrolyte systems,

taken from the literature.

3.1.1 Electrostatic persistence length

The ionic strength I is a function of the concentration of ions in solution, given by:

$$I = \frac{1}{2} \sum_i^n c_i z_i^2$$

where c_i is the concentration of species i ions in molar units and z_i is the valency of the ion. The inverse Debye screening length κ^{-1} is the distance at which a probe charge inserted in a solution becomes screened [7, 8]. For a polyelectrolyte/salt/solvent mixture it is given by:

$$\kappa^{-1} = (4\pi l_B (2c_s + f c_p))^{-1/2}$$

where c_p and c_s are the polymer and added salt concentration in molar units respectively and f is the fraction of free counter ions.

The total persistence length (L_T) of polyelectrolytes is given by a sum of two terms:

$$L_T = L_0 + L_e$$

where L_0 is the intrinsic persistence length, which arises due to the rigidity of the uncharged polymer backbone and L_e is the electrostatic persistence length which arises due to repulsion between charges along the polymer backbone. The variation of the electrostatic persistence length with ionic strength is still a subject of debate in the literature. The classical theory developed by Odijk, Schoknik and Fixman (OSF) predicts:

$$L_e = \frac{(l_B/b)^2}{4l_B\kappa^2} \quad (3.1)$$

This expression is expected to hold when $L_e \leq L_T$. Barrat and Joanny [9] later predicted L_e to have a linear dependence on κ^{-1} in contradiction with the OSF formula. A recent theory developed by Dobrynin also predicts L_e to vary linearly with κ^{-1} [10]:

$$L_e = 0.36 \frac{f^2 l_B}{b\kappa} \quad (3.2)$$

Experimental data from SANS, light scattering, and viscosimetry experiments show a power

law dependence of L_e on κ^{-1} between $2/3$ and 2 [11,12], depending on the system and technique. Extensive data for L_e as a function of c_s exists, to the best of our knowledge for two systems, NaPSS and NaHA. We have analysed the available data for these two systems to test whether any theory gives an accurate description of the data, this is shown in the section 3.5. We conclude that no theory can give a quantitative prediction of L_e although the OSF prediction gives a reasonable description for the NaHA system, which is a close analogue to NaCMC in terms of molecular structure (i.e. charge density, L_0 , cross sectional radius etc).

3.1.2 Wormlike chain model

Polyelectrolytes in solution are often modelled as worm like chains. The wormlike chain is characterised by three parameters: the persistence length L_T , the contour length L and the cross sectional diameter d . When excluded volume effects are taken into account, an additional parameter z is needed, which will be described later. The mean square end-to-end distance R_{ee} , radius of gyration R_g and intrinsic viscosity $[\eta]$ for an ideal (i.e. no excluded volume) worm like chain are given by [13]:

$$\langle R_{ee}^2 \rangle = 2L_T L - 2L_T^2 (1 - e^{-L/L_T}) \quad (3.3)$$

$$\langle R_g^2 \rangle = LL_T/3 - L_T^2/6 + 2L_T^3/L - 2L_T^4/L^2 (1 - e^{-L/L_T})$$

$$[\eta] = \Phi L_T^{3/2} / M$$

where Φ is a function of d , L and L_T , which tends to the Flory constant Φ_0 in the limit of infinite length. Values for Φ are tabulated in ref [14].

The intrinsic viscosity represents a measure of the volume occupied by a chain at infinite dilution ($\sim R^3/M$). If the chain conformation does not change with concentration in the dilute regime, it follows that $c^* \simeq 1/[\eta]$. This is an approximate relationship [15] as we have ignored pre factors in the definition of c^* .

The viscosity of dilute polymer solutions is given by the Huggins equation:

$$\eta_{sp} = [\eta]c_p + ([\eta]c_p)^2 k_H \quad (3.4)$$

where k_H , the Huggins coefficient is approximately 0.7-0.5 for polymers in theta solvents and 0.3 for polymers in good solvents, independent of molecular weight [16]. The specific viscosity at c^* is therefore $\eta_{sp}(c^*) \simeq 1-1.7$. As mentioned in the previous chapter, using $\eta_{sp}(c^*) \simeq 1$ may not apply to polyelectrolytes in salt free solutions as the required relationship $\eta_{sp}(c) \propto [\eta]c_p$ may [17] or may not [18] hold. In the high salt limit on the other hand where the properties of polyelectrolyte solutions reduce to those of neutral polymers in good solvent, the relationship should become more accurate. Cho et al [19] determined the overlap concentration for chitosan with high added salt solutions from $\eta_{sp}(c^*) \simeq 1$ and equation 3.4 and found reasonable agreement between both.

Form Factor

The form factor of a worm like chain with no excluded volume for $qL_T \leq 4$, where q is the scattering wavevector was calculated by Sharp and Bloomfield as [20, 21]:

$$P(u)_{SB} = 2 \frac{e^{-u} + u - 1}{u^2} + \frac{2L_t}{15L} \left[4 + \frac{7}{u} - \left(11 + \frac{7}{u} \right) e^{-u} \right] \quad (3.5)$$

where $u = q^2 LL_T$. At high q values, we use an expression [20] derived by Burchard:

$$P(q)_B = \frac{1}{2LL_T q^2} + \frac{\pi}{Lq} \quad (3.6)$$

The following expression is used to interpolate between the above two formulae:

$$P(q) = P(u)_{SB} \exp[-((2qL_T/q_1)^{p_1})] + P(u)_B (1 - \exp[-((2qL_T/q_1)^{p_1})]) \quad (3.7)$$

where $p_1 = 5.33$ and $q_1 = 5.53$, as given by reference [20]. The finite thickness of the chain may be taken into account by multiplying the previous form factor by:

$$P_{cs} = \left(\frac{2J_1(qr_p)}{qr_p} \right)^2 \quad (3.8)$$

where r_p is the cross sectional radius of the polymer chain as described in the previous chapter.

Excluded volume effects

The end-to-end distance of a worm like chain with excluded volume can be calculated by mul-

tipling the ideal value by an expansion factor (α_S), i.e.:

$$\langle R_{ee}^2 \rangle = \alpha_S^2 \langle R_{ee,0}^2 \rangle \quad (3.9)$$

The expansion factor within the quasi-two parameter (QTP) theory of Yamakawa and co-workers [22, 23] is given by:

$$\alpha_S^2 = (1 + 10z' + 70\pi/9)z'^2 + 8\pi^{3/2}z'^3)^{2/15} (0.933 + 0.067e^{-0.85z' - 1.39z'^2}) \quad (3.10)$$

z' is a excluded volume parameter given by

$$z' = \frac{3}{4}K(L/L_T)z \quad (3.11)$$

where

$$\begin{aligned} K(L/L_T) &= 4/3 - 2.711(L/2L_T)^{-1/2} + 7/6(L/2L_T)^{-1} \text{ for } L \geq 12L_T \text{ and} \\ K(L/L_T) &= (L/2L_T)^{-1/2} \exp(-6.611(L/2L_T)^{-1} + 0.9198 + \\ &\quad 0.03516(L/2L_T)) \text{ for } L \leq 12L_T \end{aligned} \quad (3.12)$$

and

$$z = (3/2\pi)^{3/2} B' / (2L_T)(L/2L_T)^{1/2} \quad (3.13)$$

where

$$B' = \beta / L_T^2 \quad (3.14)$$

β is the binary cluster integral, generally modelled as the sum of three terms:

$$\beta = \beta_{hc} + \beta_{el} + \beta_a \quad (3.15)$$

where β_{hc} is the contribution from the hard core chain radius contribution, which is known to be well modelled by [13]:

$$\beta_{hc} = \frac{\pi}{2} L_T^2 d_c \quad (3.16)$$

where d_c is the chain diameter. β_{el} arises due to electrostatic excluded volume, which significantly harder to model and has been found experimentally (see section 3.5) to vary as:

$$\beta_{el} \sim L_T^2 \kappa^{-1} \quad (3.17)$$

and β_a takes into account the (typically short ranged) attractive contributions between chains. This term is often only important for high salt solutions. Due to the difficulty in modelling this term [24], it is often assumed to be a constant. Davis estimated it to be $\sim -200 \text{ nm}^3$ for NaCMC based on light scattering results by Brown et al. [25].

Experimental results for β show that current theories are not capable of accurately describing the variation of β with c_s [1–3]. Systematic studies on $\beta(c_s)$ have been performed by Noriyime and co-workers for several polyelectrolytes in aqueous NaCl solutions. An analysis of their results as well as other literature data on $\beta(c_s)$ is provided in section 3.5 of this chapter.

3.1.3 Scaling theory for flexible polyelectrolytes

For dilute solutions with high added salt (in the dilute flexible regime as defined in ref [4]), the end-to-end distance of a polyelectrolyte chain is given by [4].

$$R = bN^{3/5}(c_p b^3)^{1/2}(1 + 2Ac_s/c_p)^{-1/5}$$

The overlap concentration is given by $c^* = N/R^3$:

$$c^*(1 + 2Ac_s/c^*)^{-3/2} = N^{-2}B^{-3} \quad (3.18)$$

This expression remains valid for both high and low added salt concentrations. Above c^* chains overlap. The conformation of polyelectrolytes in solutions with added salt in the semidilute regime is treated in the same manner as in salt free solutions. Recall that for locally stiff polyelectrolytes (solvent quality parameter $B = 1$) in salt free solution the correlation length is given by

$$\xi = b(c_p b^3)^{-1/2}$$

which we validated in the previous chapter. Scaling theory assumes the following functional form for the dependence of ξ , the end-to-end distance on R_{ee} :

$$\xi = R_{ee}(c_p)[f(c_p)/f(c^*)]^{-m}$$

where $f(c)$ and m are chosen such that ξ is molecular weight independent, giving:

$$f(c_p) = c_p(1 + Ac_p/c_s)^{-3/2}$$

and $m = 3/10$, thus:

$$\xi = b(c_p b^3)^{-1/2}(1 + 2Ac_s/c_p)^{1/4} \quad (3.19)$$

The osmotic pressure of semidilute polyelectrolyte solutions with added salt contains two terms, as in the case of salt free solutions accounting for the polymer contribution and the ion contribution. The polymer contribution remains the same as in the salt free case, i.e. $k_B T$ per correlation blob and the ionic term now takes into account the salt ions as well as the counter ions. The full expression is given by [4]:

$$\Pi = k_B T \left(\frac{c_p^2}{(4A^2 c_s + A c_p)} + \xi^{-3} \right)$$

The compressibility $d\Pi/dc_p$ can then be worked out to be:

$$\frac{d\Pi}{dc_p} = k_B T \left[\frac{c_p(8Ac_s + c_p)}{A(4Ac_s + c_p)^2} + \frac{3(b^3 c_p)^{1/2}(3Ac_s + c_p)}{2B^{3/2} c_p \left(\frac{2Ac_s + c_p}{c_p} \right)^{7/4}} \right] \quad (3.20)$$

the polymer and ionic contributions in the high salt regime reduce to $\frac{d\Pi_p}{dc_p} \propto c_p^{1.25} c_s^{-0.75}$ and $\frac{d\Pi_i}{dc_p} \propto c_p^1 c_s^{-1}$ respectively .

The dynamics are calculated in the same manner as before, for length scales larger than ξ , hydrodynamic interactions are screened and the Rouse model applies, while for length scales smaller than ξ , chain relaxations can be treated by the Zimm model. For unentangled solutions, the specific viscosity (η_{sp}) is given by:

$$\eta_{sp} = N(c_p b^3)^{1/2}(1 + 2Ac_p/c_s)^{-3/4} \quad (3.21)$$

The entanglement concentration c_e is predicted to be

$$c_e(1 + 2Ac_s/c_e)^{-3/2} = n^4 N^{-2} b^{-3} \quad (3.22)$$

with

$$n = (c_e/c^*)^{1/4} \left(\frac{1 + 2Ac_s/c^*}{1 + 2Ac_s/c_e} \right)^{3/8} \quad (3.23)$$

experimentally, a much weaker dependence of c_e on N ($c_e \sim N^{-0.6}$) is observed for flexible, salt free, polyelectrolyte solutions, for which there is currently no satisfactory explanation, although a chain length dependence of n has been tentatively postulated [26]. The viscosity in this regime is predicted to be:

$$\eta_{sp} = n^{-4} N^3 (cb^3)^{3/2} (1 + 2Ac_p/c_s)^{-9/4} \quad (3.24)$$

the viscosity at the entanglement concentration is predicted to be $\eta_{sp}(c_e) \simeq n^2$. The concentration dependence of η_{sp} is in good agreement with both flexible and semiflexible salt free polyelectrolyte solutions [27].

3.1.4 Semiflexible polyelectrolytes in the OSF limit

An alternative theory to the de Gennes-Pfeuty-Dobrynin (GPD) approach outlined above, taking into account the intrinsic rigidity of chains was developed by Odijk [6]. Odijk developed the theory for both the high salt and salt free limits, noting that the latter was more speculative. One prediction of the salt free limit theory is that the correlation length should vary as $\xi \sim c^{-5/8}$ for $L_e \ll L_0$ and as $\xi \sim c^{-3/8}$ for $L_e \gg L_0$. Since we observed a constant power law of $\xi \sim c^{-1/2}$ throughout the whole concentration range in the previous chapter, we conclude the theory is not valid in the low salt limit. We therefore examine only the high salt limit, in which the theory may still be valid.

Static properties of semiflexible polyelectrolytes

Odijk approximates the electrostatic binary cluster integral of a segment by that of a hard cylinder of length L_T and radius κ^{-1} :

$$\beta = L_T^2 \kappa^{-1}$$

The Flory radius of a chain (R_F), (which we use to refer to the chain's radius in dilute solution, as opposed to R , the radius in semidilute solutions) is then given by:

$$R_F \simeq L^{1/2} L_T^{1/2} z_{el}^{1/5} \simeq L^{3/5} L_T^{1/5} \kappa^{-1/5}$$

where z_{el} is the electrostatic excluded volume parameter. The assumption here is that $\alpha_s = z^{0.2}$, which is the high z ($z \geq 1$) limit of equation 3.10. This condition is always satisfied in the high N limit (see section 3.6.2). z_{el} is given by:

$$z_{el} \simeq \beta_{el} L^{1/2} L_T^{-7/2} \simeq L^{1/2} \kappa^{-1} L_T^{-3/2}$$

The overlap concentration is given by $c^* = N/R_F^3$ (with $N = L/b$). Requiring $R_F(c^*) = \xi(c^*)$ and that ξ must be independent of N it follows that, in the high salt limit:

$$\xi = L_T^{-1/4} \kappa^{1/4} (bc)^{-3/4} \quad (3.25)$$

Inside the correlation blob, where dilute solution statistics apply, there are g_L segments of length L_T following excluded volume statistics.

$$\xi = g_L^{3/5} L_T^{4/5} \kappa^{-1/5}$$

$$g_L = (\xi L_T^{-4/5} \kappa^{1/5})^{5/3} = \xi^{5/3} L_T^{-4/3} \kappa^{1/3}$$

For length scales larger than the correlation blob, the chain is modelled by a random walk of $L/(g_L L_T)$ steps of length ξ :

$$R(c) = \xi \left(\frac{L}{L_T g_L} \right)^{1/2} = L^{1/2} L_T^{1/8} \kappa^{-1/8} (bc)^{-1/8}$$

Comment on Odijk's theory

Odijk's approach is fundamentally different from the de Gennes-Pfeuty-Dobrynin theory in that

is assumes the chains flexibility varies quadratically with κ^{-1} instead of linearly. Therefore, Odijk's theory in the limit $L_0 = 0$ does not reduce to the theory of flexible polyelectrolytes. Equation 3.25 and the quantities derived from it are valid only in the high salt limit ($c_s \ll c_p$). The predictions for R_F and c^* could remain valid over the whole c_s range.

We consider two sub regimes of the high salt case: $L_0 \ll L_e$ and $L_0 \gg L_e$ corresponding to intrinsically flexible and intrinsically semiflexible polyelectrolytes respectively.

Flexible case $L_0 \ll L_e$: Achieving simultaneously $c_s \ll c_p$ and $L_0 \ll L_e$ is restricted by both a lower and upper bound of c_s , as c_s increases, L_e decreases and thus, the second condition becomes harder to meet. The experimental data on NaPSS shows this regime does however apply up to relatively high salt concentrations ($c_s \sim 3\text{M}$ for $c_p \sim 0.17$), which are experimentally achievable (figure 3.18). The different properties of the chains vary as follows:

$$\begin{aligned}
R_F &\propto L^{3/5} c_s^{-3/10} \\
c^* &\propto L^{-4/5} c_s^{9/10} \\
L_T &\propto c_s^{-1} \\
\xi &\propto c_s^{3/8} c_p^{-3/4} \\
R(c) &\propto L^{1/2} c_s^{-3/16} c_p^{-1/8}
\end{aligned} \tag{3.26}$$

The predicted quantities in the flexible case depend more strongly on c_s than in de Gennes-Pfeuty-Dobrynin's (GPD) theory due to the quadratic dependence of L_e on κ^{-1} . If we substitute the OSF equation by, for example Dobrynin's relation for L_e (eq. 3.2), we recover the GPD power laws.

Semiflexible case $L_0 \gg L_e$: This limit is easily achieved for semiflexible polyelectrolytes in the high salt regime, e.g. NaHA (fig 3.19). The predictions are now:

$$\begin{aligned}
R_F &\propto c_s^{-1/10} \\
c^* &\propto L^{-4/5} c_s^{-3/10} \\
L_T &\propto c_s^0 \\
\xi &\propto c_p^{-3/4} c_s^{-1/8} \\
R(c) &\propto L^{1/2} c_s^{-1/16} c_p^{-1/8}
\end{aligned} \tag{3.27}$$

which are weaker than the GPD power laws. We may have expected that since L_T is independent of salt content, the other properties should be too. The reason for the weak dependence on c_s of R_F , c^* , ... is that the expansion factor $\alpha \sim z^{0.2}$ keeps decreasing with salt content as z tends to zero. This is an artefact of the approximation used by Odijk. At $z = 0$, the chain should be unperturbed and thus reach its theta condition $R_F \sim L_T N^{1/2}$. The use of a more accurate form of α leads to the correct result $\alpha = 1$ at $z = 0$. In this limit the power laws reduce to that of neutral polymers in theta solvents. A more realistic estimate may be to introduce a limiting value of z , corresponding to contribution of the hard core repulsion (i.e. β_{hc}), which is salt independent. In this case, z will tend to a fixed value and the predicted laws will be those of a neutral polymer in good solvent, independent of salt content.

Extension of Odijk's theory to the dynamic properties of semiflexible polyelectrolytes

Odijk's original work did not calculate the dynamic properties (viscosity and relaxation time) of semiflexible solutions, these are calculated here using the standard scaling approach. Below the correlation length, Zimm statistics apply, the relaxation time of one blob is therefore given by:

$$\tau_Z = \eta_s \xi^3 / k_B T$$

The longest relaxation time of the chain is given by a Rouse chain of $L/(g_L L_t)$ correlation blobs.

$$\tau_R = \tau_Z \left(\frac{L}{L_t g_L} \right)^2$$

which simplifies to:

$$\tau_R = \frac{\eta_s}{k_B T} L^2 L_T^{3/4} \kappa^{-3/4} (bc)^{1/4}$$

Estimating the polymer contribution to the viscosity as the product of the longest relaxation time and the modulus, taken here to be $k_B T$ per chain:

$$\eta_{sp} = L L_T^{3/4} \kappa^{-3/4} b^{13/4} c^{5/4} \quad (3.28)$$

We thus recover the $\eta_{sp} \sim c^{1.25}$ limit at high salt, the same as for neutral polymers in good solvent. Since $L_T \sim L_0$, $\eta_{sp} \sim L_0^{3/4}$, the viscosity thus increases with intrinsic rigidity.

The above equation reduces to GPD theory when $L_0 = 0$ and $L_e \sim \kappa^{-1}$. For $L_e \gg L_0$, the flexible chain limit, we can approximate $(L_e + L_0)^{3/4} \simeq L_e^{3/4} (1 + \frac{3}{4} L_0 L_e^{-0.75})$. Thus, the viscosity predicted by GPD theory η_{sp}^{GPD} can be corrected to account for intrinsic stiffness in the limit of $L_e \gg L_0$ as:

$$\eta_{sp} \simeq \eta_{sp}^{GPD} (1 + \frac{3}{4} L_0 L_e^{-0.75})$$

3.1.5 Small angle neutron scattering

Polyelectrolyte solutions with added salt are four component solutions: solvent, counter ions, co-ions and poly-ions. Treating the salt and solvent as one component and neglecting the contribution from the counter ions, which have weak contrast compared to the polymer in D₂O, the differential cross section of scattered intensity per unit volume in a SANS experiment may be written as:

$$I(q) = \rho k^2 S(q)$$

where ρ is the concentration in number of species per unit volume and $k = b_p/v_p - b_s/v_s$; b is the coherent scattering length and v is the partial molar volume. The subscript p refers to the polymer and s refers to the solvent (D₂O + NaCl in our case). $S(q)$ is given by the random phase approximation (RPA) for semidilute polymer solutions:

$$1/S(q) = 1/N\phi v_p P(q) + 1/(1 - \phi) v_s + 2\chi/v_0 \quad (3.29)$$

where ϕ is the polymer volume fraction, χ is the Flory-Huggins interaction parameter, v_0 is

a reference volume and $P(q)$ is the form factor, which describes the scattering of a particle at infinite dilution. The RPA is known to be inappropriate for polyelectrolyte solutions with low added salt due to the strong interaction between chains. In the high salt limit however, where polyelectrolytes are analogous to neutral polymers in good solvent, the RPA is expected to be valid. For polydisperse systems, the above expression becomes more complicated as both $P(q)$ and χ are molecular weight dependent. The full expression of $I(q)$ is therefore complex (see eq. 51 of ref [21]) and we choose a simplified version named the local monodisperse approximation. The latter is given by:

$$I(q) = \rho k^2 \int D(M) V^2(M) P(q, M) S(q, M) dM \quad (3.30)$$

We make a further simplification to this by approximating χ as being independent of molecular weight. This seems reasonable as the second virial coefficient (A_2) is known to vary weakly with molecular weight for polymers in good solvent $A_2 \propto M_w^{-0.2}$.

The scattered intensity at $q = 0$ is related to the compressibility by [70]

$$I(0) = k^2 k_B T \phi \frac{d\phi}{d\Pi} \quad (3.31)$$

3.2 Methods

Two NaCMC grades were used in this study, the first is the same as in the previous chapter, $M_w \simeq 280\text{kg/mol}$ and D.S. $\simeq 1.17$. The second, also obtained from sigma Aldrich has nominal $M_w \simeq 90\text{kg/mol}$ and D.S. $\simeq 0.7\text{-}0.9$. The 90k sample will be used only for the determination of the persistence length and correlation length using SANS, for which exact values of M_w and D.S. are not required precisely. We therefore use the manufacturer's values throughout this chapter.

SANS experiments were carried out on the D22 beam line at the ILL (Grenoble, France) with $\lambda = 6\text{\AA}$ and sample-detector distances of 1.5 m, 5.6 m, 17.6 m yielding $0.003\text{-}0.6\text{ \AA}^{-1}$. Quartz Hellma cells of path length 5mm were employed. The data was reduced using standard procedures with GRASP.

The viscosity measurements in salt free solution were taken from the previous chapter and the measurements in salt solutions for the 280kg/mol sample were made on an LV-DVI-Prime Brookfield viscometer with a Couette geometry. Readings were taken at a shear rate lower than the onset of shear thinning for the salt free samples. Since the relaxation times increase upon addition of salt, we take this to be the zero shear rate value. Viscosity reading for the 90k sample were measured on a Anton Paar Physica MCR 301 rheometer using a cone and plate geometry.

3.3 Results and discussion

3.3.1 Determination of intrinsic persistence length and correlation length

Figure 3.1 shows a Huggins plot ($\eta_{red} \equiv \eta_{sp}/c$ vs. c) for NaCMC 90k in 2M NaCl aqueous solutions. The black line is a fit to the Huggins equation for the four lowest concentrations. The data deviates upwards for higher concentrations as the polymer chains become entangled. The best fit parameters are $[\eta] = 0.276\text{ L/g}$ and $k_H \simeq 0.25$. The latter is close to that for neutral polymers in good solvents ($\simeq 0.3$ [16]), and similar to that found by Brown et al [25] for NaCMC in Cadoxen, a high ionic strength solvent.

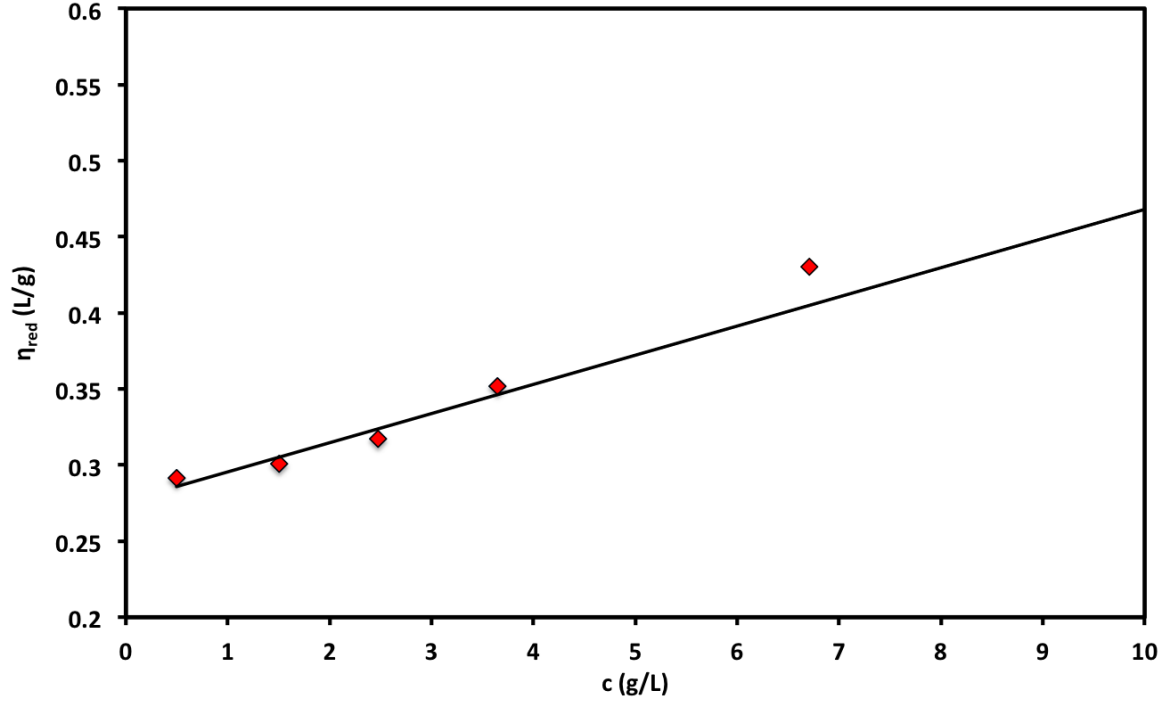


Figure 3.1: Huggins plot for NaCMC 90k as in 2M NaCl aqueous solution. Black line: Fit to the Huggins equation (Eq 3.4), only four lowest points are considered for the fit.

Figure 3.2 shows the specific viscosity of the 90k sample in a $\simeq 2$ M NaCl aqueous solutions as a function of polymer concentration. The grey and black solid lines indicate the dilute ($\eta_{sp} \sim c^1$) and entangled ($\eta_{sp} \sim c^{3.75}$) scaling predictions for neutral polymers in good solvents. The blue dashed lines indicate the c^* value obtained from $\eta_{sp} = 1$, which yields $c^* \simeq 3.4$ g/L. The red line indicates the prediction for the Huggins equation (Eq 3.4) with the values obtained above. Clearly, it provides a good description of the dilute regime and breaks down when entanglement effects become important. The green dashed lines indicate $c^* = 1/[\eta]$, which yields $c^* = 3.6$ g/L and $\eta_{sp} \simeq 1.2$, in fair agreement with the previous criterion.

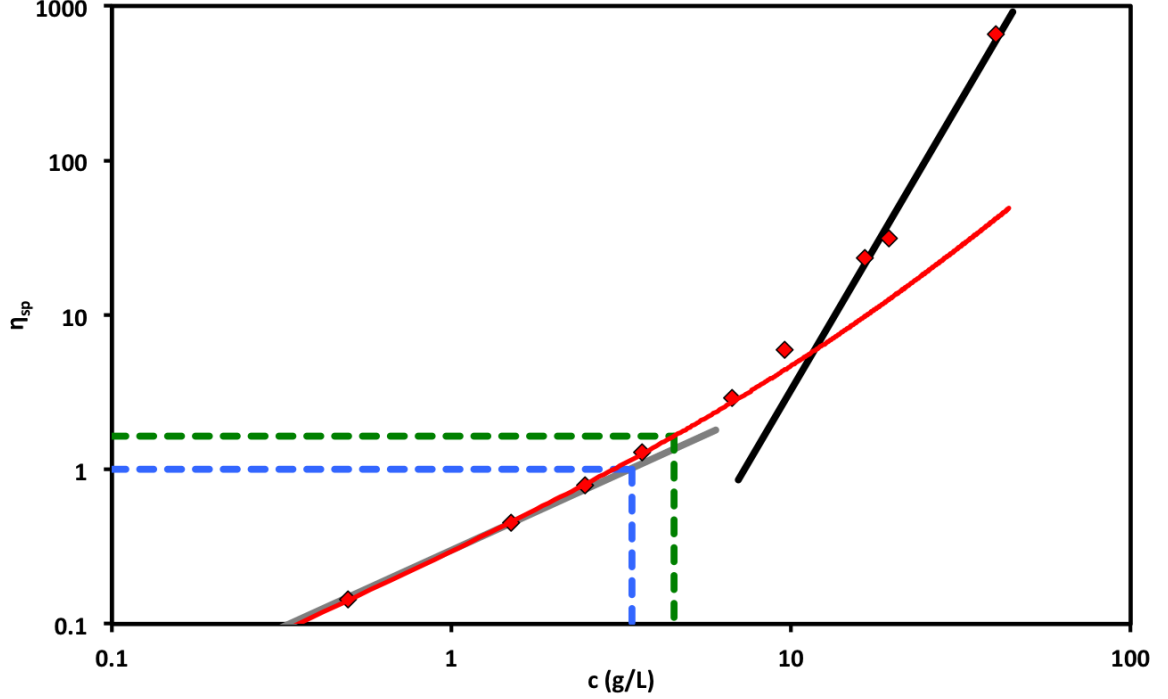


Figure 3.2: Specific viscosity of 90k NaCMC sample as a function of polymer concentration in 2M NaCl aqueous solution. Red points: data. Grey line: best fit line to $\eta_{sp} \sim c^1$. Black line: best fit line to $\eta_{sp} \sim c^{3.75}$. Red line line: Huggins equation with $[\eta]$ and k_H obtained above. Dashed blue lines: c^* from $\eta_{sp}(c^*) = 1$. Dashed green lines: $c^* = 1/[\eta]$.

Figure 3.3 shows the scattering curve for a 24 g/L NaCMC in a 2M aqueous NaCl solution. Unlike the salt free samples, and as expected, the profile resembles that of a neutral polymer. The data is well fitted by the RPA using a worm like chain form factor with no excluded volume, calculated by equations 3.5-3.8 and 3.29. We expect excluded volume to be partially screened at $c = 24 \text{ g/L} \simeq 6c^*$. The small upturn at low q ($q \leq 0.005 \text{ \AA}^{-1}$) reveals the presence of large aggregates or clusters, which have also been observed in semidilute solutions of neutral polymer solutions [29–31]. Unfortunately, this small upturn makes the determination of χ difficult, additionally, χ is coupled with the molecular weight and its distribution for which we do not have precise values. The value of the persistence length can however be determined to be 50 - 55 $\text{\AA}$ and is not affected by the value of M_w , χ or PDI significantly.

Experiments for the same polymer concentration with added salt concentrations of 0.7, 1.2 and 3 M yield the same result for the persistence length. This is expected at high ionic strengths,

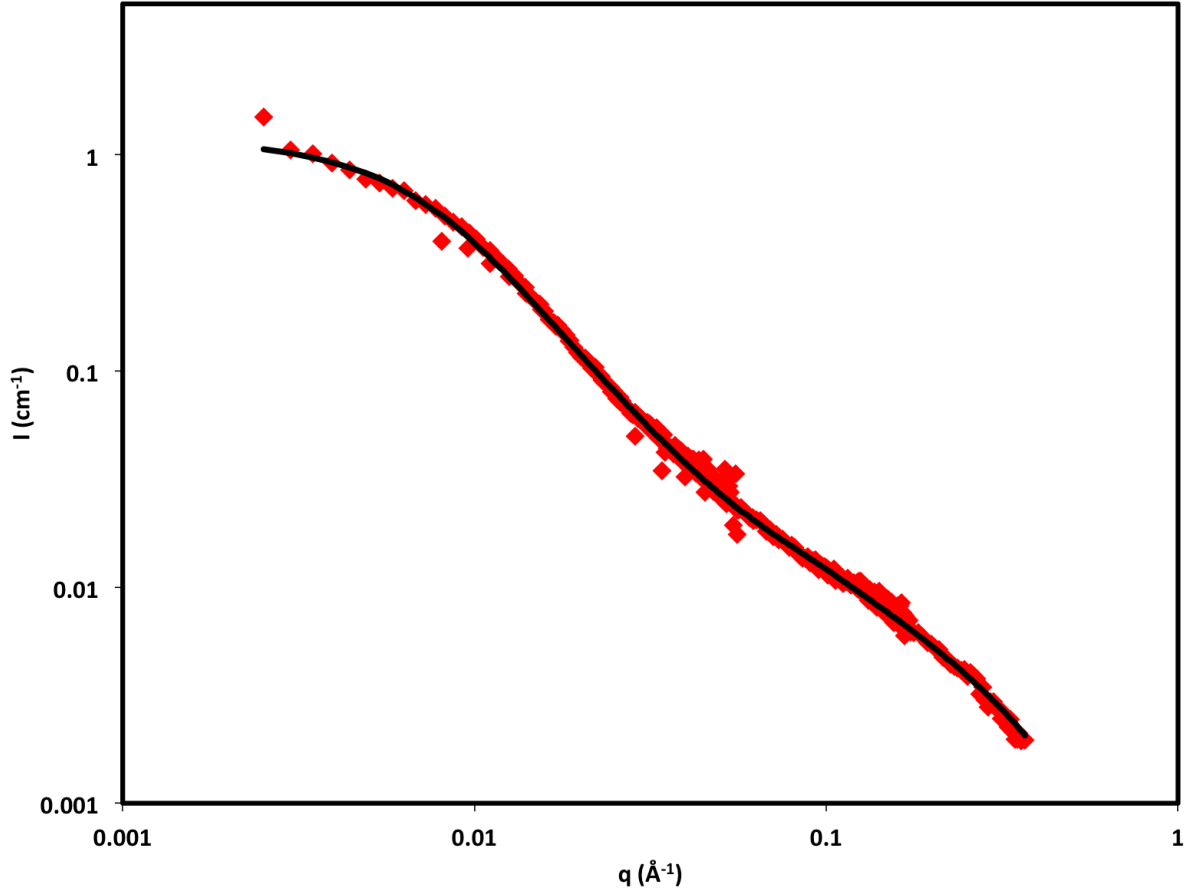


Figure 3.3: SANS profile for NaCMC 24g/L in a 2M NaCl solution in D₂O. Data: red squares. Black line: RPA fit using a WLC form factor.

where $L_e \ll L_0$ and therefore $L_T \simeq L_0$. Our value for L_0 is in agreement with some reported values in the literature [32–34], but not with others [35–37]. A number of estimates for L_0 are based on intrinsic viscosity data [33, 36]. Figure 3.6.6 compiles data for $[\eta]$ at $c_s = 0.01\text{M}$. A large disagreement exists between measurements and we cannot determine which data is more reliable, we therefore do not consider those reported values here. The value of $150\text{ \AA}$ reported by Hoogendam et al. differs strongly from ours and deserves some comment. Hoogendam et al. [35] measured R_g as a function of M_w for several NaCMC samples using GPC. Their data was fitted using using a worm like chain model within the quasi two parameter (QTP) framework for excluded volume. The electrostatic persistence length and excluded volume were calculated from the theory of Davis et al. [32] and the intrinsic persistence length was left as a free parameter. A possible reason for the disagreement could be that the calculated values of L_e or B' from Davis'

theory significantly deviate from the real values and thus lead to an artificially high L_0 value. Our estimate on the other hand is more direct, and does not rely on modelling of the excluded volume or L_e , which, as explained above, are problematic.

A correlation length (ξ_{OZ}) may also be extracted from the data by fitting it to a Ornstein-Zernike equation

$$I(q) = \frac{I(0)}{1 + (q\xi_{OZ})^m}$$

where $I(0)$ is the scattering at zero wave-vector and m gives the limiting power law at high q . $m = 2$ for polymers in theta solvents and 1.7 for polymers in good solvent. We have fitted our data fixing $m = 2$ and leaving m as a free parameter. Both methods yield similar results and the best fit m is always between 2 and 2.15. A fit to this function with $m = 2$ is shown in fig 3.4, in a standard I vs. q and in the Debye representation, yields $\xi = 140 \text{ \AA}$ and $I(0) = 0.95 \text{ cm}^{-1}$.

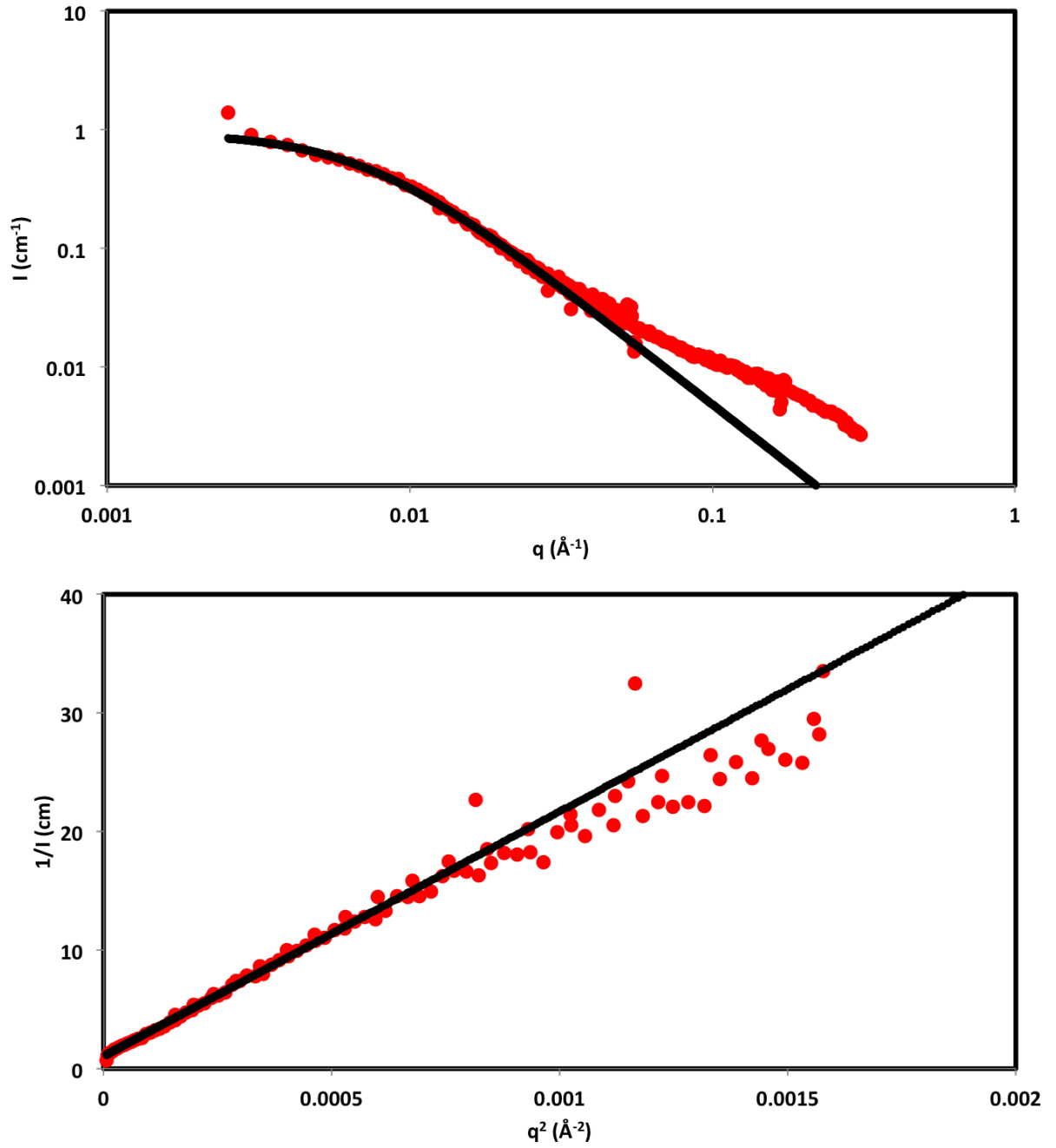


Figure 3.4: SANS profile for NaCMC 24g/L in a 2M NaCl solution in D_2O . Top: I vs. q . Data: red squares. Black line: fit to the Ornstein-Zernike function. Bottom: $1/I$ vs. q^2 , symbols same as for top panel.

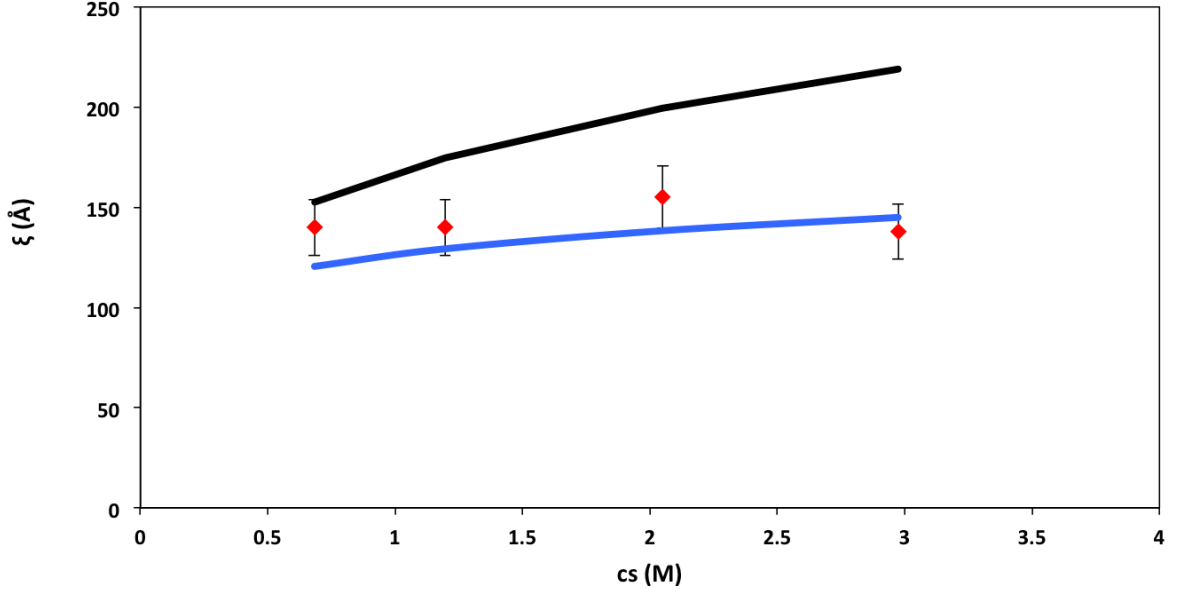


Figure 3.5: Correlation length obtained from an OZ fit as a function of added salt. Red diamonds: data. Black line: flexible scaling theory prediction, equation 3.19. Blue line: Odijk's scaling theory prediction, equation 3.25.

Figure 3.5 shows the correlation length for four NaCMC solutions with $c_p = 24$ g/L as a function of added salt. Contrary to the theoretical predictions from equations 3.19 and 3.25, the correlation length is independent of added salt within experimental error in the range studied. This result anticipates what is found throughout this chapter, i.e. an independence of the static and dynamic properties of NaCMC solutions on c_s for high values of c_s . It is worth noting however, that flexible scaling theory (blue line) does yield a reasonable value for the correlation length, the largest deviation from the data being a factor of $\simeq 2$. Odijk's theory gives a better prediction for ξ , with a weaker power law dependence on added salt ($\xi \sim c_s^{0.125}$) and values closer to the data than the flexible scaling theory prediction. $I(0)$ is independent of c_s at a value of $\simeq 1 \text{ cm}^{-1}$. The osmotic compressibility, calculated using equation 3.31 is found to be constant within experimental error at a value of $\frac{d\Pi}{d\Phi} \simeq 6000 \text{ Pa}$, in disagreement with equation 3.20.

Using the relation for the correlation length measured in the previous chapter, the correlation length for $c = 24 \text{ g/L}$ in salt free solution is $\xi \simeq 60 \text{ Å}$. The correlation length therefore increases with added salt as expected from theory. We note however, that this is not observed for other systems. To the best of our knowledge, the only other study to compare the correlation length

values in salt free and with high added monovalent salt is that of Spiteri [11]ⁱ. Semidilute NaPSS solutions show and increase in the correlation length when increasing the salt content from 1.5M to 3M, but both values are significantly lower than the salt free value (The values are plotted in section 3.6.5). This suggests that the length scale associated with the peak position ($2\pi/q^*$) may be of a different nature to the correlation length from an OZ fit.

Within the framework of scaling theory, both quantities should be equivalent, they represent the length scale below which dilute solution statistics apply and above which excluded volume is screened and Gaussian statistics apply. The correlation length obtained from the peak position in $I(q)$ need not correspond to the scaling picture, for example, when $L_T \geq \xi$, Gaussian statistics do not apply for length scales larger than ξ . For the NaPSS solutions studied in ref [11], L_T is smaller than ξ or ξ_{OZ} for all cases (for the high salt solutions, $\xi_{OZ} \sim 2L_T$). For our salt free sample $\xi(24g/L) \simeq 60\text{\AA}$ and $L_0 \simeq 55\text{\AA}$, it is thus possible that some rigidity remains above the correlation length in the salt free case. For the high salt case however, where $L_T \simeq 55\text{\AA}$ and $\xi_{OZ} \simeq 140\text{\AA}$ this should not be the case. Thus the intrinsic rigidity should not be the origin of the different behaviour between these two systems. It is not clear to us at this point why different behaviour is observed and we conclude that ξ and ξ_{OZ} represent different (yet similar) quantities.

ⁱHorkay [38] et al. measured the correlation length of Chondroitin sulfate in salt free and NaCl/solutions. Their fitting procedure is however significantly different from ours and we therefore do not consider their data here.

3.3.2 Viscosity as a function of added salt

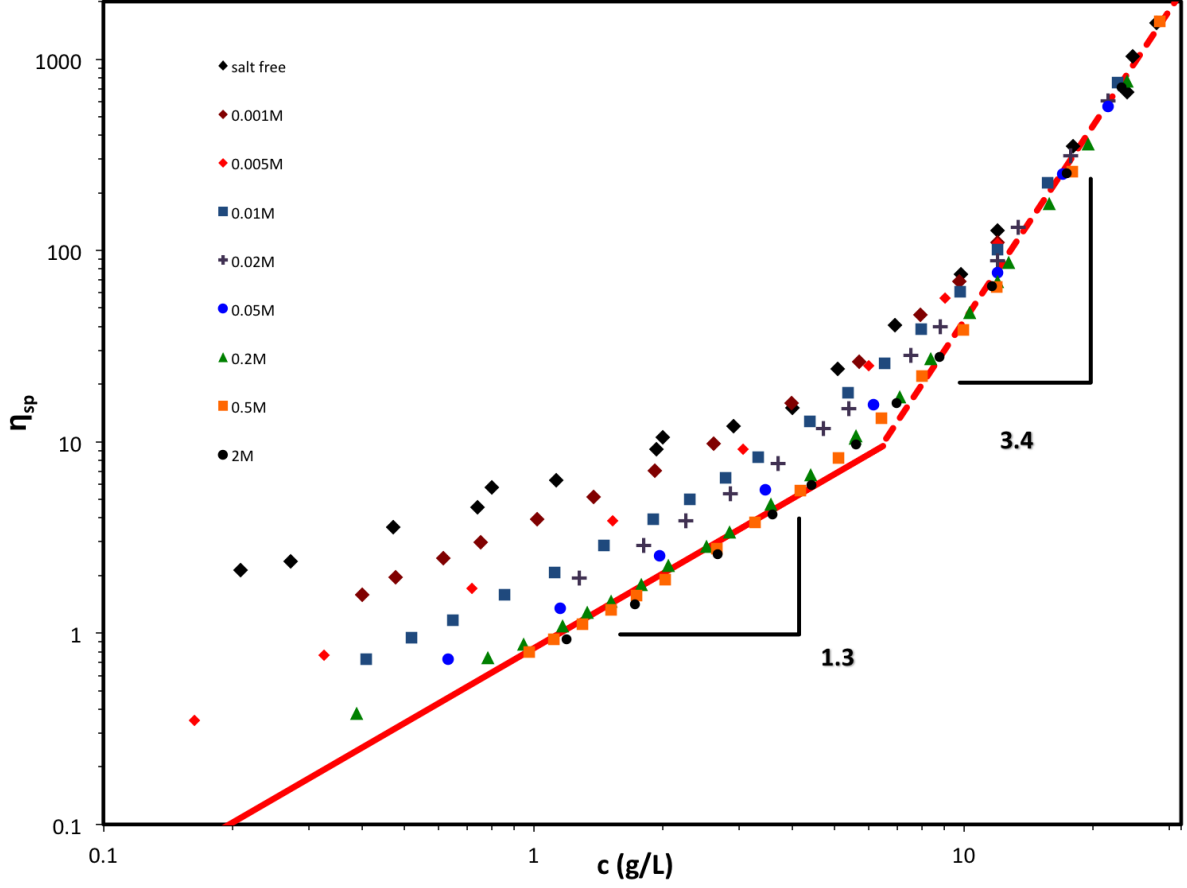


Figure 3.6: Specific viscosity as a function of polymer concentration at different concentrations of added salt for NaCMC D.S. = 1.2 and $M_w = 280$ kg/mol. Lines indicate power laws of $\eta_{sp} \sim c^{1.3}$ and $\eta_{sp} \sim c^{3.4}$. Added salt concentration is given in the legend.

Figure 3.6 shows the specific viscosity of NaCMC (D.S. = 1.2 $M_w = 280$ kg/mol) solutions in deionised water and in aqueous solutions of NaCl ($c_s = 0.001 - 2$ M). The viscosity of the aqueous NaCl solutions was calculated from reference [39]. As expected the viscosity decreases as the salt content increases and for the high salt samples follows the neutral polymer in good solvent power laws of $\eta_{sp} \sim c^{1.3}$ for semidilute unentangled solutions and $\eta_{sp} \sim c^{3.4}$ for semidilute entangled solutions. Later, we will calculate the relative decrease of the specific viscosity upon salt addition. For this purpose we interpolate the salt free data by fitting the data with a sixth order polynomial, as shown in section 3.6.1.

We estimate the overlap concentration from $\eta_{sp}(c^*) = 1$. This method underestimates c^* as

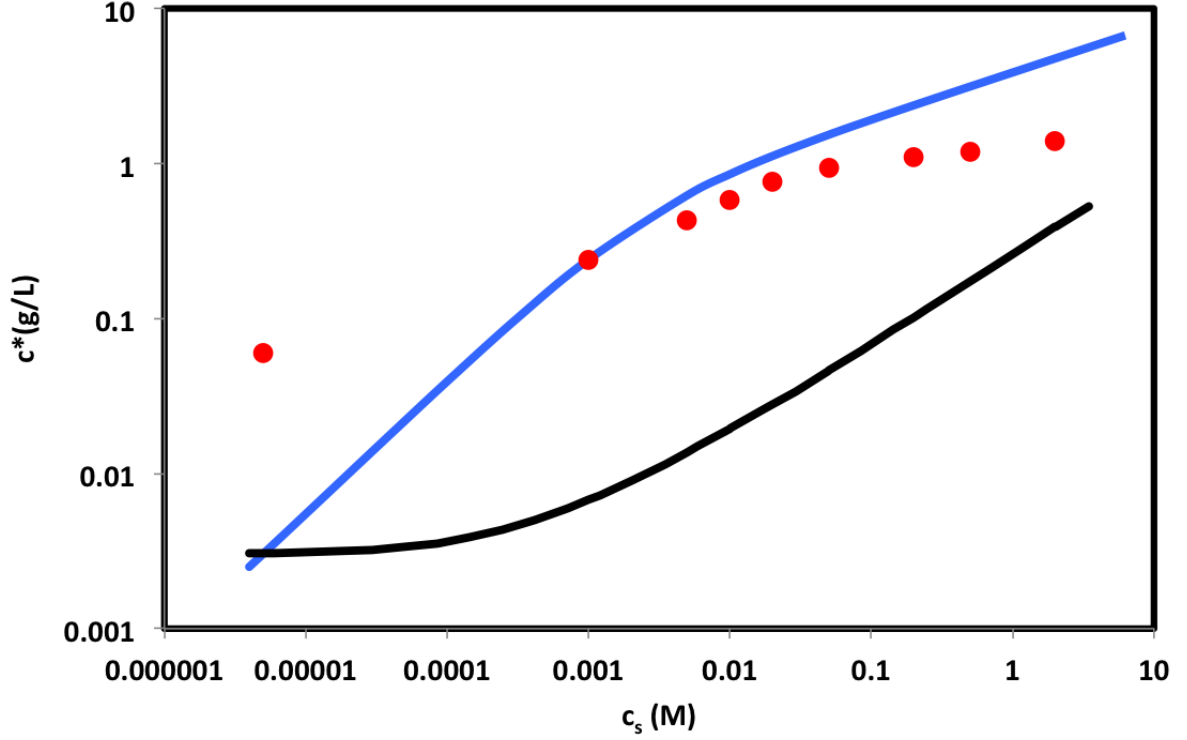


Figure 3.7: Overlap concentration determined from $\eta_{sp}(c^*) = 1$. Black line: Flexible scaling theory prediction. Blue line: Odijk's scaling theory. Both calculations assume a residual salt of $c_s = 5 \cdot 10^{-6}\text{M}$.

explained in the introduction, but it yields fairly similar results to other methods, see figure 3.2 or for example reference [19]. The results are plotted in figure 3.7. At low added salt levels, c^* follows a power law dependence of $c^* \sim c_s^{0.3-0.4}$. This is weaker than the flexible scaling theory prediction of $c^* \sim c_s^{0.6}$, shown by the black line, which has been observed for example for NaPSS, see section 3.6.3 for a comparison. For salt concentrations greater than $\approx 0.01\text{M}$, the dependence of c^* on c_s becomes weaker ($c^* \sim c_s^{0.1}$) and appears to flatten out. The prediction from Odijk's theory, shown by the blue line gives a better description of the data but still fails, specifically at high and low ionic strengths, where it predicts power laws of $c^* \sim c_s^{0.3}$ and $c^* \sim c_s^{0.9}$ respectively. The failure at low ionic strengths is not significant, as the $\eta_{sp}(c^*) = 1$ criterion becomes less valid.

Four representative plots of the specific viscosity vs. polymer concentration for different added salt levels are shown in figure 3.8 along with power law fits. The lower power law (ν) corresponds to the semidilute unentangled regime, which is plotted as a function of c_s in figure 3.9. ν is seen

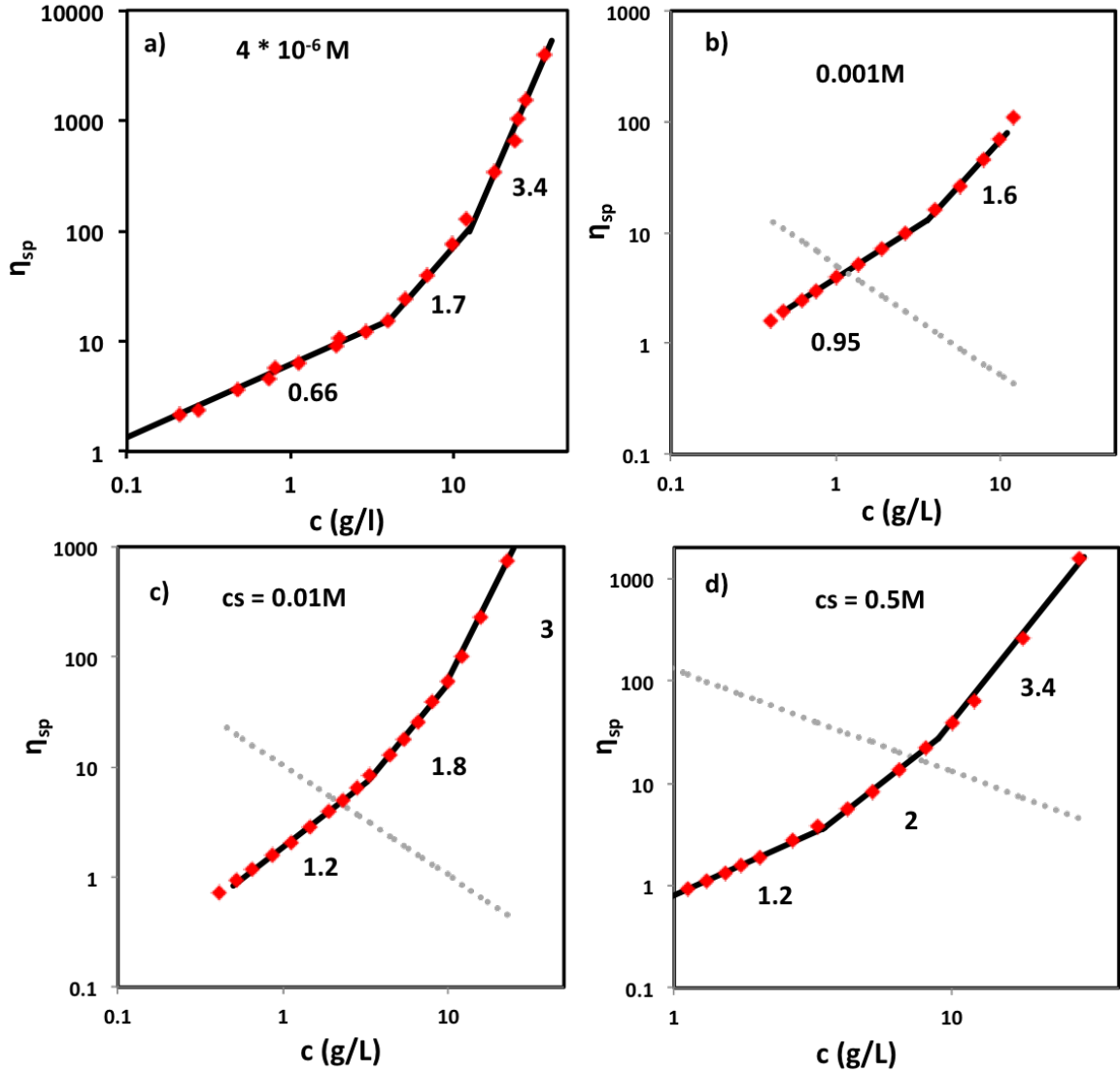


Figure 3.8: Specific viscosity vs. concentration and power law fits. The grey dotted lines indicate c_s/c_p on the same scale as the specific viscosity.

to increase with c_s from a near Fuoss value (0.66 ± 0.02) in salt free conditions to the expected value $\simeq 1.3$ at high salt.

The power law at high concentrations, corresponding to the entangled and/or concentrated regime shows a value of $\simeq 3.4 \pm 0.3$ which is approximately salt independent. Between these two regimes an intermediate power law of $\eta_{sp} \sim c^2$ is observed. This could correspond to a transition between the two regimes. Given the large polydispersity of the system, entanglement is likely a gradual process. Additionally, the unentangled to entangled crossover occurs at the same time

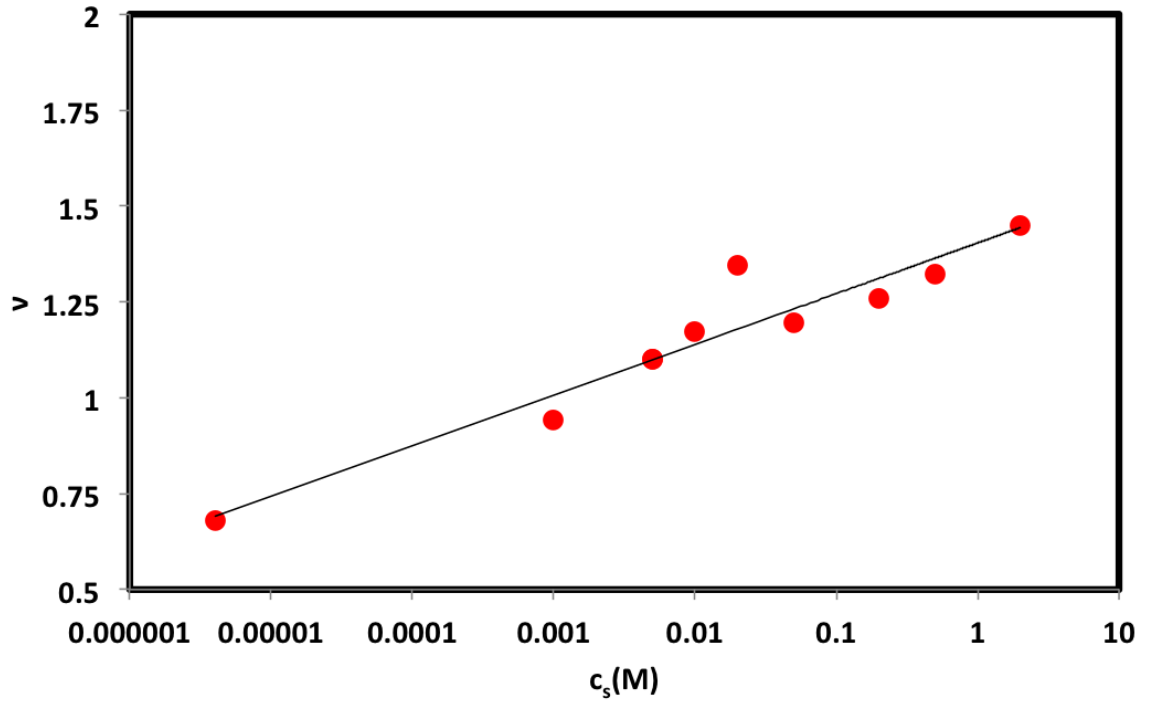


Figure 3.9: Power law exponent of the specific viscosity with concentration in the semidilute unentangled regime as a function of added salt. Red points: data. Black line: empirical fit to logarithmic function $\nu = 0.0574\ln(c_s) + 1.4036$.

as the low c_s/c_p to high c_s/c_p crossover, indicated by the grey dotted lines.

We estimate c_e from the crossover between the unentangled and intermediate power law. Different methods for estimating c_e were considered and the results are shown in section 3.6.4. The results agree well up to a pre factor. The values of c_e as a function of c_s are plotted in figure 3.10. We observe almost no variation of c_e with c_s , a similar result was reported for chitosan in the c_s range 0.009 - 0.46M [19]. Other polyelectrolytes however, show an increase in c_e (by a factor of 2) from salt free to high salt conditions [40]. This weak variation is in disagreement with the flexible scaling theory prediction in the high salt regime $c_e \sim c_s^{1.5}$ (eq 3.22). The weak variation of c_e with salt contrasts with the stronger dependence of c^* on c_s . Scaling theory predicts $c^* \propto c_e$, in clear disagreement with our results. This discrepancy could be accounted for in the scaling picture by assuming a c_s dependent number of chain overlaps needed to form an entanglement (n). Given equation 3.23, n can be estimated from the measured values of c_e and c^* . In order to check for self consistency, we also calculate n from the scaling prediction $\eta_{sp}(c_e) = n^2$. The results are plotted in figure 3.11 along with the ratio between the two methods.

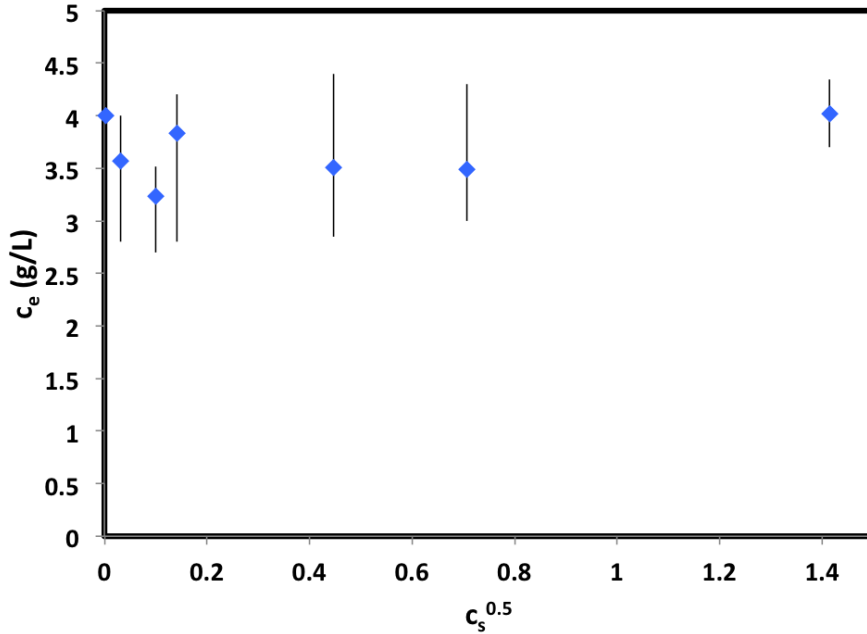


Figure 3.10: Entanglement concentration determined from the departure from the unentangled slope as a function of added salt.

Both methods agree well up to a pre factor and show that n decreases with increasing salt content with an approximate power law dependence of $n \sim c_s^{-0.06 \pm 0.03}$. We note that the n values obtained, specially at high salt ($n \simeq 2$ appear to be too low compared to the typical value of $n \simeq$

5-10 and are therefore likely incorrect, at least up to a prefactor.

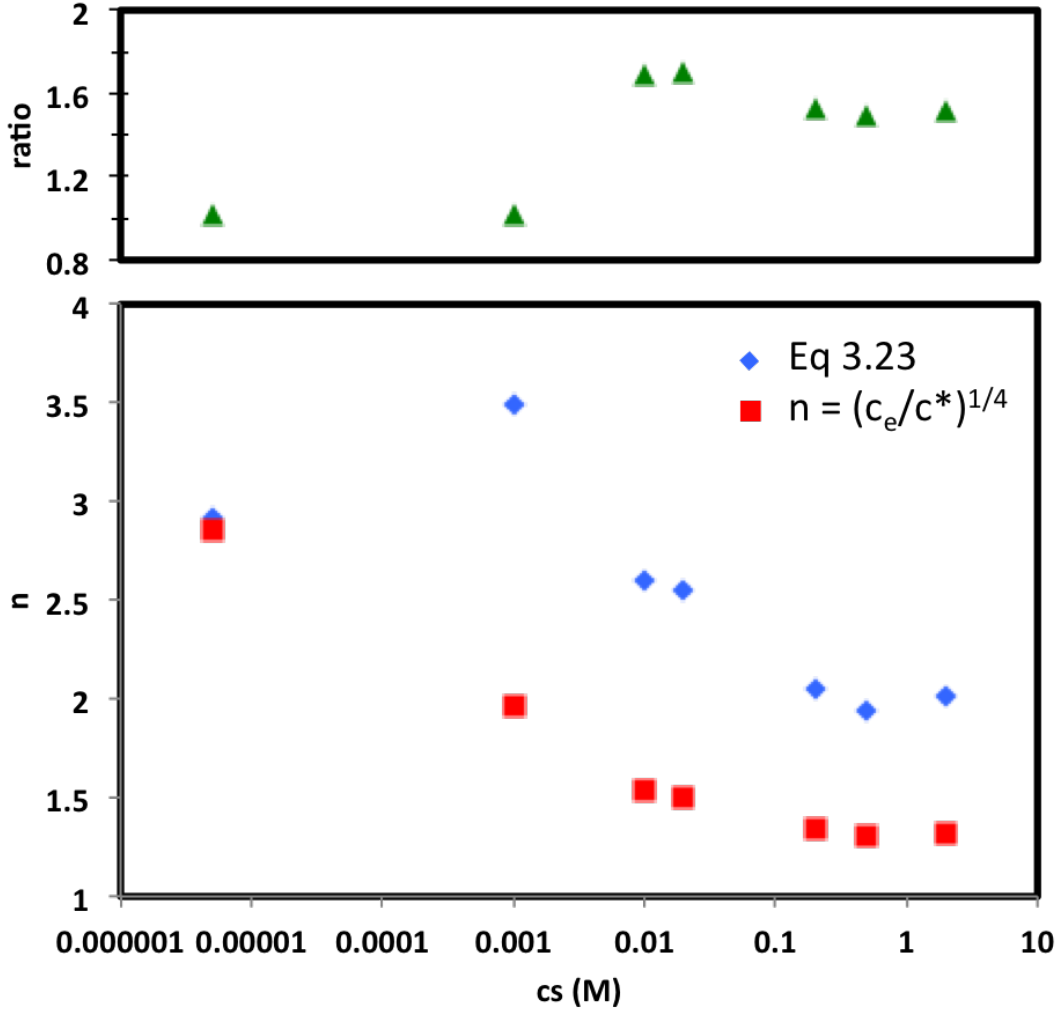


Figure 3.11: n vs. c_s calculated by two different methods as explained in the text. Green triangles: ratio between the two methods.

Figure 3.12 shows the dependence of the relative decrease in viscosity with respect to the salt free case i.e. η_{sp}/η_{sp}^{sf} as a function of c_s/c_p . Scaling theory for flexible polyelectrolytes predicts all entangled points and all unentangled points should collapse into a single line, with the form $\eta_{sp}/\eta_{sp}^{sf} = (1 + 2Ac_s/c_p)^\alpha$, where $\alpha = -0.75$ for the unentangled and -2.25 for the entangled case 3.24. This is clearly not observed in figure 3.12. First for $c_s \geq 0.01\text{M}$ the data deviates from the lower c_s data. For $c_s \leq 0.01\text{M}$ the data collapses reasonably well, as shown in further detail in figure 3.13. This is surprising as according to scaling theory a much stronger decrease is predicted for entangled samples than for unentangled samples. Figure 3.12 clearly shows that

entanglement does not affect η_{sp}/η_{sp}^{sf} when plotted against c_s/c_p . Even at high c_s/c_p where the data deviates from a single line, there is no evidence of a change in slope either as a function of c_s or due to entanglement. We have analysed additional data sets from the literature, shown in section 3.7. Strong disagreement with scaling theory is also found, specially with respect to the entangled predictions.

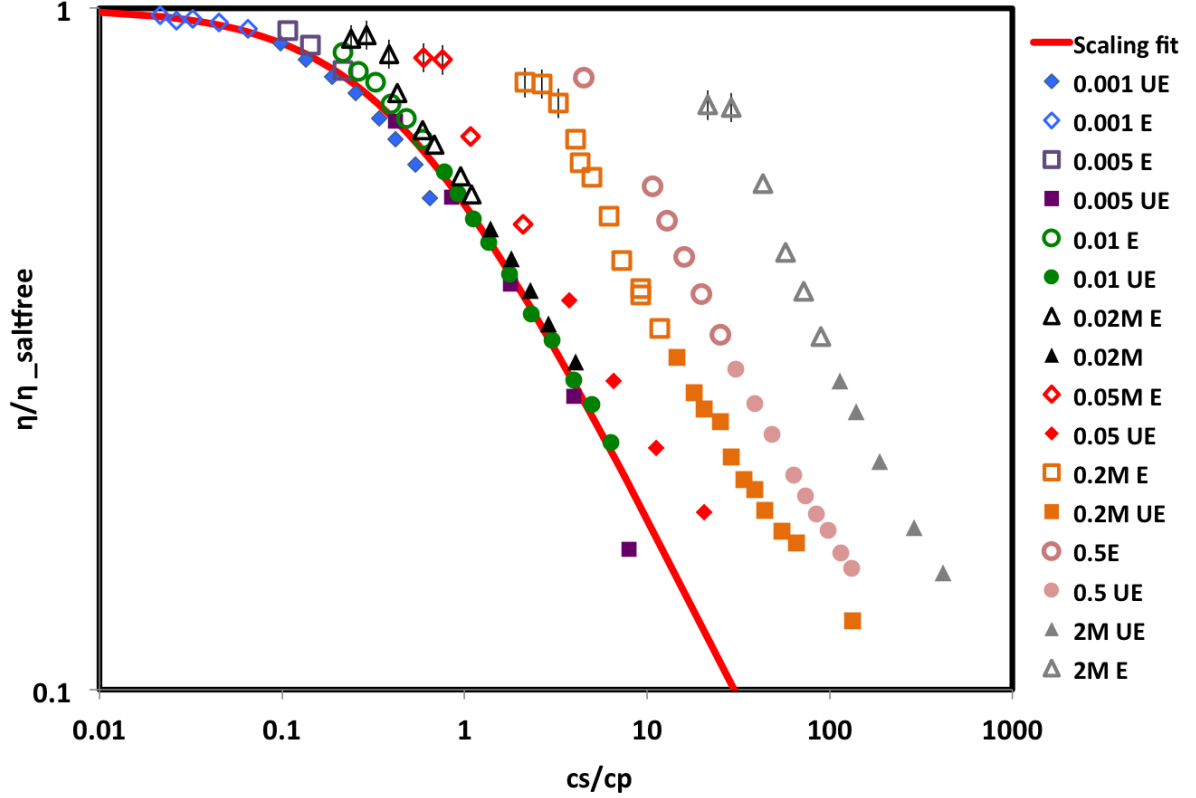


Figure 3.12: $\eta/\eta_{saltfree}$ vs. c_s/c_p . Open symbols correspond to entangled solutions (E) and closed symbols correspond to unentangled solutions (UE). Vertical bars indicate samples in the concentrated regime.

While we do not have sufficient data to clearly assess what happens upon salt addition in the concentrated regime it appears that the concentrated data points in Figure 3.12 (symbols with vertical bars) show a very weak dependence of η_{sp}/η_{sp}^{sf} on c_s/c_p . This can be seen, for example in the flattening of the 0.2M curve at low c_s/c_p , while this is only observed for two points, η_{sp}/η_{sp}^{sf} must go to 1 as c_s/c_p tends to zero, thus leading to a very weak power law $\eta_{sp}/\eta_{sp}^{sf} \sim (c_s/c_p)^{-0.05}$.

Figure 3.13 shows a plot of the data for $c_s \leq 0.01M$, the region where the data approximately collapse, along with a scaling fit to the function $\eta_{sp}/\eta_{sp}^{sf} = (1 + 2Ac_s/c_p)^\alpha$ yielding $\alpha = -0.58$ and

$A = 0.97$ which is in reasonable agreement with the expected values of $A = 2.4 - 1$ [35,41] and $\alpha = -0.75$. Also shown in the figure is data for NaPSS, from ref [26]. The best fit values to the NaPSS data are $A = 3$ and $\alpha = -0.9$. The value for A agrees with independent estimates from conductivity and osmotic pressure ($A = 3 - 5$) [4,42,43], while α shows a similar deviation from the scaling prediction as for NaCMC but in the opposite direction. The comparison with NaPSS allows us to conclude that the deviations of scaling theory from the data, at least in the low added salt cases cannot be uniquely assigned to the semiflexible nature of NaCMC.

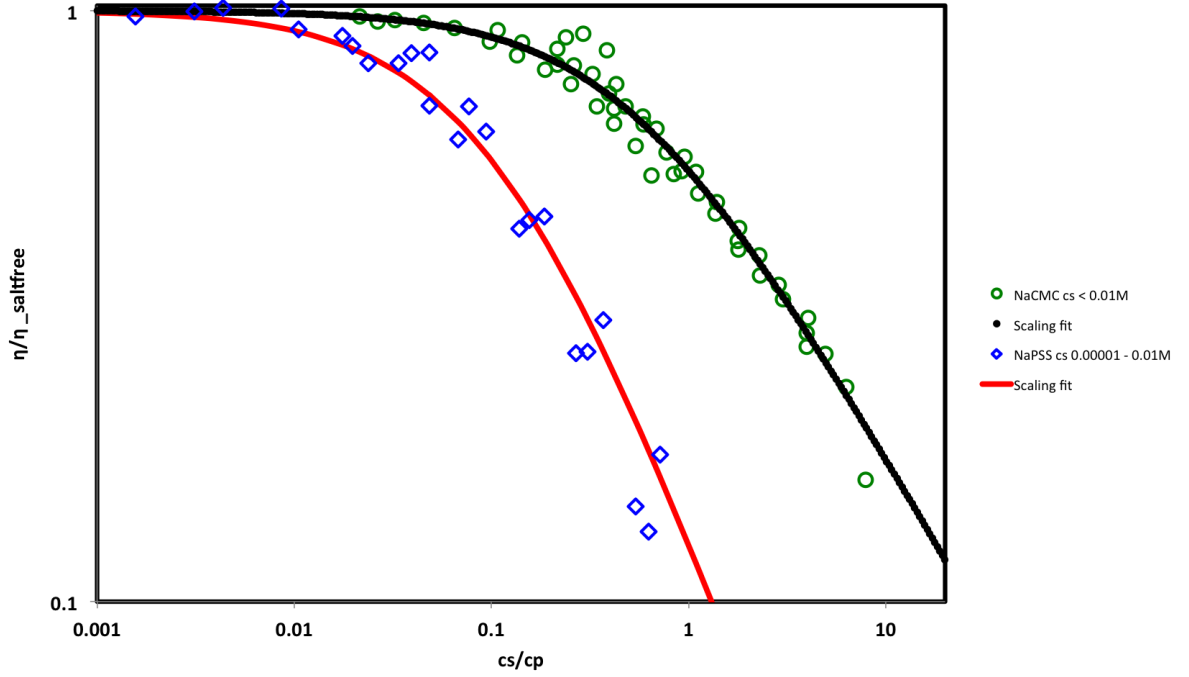


Figure 3.13: $\eta/\eta_{saltfree}$ vs. c_s/c_p for $c_s \leq 0.01M$. Green circles NaCMC, Blue diamonds NaPSS. Lines are best fit to $\eta/\eta_{saltfree} = (1 + 2Ac_s/c_p)^\alpha$

We next consider the variation of the solution viscosity as a function of added salt for a fixed polymer concentration. Figure 3.14 shows the relative decrease in specific viscosity as a function of added salt content for an entangled and an unentangled solution of NaCMC. Data for an unentangled solution of NaPSS (from ref [26]) is also shown for comparison. Dotted lines represent the flexible scaling predictions from equations 3.21 - 3.24. We can see that the viscosity of NaPSS decreases more rapidly and to a much lower value as a function of c_s compared to NaCMC. We can intuitively interpret this as follows: given the larger value for L_0 of NaCMC, we expect it to remain reasonably extended even at high salt compared with NaPSS ($L_0 \approx 10\text{\AA}$).

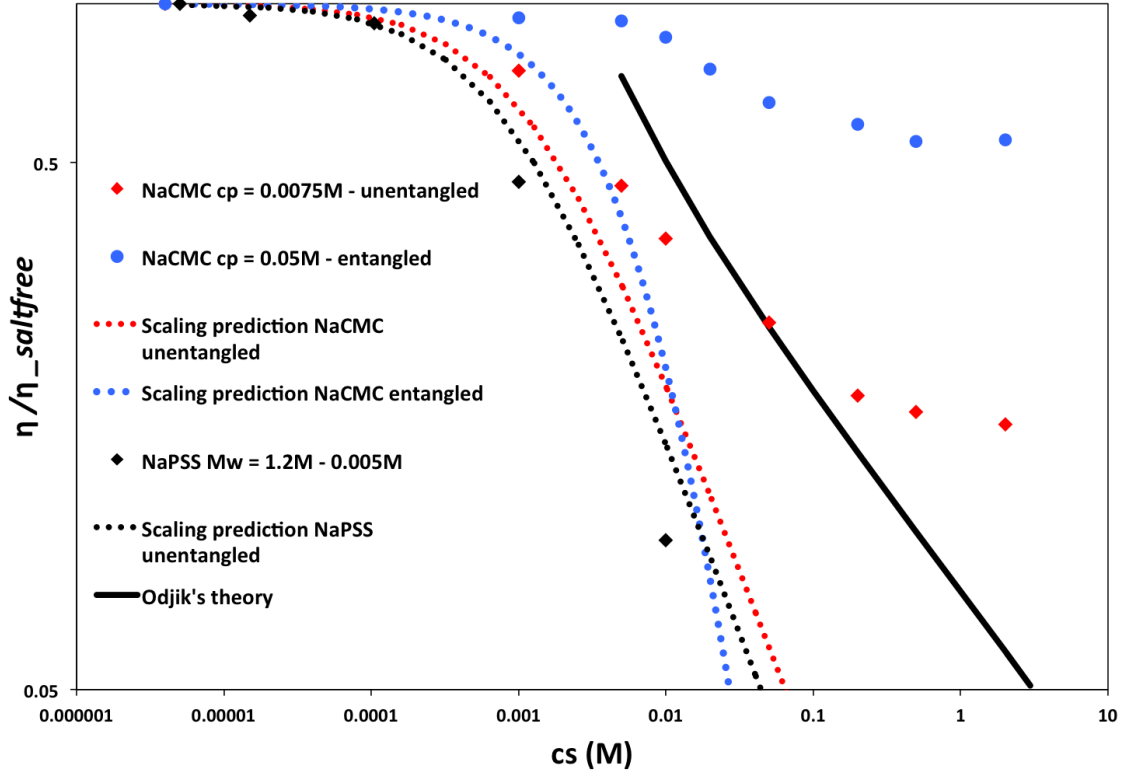


Figure 3.14: $\eta/\eta_{saltfree}$ vs. c_s . for entangled (blue circles) and unentangled (red diamonds NaCMC and black diamonds NaPSS) along with scaling prediction blue dotted line for entangled, red dotted line for unentangled NaCMC and black dotted line for unentangled NaPSS. Solid black line is the prediction of Odijk's theory adjusted to match the experimental data at $c_s = 0.05M$.

The scaling prediction for the unentangled cases seems to follow the data qualitatively at low c_s , deviating from it further as c_s increases. This is specially true for the NaCMC case, where the data is nearly flat for $c_s \geq 0.1M$ while flexible scaling theory predicts a limiting slope of -0.75. Odijk's prediction is adjusted to $c_s = 0.05M$, as it is derived for $c_s \gg c_p$. While it fails to describe the data, it gives a weaker dependence of c_s , $\eta_{sp} \propto c_s^{-3/8}$ vs. $\eta_{sp} \propto c_s^{-3/4}$ of flexible scaling theory and is thus closer to experimental values.

A much stronger deviation from the scaling prediction is observed for the entangled case. Even for relatively low $c_s = 0.001M$, the deviations between theory and experiment are significant. As in the previous case, the difference between theory and experiment increases as c_s increases, with the data showing $\eta_{sp} \sim c_s^0$ and theory predicting $\eta_{sp} \sim c_s^{-2.25}$. Given the relatively large polymer concentration, $c_p = 0.05M$ ($I \simeq 0.015 - 0.024M$), the intrinsic persistence length is likely

to dominate over the electrostatic one even at low added salt. We note here that the variation of $n^{-4} \sim c_s^{0.2}$ is too weak to reconcile the prediction with our experimental data. Interestingly, incorporating $n^{-4} \sim c_s^{0.2}$ on eq 3.24 leads to a predicted small increase in viscosity for low c_s , which we do not observe.

3.3.3 Corrections to Odijk's theory

Overlap concentration

Figure 3.15 a shows the overlap concentration as a function of added salt along with several theoretical predictions. The graph in part b indicates the ratio between experiment and theory. In general, we may expect theoretical predictions to agree with the data only up to a prefactor given that c^* is determined in an approximate manner and $c^* = N/R^3$ neglects a prefactor of order unity. The black line is the prediction of Odijk's theory, already shown in figure 3.7, which fails to capture the flattening of the data at high c_s . The green line is the prediction of Odijk's theory, where the excluded volume parameter is modelled empirically, thus changing from $B' = \kappa^{-1}$ to $B' = 3.5\kappa^{-1} + 12$, as explained in section 3.5.3. As discussed earlier, introducing a term to account for the hardcore excluded volume at infinite ionic strength correctly predicts the independence of static and dynamic properties on c_s at high c_s . The green line in part b is significantly flatter than the black one, signalling a better quantitative description. The next modification to the theory is to use the full expression for the expansion factor α given by equation 3.10 instead of the simpler expression ($\alpha = z^{0.2}$) used by Odijk and to use equation 3.3 to calculate R_F . This is shown by the blue line, which, up to a prefactor ($\simeq 2$) gives a good description of the data. Thus we see that these two small modifications highly improve Odijk's theory and are able to quantitatively describe the data for c^* up to a prefactor of order unity. For reference, Odijk's theory using $B' = \kappa^{-1}$ but the expansion factor of equation 3.10 is given by the purple line. This again correctly predicts the data up to a prefactor order unity suggesting the effect of simplifying the expression for the expansion factor is more significant than neglecting the hardcore term in the excluded volume.

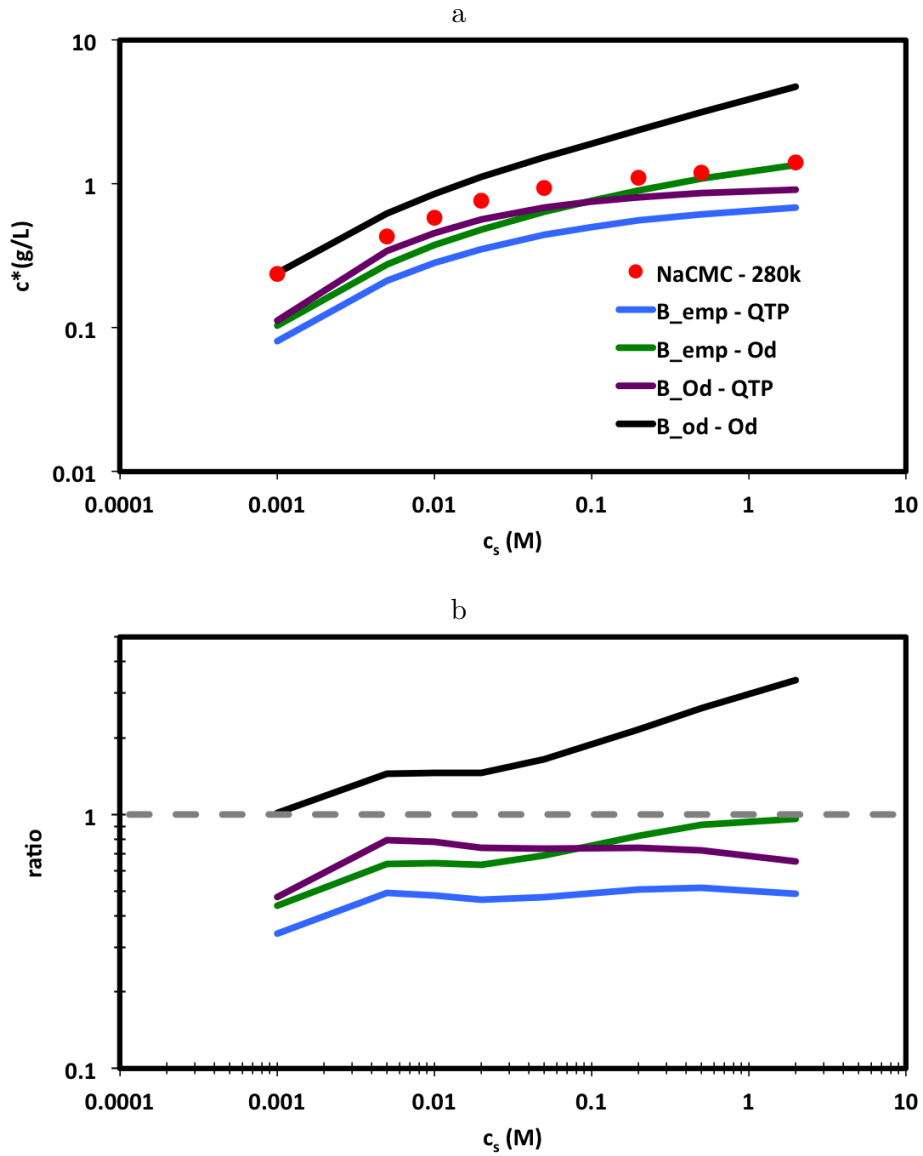


Figure 3.15: a: c^* as a function of added salt. Red circles: data. Black line: calculated from Odijk's theory. Green lines: Odijk's theory with empirical values for the excluded volume, see text. Purple line: calculated from QTP, using Odijk's value for the excluded volume. Blue line: calculated from QTP, using the empirical expression for the excluded volume B. b: ratio between theory and experiment, colours have the same meaning as in a. Dashed line indicates ratio =1.

Viscosity

Having seen the disagreement between theory and experiment for c^* can be reduced largely by introducing two small modifications to Odijk's treatment, we now consider whether the predictions for the viscosity can also be improved. The relative decrease of solution viscosity as

a function of added salt for a 0.0075M NaCMC solution is plotted in figure 3.16. It was shown in figure 3.14 that the observed results were not described by either flexible or semiflexible scaling theory. The green line shows Odijk's prediction with the modified B' , and the black dotted line, the prediction using equations 3.10 and 3.3 to calculate R_F and g_L . Both predictions are shifted vertically to match the data at $c_s = 2\text{M}$. Both cases give a much better prediction than the unmodified theory of Odijk (see figure 3.14). The prediction using the full expression for α in particular yields excellent agreement with the data for $c_s \geq 0.01\text{M}$. At lower salt concentrations, it likely the discrepancy arises, at least to some extent because equation 3.25 is not valid as the condition $c_s \gg c_p$ is not satisfied. Thus we see that more accurate (and complex), expression for α than the $\alpha = z^{0.2}$ approximation used by Odijk is required to obtain a quantitative prediction of the viscosity data.

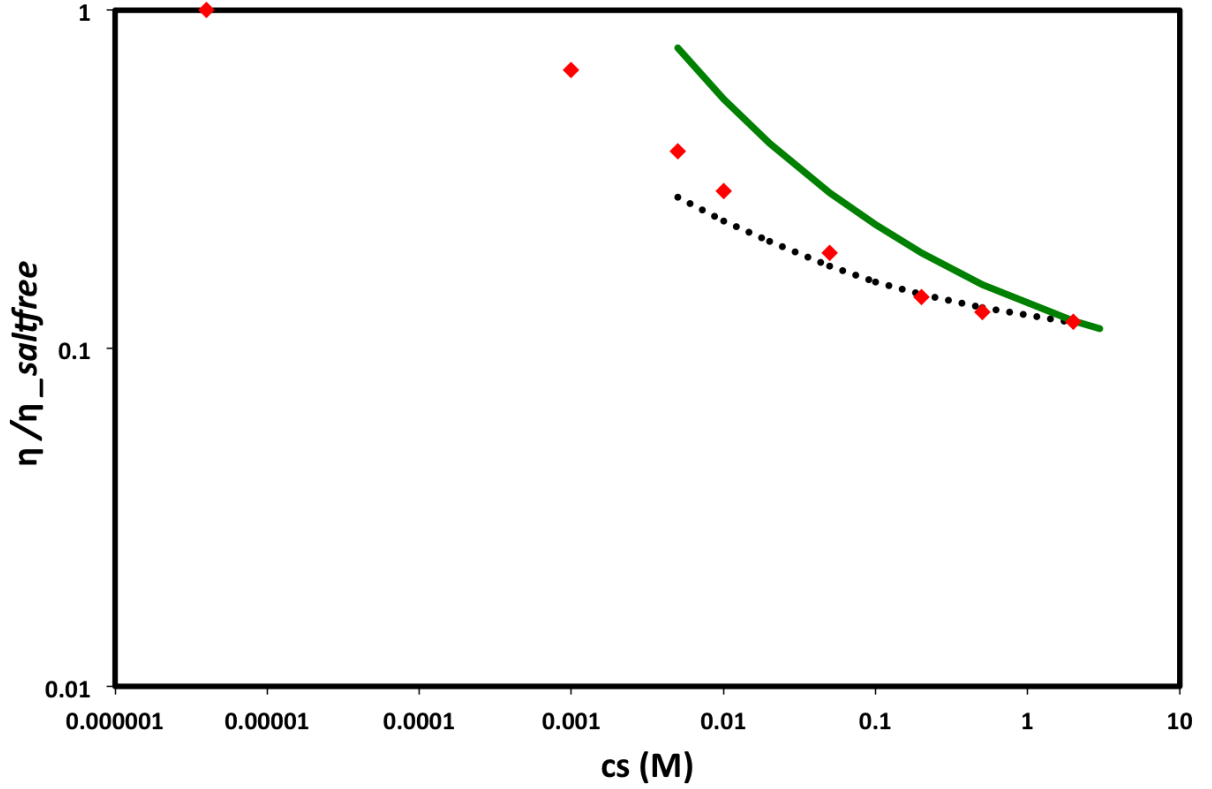


Figure 3.16: $\eta/\eta_{\text{saltfree}}$ as a function of c_s . The green line is a prediction of Odijk's theory using the empirical expression for B' explained in the text. The dotted line corresponds the prediction using the full expressions for α and R_{ee} .

3.4 Conclusions

We measure the intrinsic persistence length of NaCMC to be $L_0 = 55 \pm 10$ Å, characteristic of a semiflexible polyelectrolyte. The correlation length at $c_p = 24$ g/L is determined to be $\simeq 140$ Å independent of salt content for $c_s \geq 0.7$ M. We measure the viscosity of NaCMC solutions in the presence of NaCl as a function of polymer and salt concentration. In the high salt limit, the power laws of η_{sp} with concentration are the same as for neutral polymers in good solvent. The dependence of the overlap concentration and viscosity on c_s are not well described by either the flexible scaling theory of de Gennes, Pfeuty and Dobrynin or the semiflexible scaling theory of Odijk. It can be shown that the disagreement with the latter is, at least in part the result of two approximations: the use of a simplified expression for the expansion factor due to excluded volume and the lack of a term to take into account the hard core excluded volume which is independent of ionic strength. Once this modifications are taken into account, static and dynamic properties are predicted to be independent of c_s at high ionic strength. Interestingly, a plot of $\eta_{sp}/\eta_{sp}^{saltfree}$ vs. $1 + A c_s/c_p$ in a logarithmic representation yields a straight line for any given salt concentration, independent of whether solutions are entangled or unentangled. This is in strong disagreement with the predictions of the model of Dobrynin et al for polyelectrolyte entanglement. While our experiments indicate that n is salt dependent, this alone cannot explain this disagreement.

3.5 Annex 1: Analysis of literature data: persistence length and excluded volume

We compile experimental data on the persistence length and excluded volume of polyelectrolytes as a function of added salt. We have found two systems for which extensive data is available, namely NaPSS and NaHA. Our aim here is to find out if a proper theoretical description of the results is available and in its absence, to find empirical relationships for the aforementioned parameters.

3.5.1 Re-evaluation of Hirose's data

Hirose et al. [2] calculated the persistence length and excluded volume parameter for NaPSS in aqueous solution as a function of added salt from light scattering and viscosimetry measurements.

Their results, when compared with SANS data on semidilute solutions with or without added salt, give significantly lower values for the persistence length at a given ionic strength. Their value for the intrinsic persistence length of NaPSS, measured at theta conditions is $6.9 \text{ \AA}$, lower than the value of $\approx 10\text{--}12 \text{ \AA}$ obtained by others [11], which matches the persistence length of polystyrene ($\approx 10 \text{ \AA}$). Fitting their viscosity data, they obtain a monomer size of $2.5 \text{ \AA}$, lower than the $1.7 \text{ \AA}$ value reported by Kassapidou et al. [44] by fitting the high q range of their SANS data to a worm like chain model. Spiteri [11] and Combet et al. [45] report an intermediate value of $2 \text{ \AA}$ using the latter method. Calculating the effective monomer length from correlation length values (measured by SANS and SAXS) as explained in the previous chapter gives $b = 1.45 \text{ \AA}$. We take Kassapidou's value to be the most accurate as the counter ions were contrast matched with the solvent, hence removing any possible artefacts arising from their contribution to the scattering signal. We reanalyse the light scattering data of Hirose et al, fixing $b = 1.7 \text{ \AA}$ and leaving B' and L_T as free parameters. This gives a more reasonable value for the intrinsic persistence length of $10 \text{ \AA}$, and values of L_e in better agreement with SANS experiments. Figure 3.18 shows their data and our fit to it using the wormlike chain model with QTP for the excluded volume at $c_s = 0.5$ and $c_s = 0.05\text{M}$.

Norisuye and co-workers data [3] for NaPAMS should in principle be corrected in the same manner. unfortunately, we do not have scattering measurements of the effective monomer distance for fully charge NaPAMS. The data of Spiteri [11] however shows the contour length to be dependent on salt content for weakly charged ($f \approx 0.1$) NaPAMS. It is not clear to us if this effect will persist in fully charged NaPAMS. We may guess the correction should be similar to that of NaPSS given the value for B' is essentially the same for both polymers. We therefore reevaluate their light scattering data fixing $b = 1.7 \text{ \AA}$, noting that this is merely an approximation.

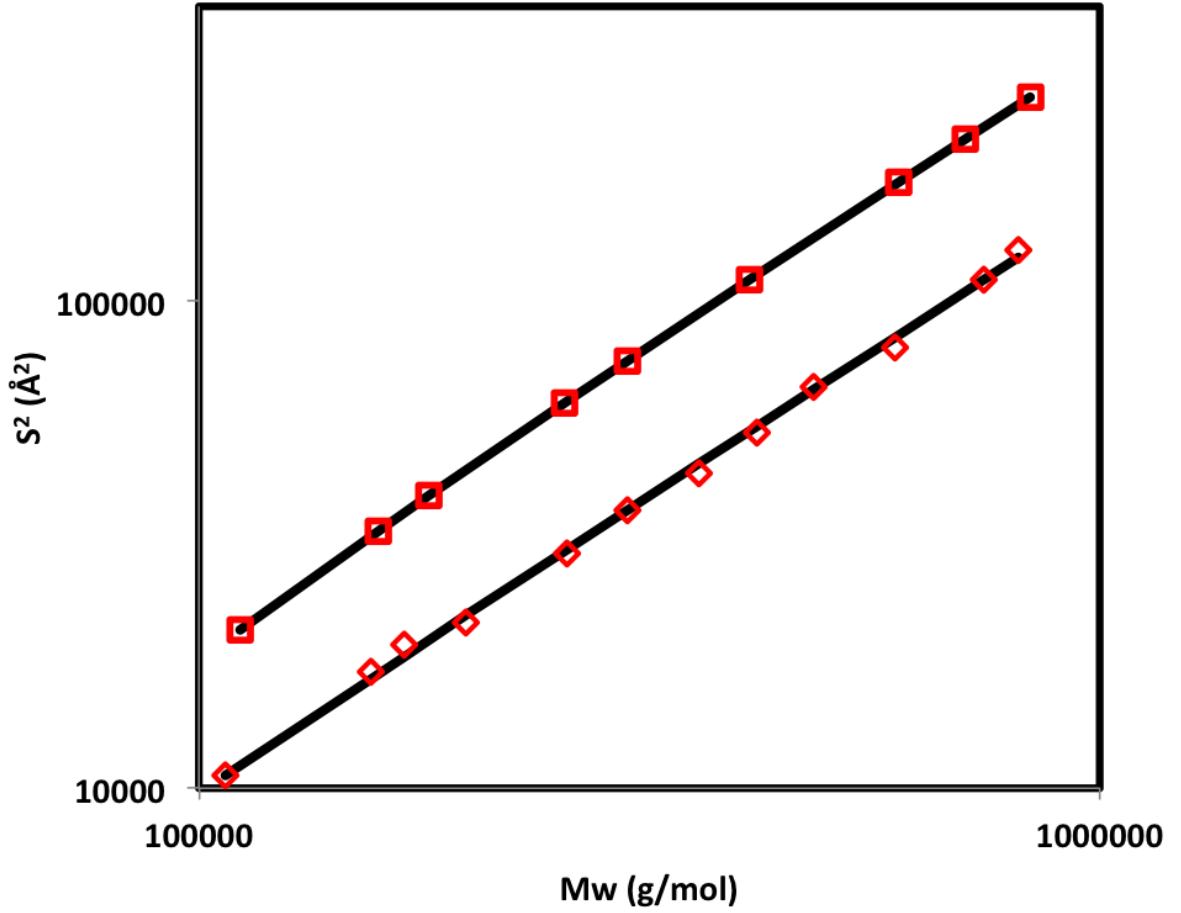


Figure 3.17: S^2 vs. M_w for NaPSS in 0.5M and 0.05M NaCl. Red symbols: data from ref [2]. Line: best fit to QTP theory using $b = 1.7\text{\AA}$.

3.5.2 Persistence length

NaPSS

Figure 3.18a shows the persistence length of NaPSS as a function of ionic strength, calculated assuming a fraction of uncondensed counterions of $1/3$ [42]. L_T values from SANS data were obtained from two different fitting routines: Spiteri [11], and Nierlich et al [46,47] fitted a worm like chain form factor with no excluded volume to the full q range. The data of Higgins and co-workers [48], Kassapidou et al [49], and Nishida et al [50] was fitted with a rod form factor at high q and a Debye form factor at low q and the persistence length was estimated from the inverse of the crossover between the two functions. The data of Hirose et al was reanalysed by us as described above. We see that there is a reasonably good overlap between different sets of

data despite the different measurement techniques and fitting procedures. Additionally, L_T is a function of the total ionic strength and not of the polymer or salt concentration specifically, this point was verified by Nishida [51] and Spiteri [11] who performed isoionic dilutions on NaPSS and found the value of the persistence length to be unchanged. The black line is a best fit to $L_T = L_0 + \alpha(c_s + c_p/6)^\beta$, where L_0 is taken to be 10 Å (indicated by the dashed line), the best fit values are $\alpha = 8.6$ and $\beta = -0.49$. The electrostatic persistence length as a function of ionic strength is plotted in figure 3.18b. The full red line indicates the OSF prediction in the zero chain radius limit, which is seen to qualitatively disagree with the data. The red dashed line is the Debye screening length κ^{-1} . The electrostatic persistence length is clearly proportional to but larger than κ^{-1} ($L_e \simeq (2.7 \pm 0.3) \kappa^{-1}$), in agreement with the predictions of ref [4]. The dashed blue line is the correlation length of NaPSS in salt free solution for the equivalent ionic strength ($\xi = 33.9c^{-0.5}$ where c is in molar units). The correlation length is proportional to L_e and of similar magnitude $L_e \simeq (0.65 \pm 0.1)\xi$, in agreement with the results of simulations by Dobrynin and Rubinstein [52]. The prediction of Dobrynin's model for the electrostatic persistence length of semiflexible polyelectrolytes (equation 3.2) is in qualitative agreement with data on NaPSS. It correctly predicts a linear variation of L_e with κ^{-1} but it gets the pre factor wrong by an order of magnitude: $0.36f^2l_B/b \simeq 0.1$ vs. the pre factor of $\simeq 2.7$ observed experimentally. A second theory developed by Dobrynin [10, 53] predicts a crossover between a κ^{-2} to a κ^{-1} dependence of L_e should be observed at $\kappa^{-1} \simeq \sqrt{L_0l_B}$, corresponding to $c_s \simeq 0.1\text{M}$ for NaPSS in water, no such crossover is observed in the data. Thus, it appears that no model can give a qualitative prediction for the electrostatic persistence length, and approximating $L_e \simeq \xi$ gives the most reasonable result.

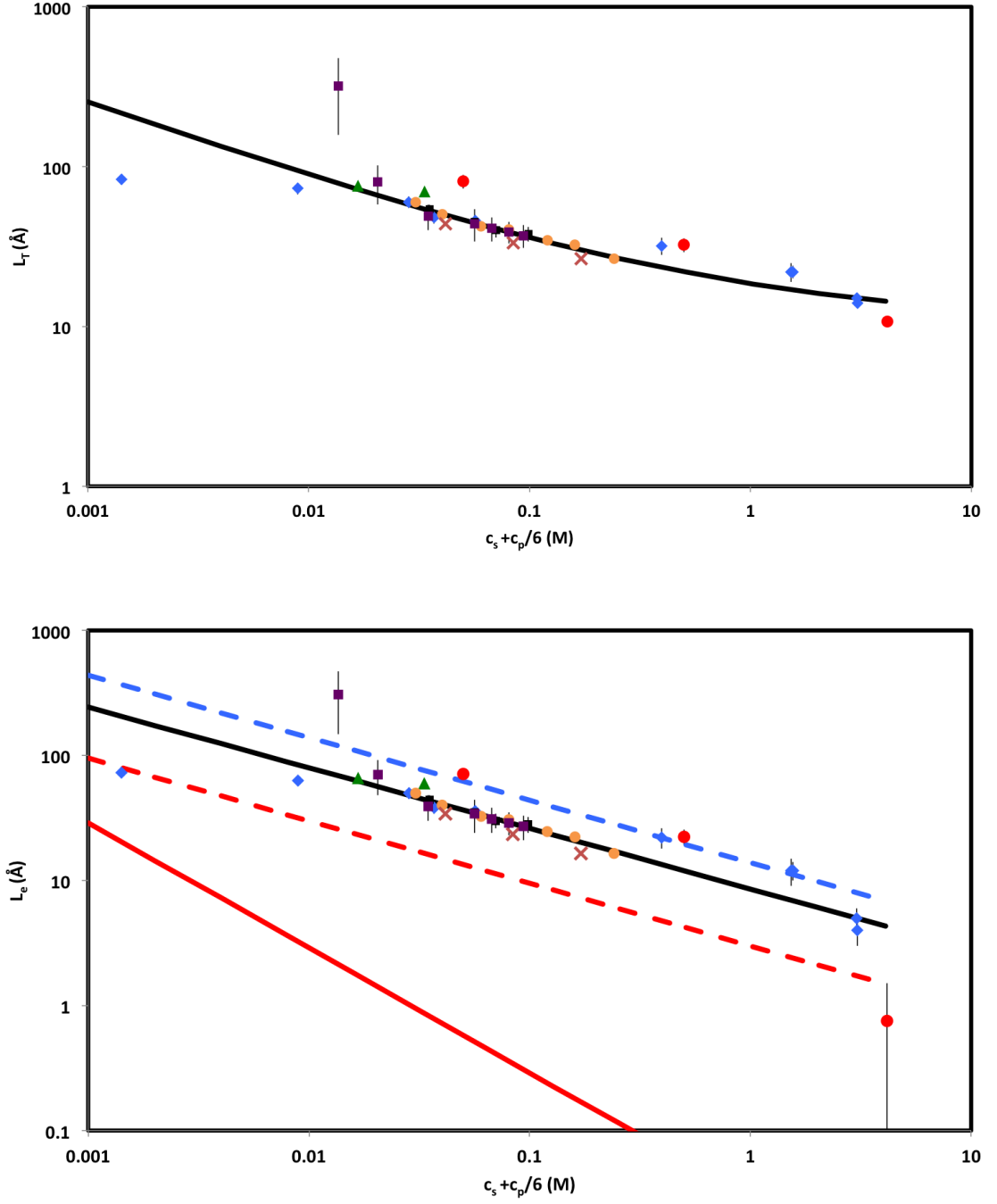


Figure 3.18: Top: Persistence length (L_T) of NaPSS as a function of ionic strength. Blue diamonds, data from Spiteri et al [11], purple squares, data by Nierlich et al [46], green triangles, data from Kassapidou et al [49], black squares, data by Nierlich et al [47], orange circles, data from ref [48], brown crosses, data from Kaji et al [50]. Black line: best fit to $L_T = 10 + \alpha(c_s + c_p/6)^\beta$ with $\alpha = 8.6$ and $\beta = -0.49$. Bottom graph: Electrostatic persistence length (L_e) as a function of ionic strength, calculated with $L_0 = 10\text{\AA}$. Symbols have the same meaning as above. Black line: $L_e = \alpha(c_s + c_p/6)^\beta$ with $\alpha = 8.6$ and $\beta = -0.49$. Full red line: OSF prediction. Dashed red line: κ^{-1} . Dashed blue line: Correlation length calculated for an equivalent ionic strength.

NaHA

We now turn to NaHA, a polyelectrolyte with a larger intrinsic persistence length ($\approx 40\text{-}90$ Å). Two studies are considered, the first is by Tsutsumi et al [1], who calculated the persistence length by fitting the intrinsic viscosity of a molecular weight series of NaHA with Yamakawa-Fujii-Yoshizaki theory for unperturbed wormlike chains combined with QTP theory for excluded-volume effects. Their light scattering and SAXS results show good agreement for $c_s \geq 0.02M$. The second data set is by Buhler and Boue [12] who obtained the persistence length from fitting a high q limit worm like chain form factor to SANS data on dilute solutions of NaHA in salt free D_2O and with added NaCl. Both sets of data are plotted in figure 3.19a. Unlike for the NaPSS case, the agreement of the data is limited. The two lowest ionic strengths measured by SANS appear to follow the values obtained by Tsutsumi et al. while the two highest ionic strengths are significantly larger for the SANS measurements than from the viscosity/LS/SAXS ones. Tsutsumi et al's data below $0.01M$ must be taken with care as it has not been verified by LS or SAXS and the authors claim the agreement between theory and experiment is limited. The data at high added salt on the other hand, verified by three different techniques should be considered as accurate. It is unclear to us why the disagreement between these two datasets exists. Figure 3.19b shows the electrostatic persistence length as a function of the ionic strength. The green and black points are the data of Buhler and Tsutsumi respectively, assuming $L_0 = 40\text{Å}$. The OSF prediction, shown by a full red line, gives a reasonable prediction for Tsutsumi's data. It is important to note however that a small change in the value of L_0 causes a significant difference in the values of L_e at high c_s . This is shown by the blue circles, which are the values of L_e for Tsutsumi's data using $L_0 = 38\text{Å}$. The high c_s data now shows a near linear dependence on κ^{-1} , the latter is indicated by the dashed red line. If we disregard Tsutsumi's data and use only Buhler's, we are left with a similar problem, subtracting a value of $L_0 = 74\text{Å}$ we find a linear dependence of L_e on κ^{-1} , while subtracting $L_0 = 80\text{Å}$, we find a quadratic dependence. For reference, the value of the correlation length, calculated for an equivalent ionic strength is shown by the dashed orange line, and clearly fails to describe L_e . We can conclude the OSF prediction gives a reasonable estimate for L_T , since, at low ionic strengths L_e appears to follow a quadratic dependence on κ^{-1} , while at high ionic strengths, the OSF relation correctly predicts a small L_e compared to L_0 . As NaCMC has similar molecular characteristics to NaHA, the OSF relation should give a reasonable prediction for L_T in the ionic strength range considered here.

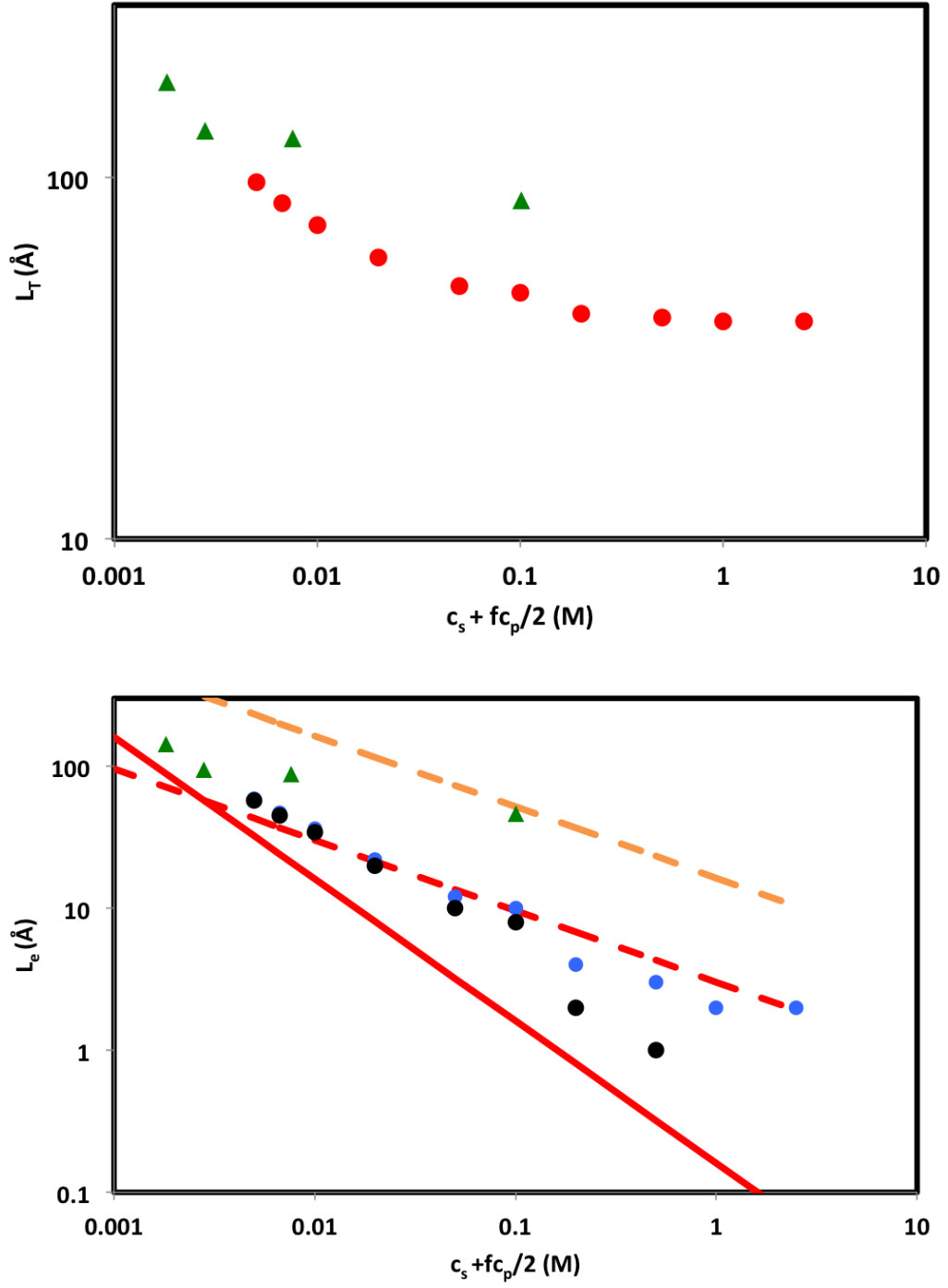


Figure 3.19: Top: Persistence length (L_T) of NaHA as a function of ionic strength. Red circles: data from Tsutsumi et al [1]. Green diamonds: data from Buhler et al [12]. Bottom: L_e as a function of ionic strength for the same two datasets. For the green triangles and black circles, a value of $L_0 = 40$ Å is assumed. For the blue circles, a value of $L_0 = 38$ Å is assumed. Full red line: OSF prediction. Dashed orange line: correlation length, calculated for an equivalent ionic strength. Dashed red line: κ^{-1} .

3.5.3 Excluded volume

Figure 3.20a shows the value of B' for NaHA (blue diamonds), as defined in section 3.1.2, vs. the inverse Debye screening length κ^{-1} in the c_s range 0.005-2.5M as blue rhombuses. The data is well described a straight line with a positive intercept. We therefore see that Odijk's approximation of $B'_{el} \sim \kappa^{-1}$ is qualitatively correct. If we neglect the attractive contribution to the binary cluster integral β_a , we can identify the intercept, corresponding to the value of B' at infinite ionic strength (where $B'_{el} = 0$) with the hardcore contribution to excluded volume B'_{hc} . Using equation 3.16, we obtain $d_c \simeq 8 \text{ \AA}$, close to the expected value of $d_c \simeq 10 \text{ \AA}$ obtained from a different procedure [1] and from bond lengths. Then assuming $B'_{el} = B' - B'_{hc}$ for all c_s , we find $B'_{el} \simeq 3.4\kappa^{-1}$. The values of B' for NaPSS, based on our analysis of Hirose's light scattering data are shown as red rhombuses, and overlap well with the NaHA data, which is somewhat surprising, given the rather large differences in molecular architecture between the two polymers. The values following their original analysis, obtained from viscosimetry are shown black squares, which also follow a linear relationship in κ^{-1} . The data for NaPAMS are also included as green circles (following our analysis) and black crosses (following the original analysis). We see that the uncorrected values overlap extremely well with those of NaHA, while the corrected values are a factor of two higher. As we explained earlier, our correction for the effective monomer length in the NaPAMS case is somewhat arbitrary and is unlikely to be exact. The assumption of a locally stiff chain, given the value of $B' \simeq 1.7$ is also unlikely to be correct. The correct values may well line between the two estimates.

Figure 3.20b shows the same values as before but now in a logarithmic representation. A power law fit to B' as a function of κ^{-1} reveals a sub linear dependence: $B' \simeq 9.5 \kappa^{-0.7}$. Compared to the previous fitting function, this one vanishes at infinite ionic strength and this is likely to be realistic when $\beta_a \simeq -\beta_{hc}$. The data does not allow the determination of which fitting function is correct. We note here that the approximation $B'_{el} \simeq \kappa^{-1}$ is a rather crude one, and it is surprising that it turns out to be relatively close to the experimental data. More sophisticated theories do not yield significantly better agreement [1].

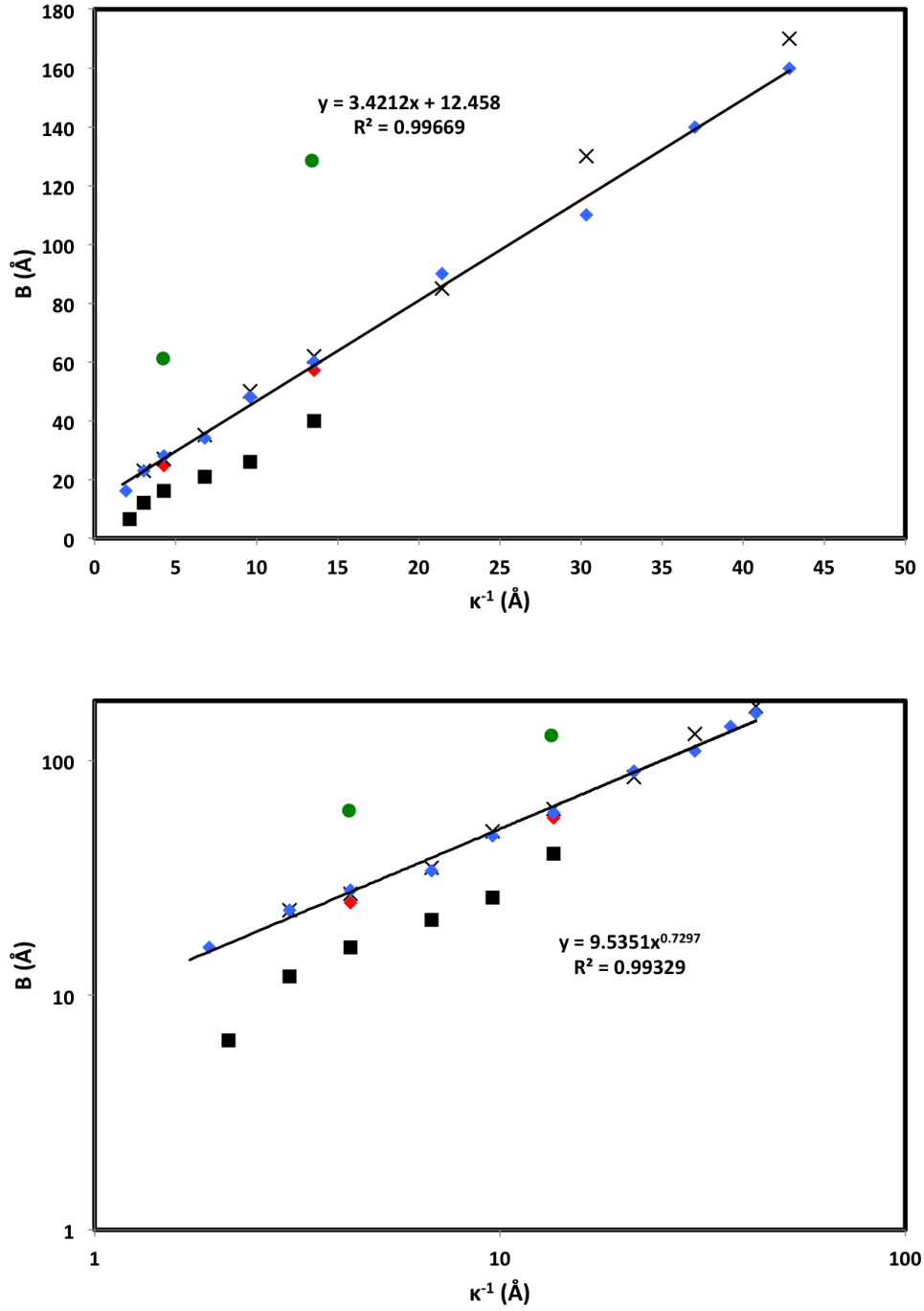


Figure 3.20: B' as a function of κ^{-1} for dilute aqueous NaCl solutions of different polyelectrolytes. Blue diamonds NaHA [1]. Corrected and uncorrected values for NaPSS [2]: red rhombuses and black squares respectively. Corrected and uncorrected values for NaPAMS [3]: green circles and black crosses respectively. Top graph, linear plot: Solid line is a best fit to a straight line for the NaHA values. Bottom graph: Logarithmic graph, solid line is a best fit power law to NaHA values.

3.6 Annex 2: Supplementary information

3.6.1 Fitting of salt free viscosity

Figure 3.21a shows the specific viscosity of salt free NaCMC solutions as a function of concentration. The black line is a sixth order polynomial fit. The ratio between data and fit as a function of concentration is shown in 3.21. The fit does not deviate by more than 10% for most values, which is within the typical error of a measurement.

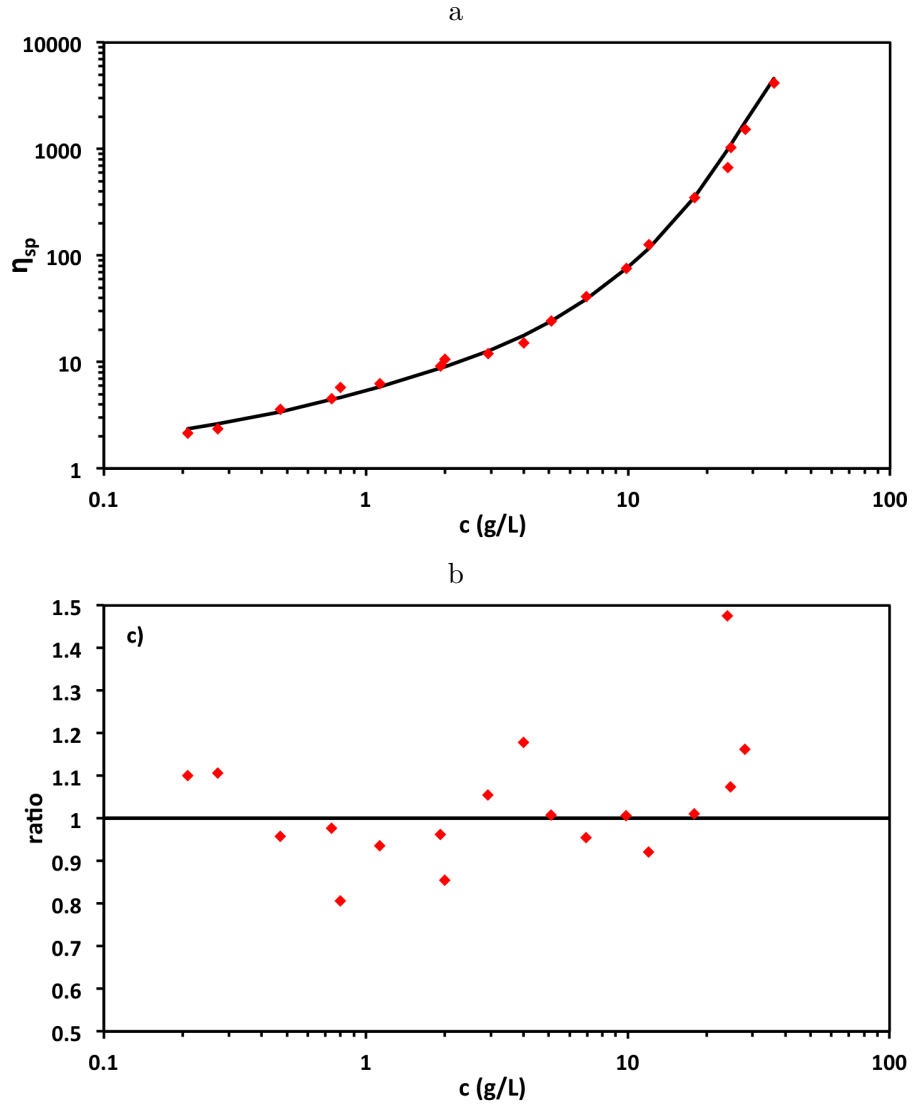


Figure 3.21: Specific viscosity as function of concentration for NaCMC in deionised water. a: Red diamonds: data Black line: sixth order polynomial fit. b: Red diamonds: ratio between fit and data. Black line: ratio = 1.

3.6.2 Expansion Factor

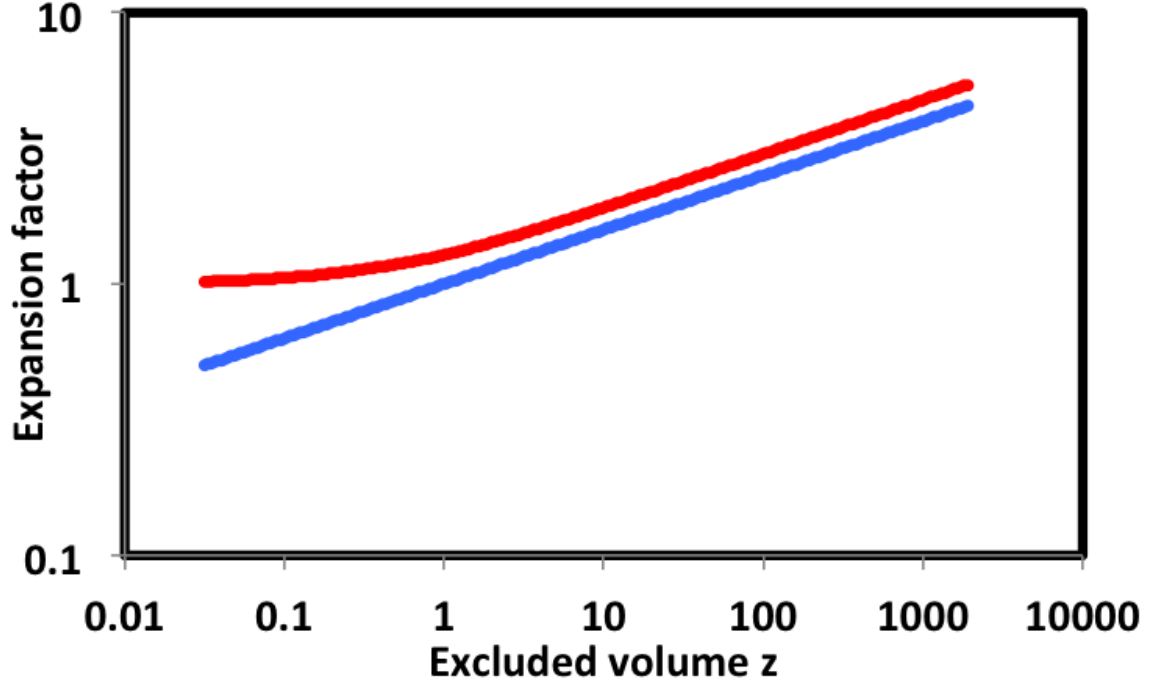


Figure 3.22: Expansion factor α calculated from the simplified formula $\alpha = z^{0.2}$ (blue line) and using equation 3.10 (red line).

Figure 3.22 shows the expansion factor α calculated from Odijk's approximation $\alpha = z^{0.2}$ and using equation 3.10. Both expressions agree up to a prefactor in the high z limit (which coincides with the high N limit as $z \propto L^{1/2}$). The $\alpha = z^{0.2}$ approximation deviates strongly from the more accurate eq 3.10 for $z \leq 1$.

3.6.3 Overlap concentration, comparison with literature data

Figure 3.23 shows the overlap concentration determined from $\eta_{sp}(c^*) = 1$ for NaCMC, as discussed earlier, NaPSS ($M_w \simeq 1.2 \cdot 10^6$ g/mol) from ref [26] and chitosan ($M_w \simeq 8.5 \cdot 10^5$ g/mol) from ref [19]. NaPSS shows the expected dependence of $c^* \sim c_s^{3/5}$ predicted by flexible scaling theory. NaCMC and chitosan show a weaker dependence ($c^* \sim c_s^{0.3}$), which flattens at high c_s . These results confirm that the deviations from GPD theory are due to the intrinsic rigidity of the chains.

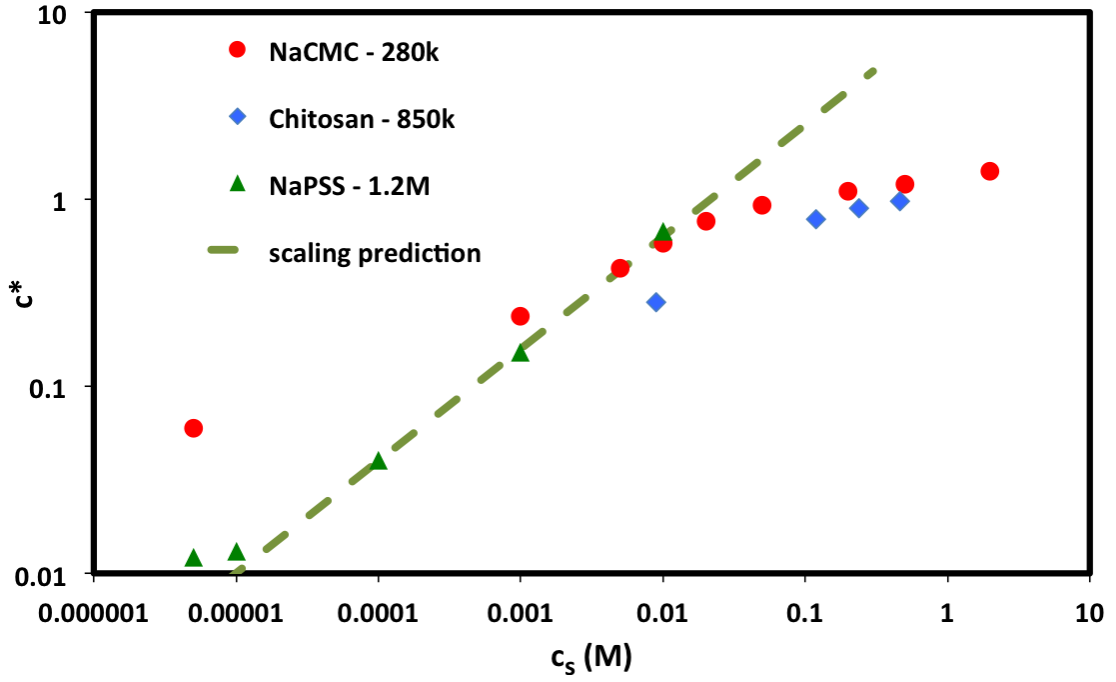


Figure 3.23: Overlap concentration determined from $\eta_{sp}(c^*) = 1$ for different systems.

3.6.4 Estimates for c_e

We consider three methods for estimating c_e . First, the crossover concentration between the unentangled and intermediate slope. Second: The crossover between the unentangled and concentrated regimes. Third: the crossover between the intermediate and concentrated regimes. The first method gives the most reasonable results. i.e. c_e does not increase with added salt. A weak variation of c_e with concentration has been observed for chitosan [19].

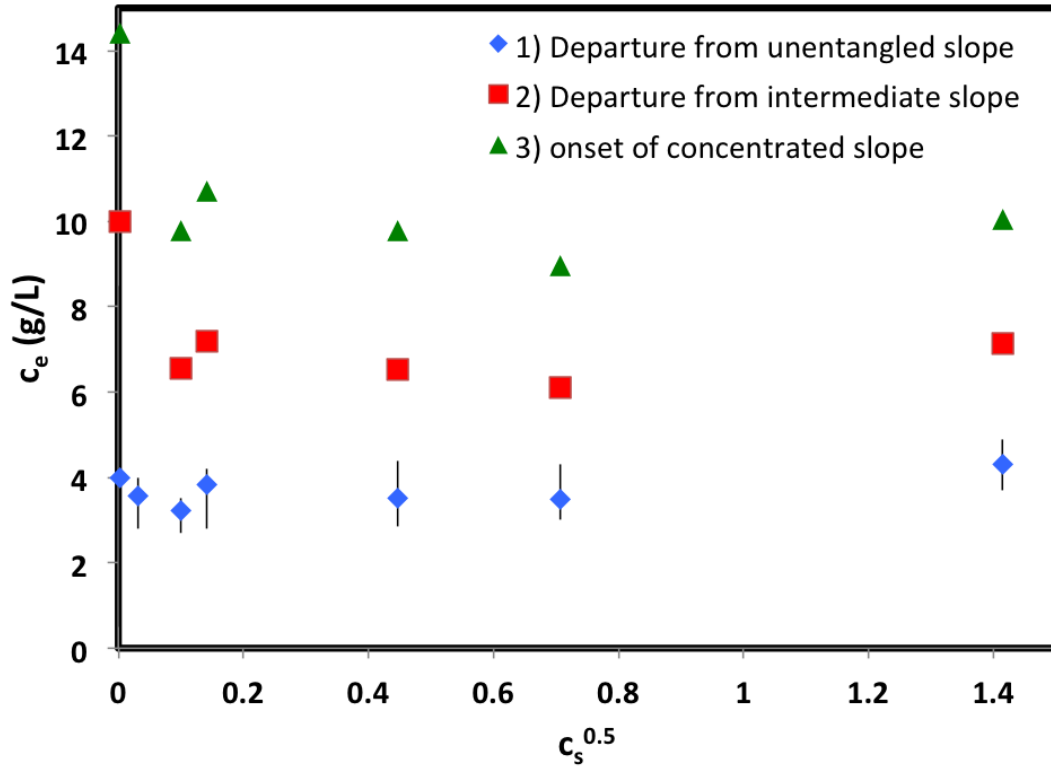


Figure 3.24: c_e determined by three different methods: 1: crossover between the unentangled and intermediate slope, 2: crossover between the unentangled and concentrated regimes, 3: crossover between the intermediate and concentrated results.

3.6.5 Correlation length NaPSS

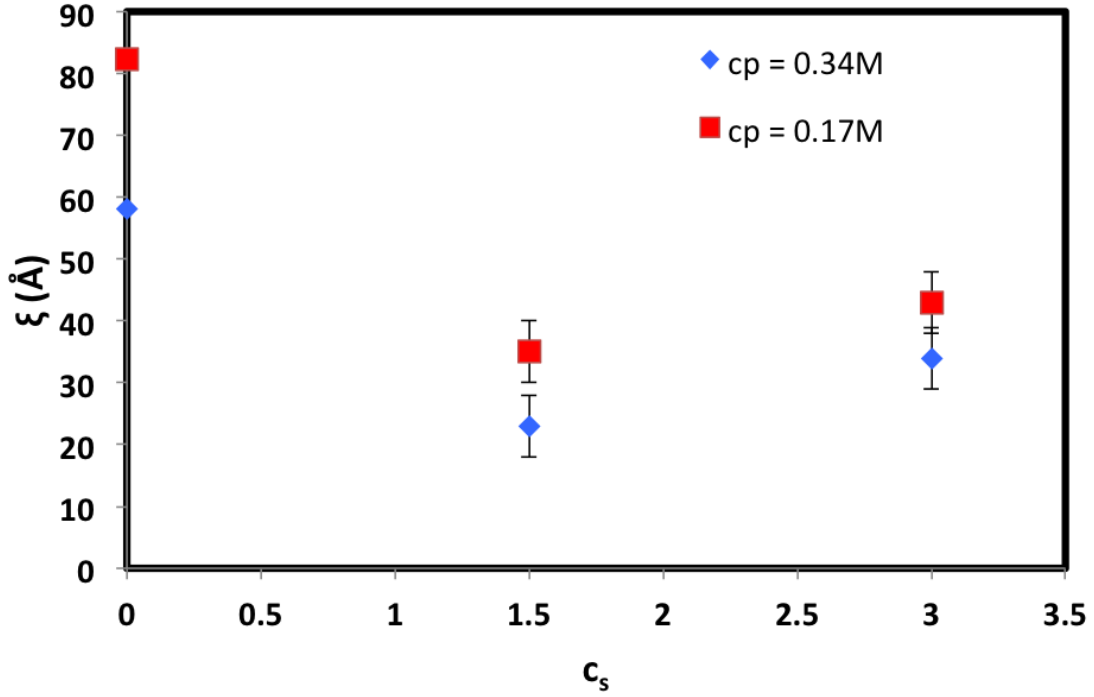


Figure 3.25: Correlation length of NaPSS solutions as a function of added salt. Results in salt solutions from reference [11]. Salt free values calculated from $\xi = 33.9c^{-1/2}$ [42].

The correlation length of NaPSS solutions as a function of added salt for two different concentrations are plotted in figure 3.25. While an increase in ξ from $c_s = 1.5M$ to $c_s = 3M$ is predicted by both flexible and semiflexible scaling theory, the larger value at $c_s = 0$ is not. The salt free correlation length is obtained from measurements of the peak position while the salt samples are obtained from an OZ fit. As mentioned earlier, it is possible that both quantities are different, which could explain the apparent decrease from $c_s = 0$ to $c_s = 1.5M$.

3.6.6 Intrinsic viscosity of NaCMC at $I = 0.01M$

Figure 3.26 shows the intrinsic viscosities of NaCMC D.S. ≈ 1 as a function of M_w at $c_s = 0.01M$ from three different studies. The reported values at high M_w vary by as much as a factor of 3, this of course translates in a large difference in L_T and B' . This likely arises from errors in both the determination of $[\eta]$ and M_w .

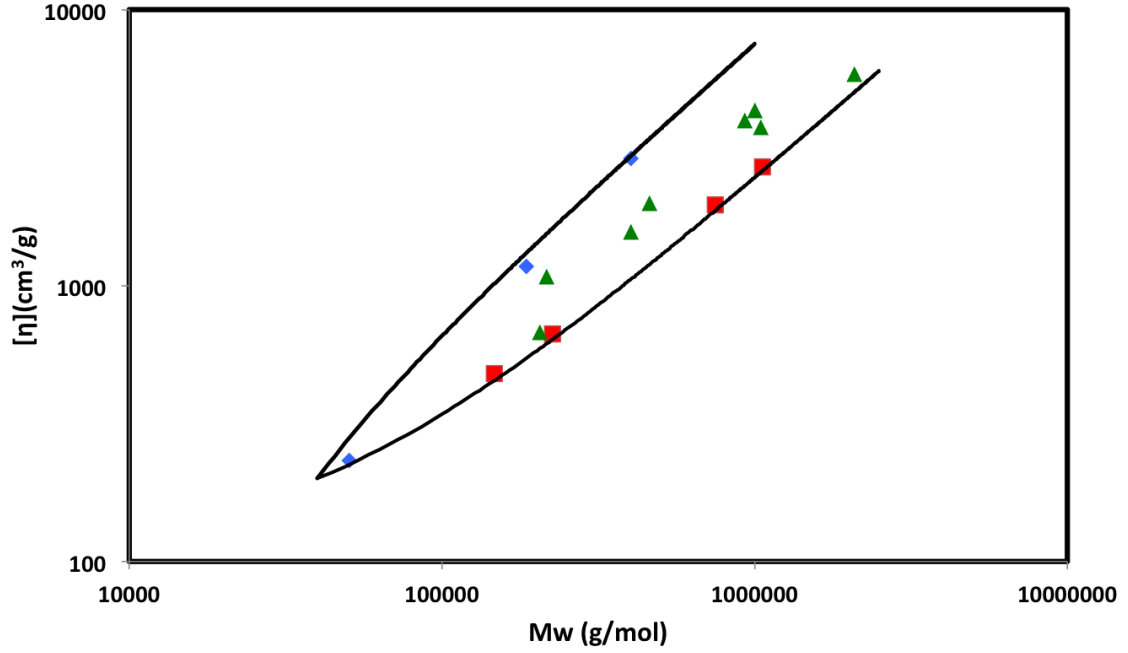


Figure 3.26: Intrinsic viscosities of NaCMC D.S. ≈ 1 as a function of M_w at $c_s = 0.01\text{M}$. Black lines represent the upper and lower bounds for the data. Blue diamonds from reference [54], Green triangles from reference [55], Red squares from reference [25]

3.7 Annex 3: Effect of added salt on solution viscosity for other systems.

Figure 3.27 shows plots of $\eta_{sp}/\eta_{sp}^{saltfree}$ vs. $1 + 2Ac_s/c_p$ for different maleate copolymers, which fall under the category of flexible polyelectrolytes. The meaning of the lines is indicated in the figure caption. Both Poly(styrene-alt-maleate) and Poly(isobutylene-alt-maleate) show similar behaviour in the dilute regime, i.e. a very weak power law, as observed before for NaPAMS by Kujawa et al [56]. The power law exponents α in the semidilute unentangled and entangled are similar for all systems with $\alpha \approx 0.6 - 0.9$. No crossover between entangled and unentangled data can be observed, although given the scatter of the data, it cannot be ruled out either.

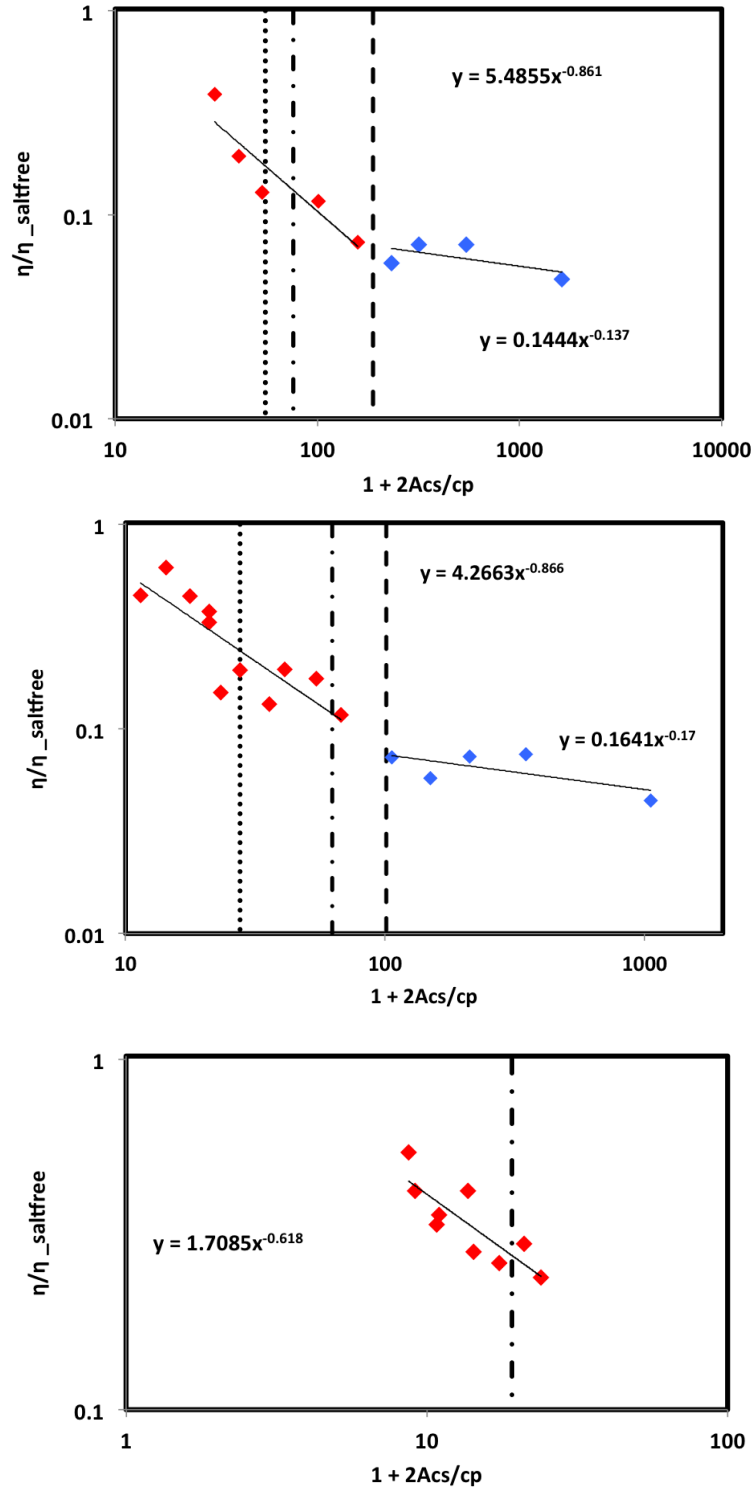


Figure 3.27: Relative decrease in viscosity as a function of $1 + 2Ac_s/c_p$ for several maleate copolymers. Top: Poly(styrene-alt-maleate). Middle: Poly(isobutylene-alt-maleate) Bottom: Poly(diisobutylene-alt-maleate). All from reference [40]. The dashed line marks the overlap concentration with added salt, the dashed dotted line marks the entanglement concentration in salt free solution and the dotted line the entanglement concentration in salt solutions. Power law fits to different regions of the datasets are indicated on the graphs.

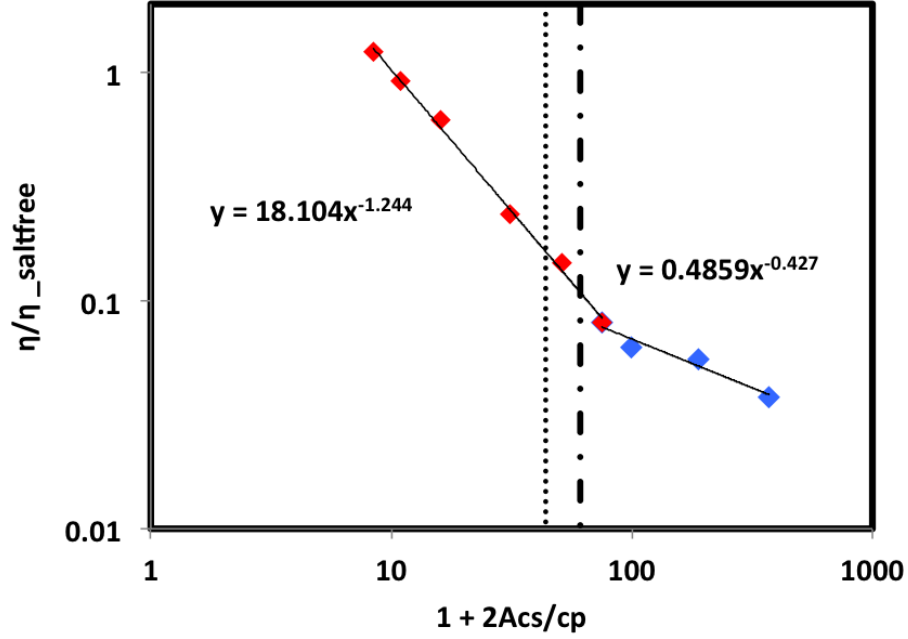


Figure 3.28: Relative decrease in viscosity as a function of $1 + 2Ac_s/c_p$ for NaHA in 0.15M NaCl solution, data taken from reference [57]. Lines have the same meaning as in previous figure.

The same plot for NaHA, a semiflexible polyelectrolyte is shown in figure 3.29. The results are quite different: a strong exponent of $\alpha \simeq -1.2$ is observed in the entangled regime, with a weaker exponent of -0.4 in the unentangled regime. While these exponents strongly deviate from scaling predictions of flexible polyelectrolytes, the strong change in α , by a factor of $\simeq 3$ is in good agreement with Dobrynin's model. NaHA does not show typical polyelectrolyte rheology. In salt free solutions, the semidilute unentangled regime shows $\eta_{sp} \propto c^1$, which is followed by an exponent of $\eta_{sp} \propto c^{3.4}$ ⁱⁱ in strong disagreement with scaling theory predictions. Finally we note that at high polymer concentrations, a slight increase in the viscosity upon salt addition is observed. This has been observed for a number of polyelectrolyte systems and is thought to arise from increased attractive intermolecular interactions [58, 59].

Last, we examine xanthan, a rigid polyelectrolyte. An even stronger exponent is found in the entangled/concentrated regime $\alpha \simeq -2.5$, here the increase in viscosity with added salt at high polymer concentrations is more significant than in the NaHA case. The unentangled regime

ⁱⁱIn the original reference, the $\eta_{sp} \propto c^1$ region was interpreted as the dilute regime, however, given the high values of η_{sp} reached (up to 170) we interpret this as the semidilute unentangled regime and identify the $\eta_{sp} \propto c^{3.4}$ regime as the semidilute entangled.

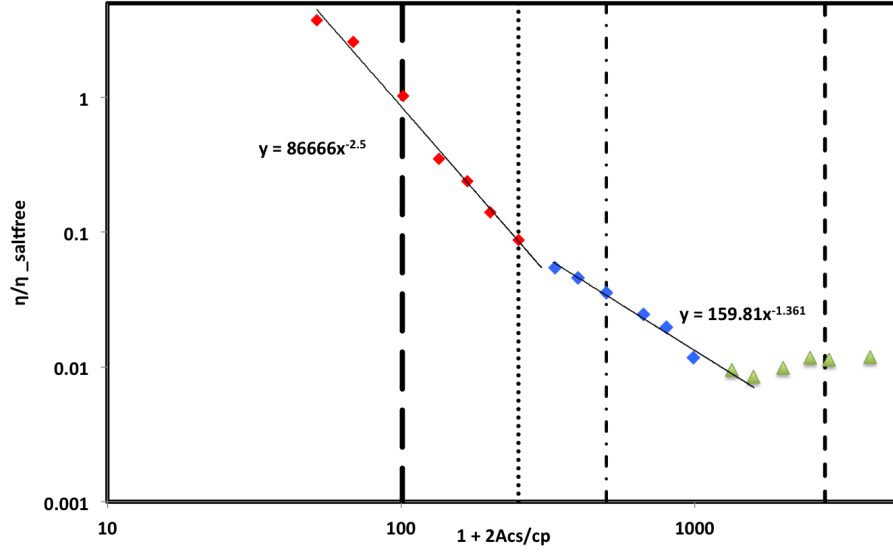


Figure 3.29: Relative decrease in viscosity as a function of $1 + 2Ac_s/c_p$ for Xanthan in 0.05M NaCl solution, data taken from reference [60]. Lines have the same meaning as in previous figure. The long dashed line marks c_D in salt free solution.

shows a much stronger power law than other systems $\alpha \simeq -1.4$ vs. the weaker 0.9-0.4 seen for NaCMC, NaHA, NaPSS etc. The behaviour of xanthan may be somewhat unique in that it adopts a double helical conformation in solution which can transition to a single helix when salt is added. It is therefore possible that at least part of the deviation between xanthan and the other systems studied is due to this and not intrinsic rigidity or any polyelectrolyte feature.

In conclusion, most systems, NaPSS, NaCMC and several maleate copolymers yield similar behaviour with power laws $\alpha \simeq 0.6-0.9$. Other polyelectrolytes such as NaHA and Xanthin show rather different behaviour, which may arise due to specific properties such as helicity. In order to validate scaling predictions, larger data sets, where both c_s and c_p is varied simultaneously are needed.

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4 Microfluidic SANS: application to complex fluids

Abstract

Understanding and engineering the flow-response of complex and non-Newtonian fluids at a molecular level is a key challenge for their practical utilization. Here we demonstrate, for the first time, the coupling of microfluidics with small angle neutron scattering (SANS). Microdevices with high neutron transmission (up to 98%), low scattering background ($\lesssim 10^{-2} \text{ cm}^{-1}$), broad solvent compatibility and high pressure tolerance ($\approx 3\text{-}15 \text{ bar}$) are rapidly prototyped via frontal photo polymerisation. Scattering from single microchannels of widths down to $60 \text{ }\mu\text{m}$, was successfully obtained in the wavenumber range $0.01\text{-}0.3 \text{ }\text{\AA}^{-1}$, corresponding to real space dimensions of $\approx 1\text{-}60 \text{ nm}$. We demonstrate our approach by investigating the molecular re-orientation and alignment underpinning the flow response of two model complex fluids, namely cetyl trimethylammonium chloride/pentanol/ D_2O and sodium lauryl sulfate/octanol/brine lamellar systems. Finally, we assess the applicability and outlook of microfluidic-SANS for high-throughput and flow processing studies, with emphasis of soft matter.

4.1 Introduction and review of the literature

The advent of microfluidics and rapid prototyping [1,2] offers opportunities to design and generate well-defined flow fields with unprecedented flexibility, ranging from extension to rotation and including pure shear [3]. Despite the general absence of non-linearity associated with inertial forces, fluids confined within microchannels ($1\text{--}1000\mu\text{m}$), exhibit unexpected and fascinating behaviour. [4] While microflows are generally characterised by low Reynolds numbers, resulting in diffusive and thus slow mixing, simple designs of both continuous and multiphase flows can reduce mixing times to the sub-millisecond range [5–7] and have enabled major advances in, for example, the study of fast reaction kinetics [5] or the rapid screening of protein crystallisation [8]. Further, microfluidic approaches are generally high throughput, either sequential or parallel, and require minimal sample consumption, in the pL- μL range. [5,9]. Complex or non-Newtonian fluids, in particular, can exhibit dramatic microflow response due to the commensurability of characteristic time and length scales. [4] Microfluidic methods can not only precisely quantify their rheological behaviour but even access hitherto unexplored phenomena that emerge, for example, when large Deborah (De) numbers and low Reynolds (Re) numbers are achieved simultaneously [10]. Soft matter generally respond strongly to flow perturbations exhibiting shear thinning or thickening, thixotropy or rheopexy, but also flow-induced transitions, such as gelation or phase separation [11–15]. The understanding of these non-equilibrium phenomena and mapping of ‘flow phase diagrams’ [15,16] can now be greatly expanded with the plethora of flow types and magnitudes available via rapid prototyping microfluidics.

In this section, we review the different applications of microfluidic-small angle scattering. We do not aim to provide a full review of the progress made on this field but rather to give representative examples of the different applications and opportunities, which may in the future be extended to microfluidic SANS.

4.1.1 High throughput screening of solutions.

Microfluidic mixers have been integrated with SAXS beam lines for rapid screening of protein solutions. The mixer acts as a formulation unit, where a solution of a given composition is made and then measured using SAXS in an observation window which can be part of the same device or a separate one connected to the mixer [17,18]. The main advantages over using capillary tubes are the low volume required per sample, and the increased efficiency in samples/time. This

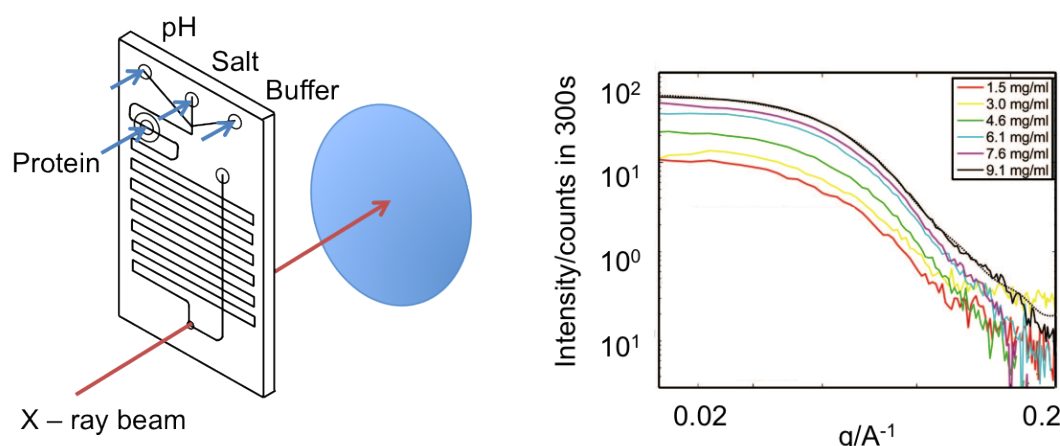


Figure 4.1: a) Schematic of setup used by Arleth and co-workers [17] for automated screening of solutions, four components are mixed and the resulting solution is studied with SAXS., b) representative scattering profiles for BSA solutions. Image adapted from reference [17].

method is particularly suited for samples which are susceptible to damage from X-ray radiation, such as proteins: by having a continuous stream of solution, the exposure time of any single molecule in solution is minimised. Examples of this are the work of Arleth and co-workers [17], who used a microfluidic mixer to generate dilutions of Bovine Serum Albumin (BSA) in water at controlled pH and ionic strength, and coupled this to a polystyrene observation window. A schematic of their setup is shown in figure Figure 4.1. They further developed their method [18] and were able obtain readings with 15 μ l per sample. A current aim with these systems is to implement software which provides real time feedback on experimental results, thus allowing automation of experiments.

Chastek et al. designed a microfluidic device to synthesise block copolymer micelles. After synthesis, a small amount ($\approx 4\mu$ l) passed through a fiber optic channel coupled to a dynamic light scattering (DLS) from which a particle size distribution could be obtained. Further details on microfluidic-DLS can be found in reference [19]. The coupling of these two techniques provides a way to monitor polymerisation reactions in real time and characterise the final product. Another example of the coupling of microfluidics with light scattering is the work of Beersjo and co-workers [7]. Using a rapid prototyping micro fabrication technique, a mixer was coupled to an observation window, which allowed the monitoring of diblock copolymers aggregation into multilamellar vesicles in aqueous solution.

Finally, we discuss the use of microfluidic combined with X-ray diffraction (XRD) for protein

crystallisation [21–23]. For a review of the topic see reference [24]. Ismagilov and co-workers [23,24] used a PDMS droplet mixer (similar geometry to figure 1.10c) connected to a capillary tube to produce droplets containing protein, buffer and precipitant at given ratios. These are then transferred to a borosilicate capillary tube where the solutions are studied by X ray diffraction (XRD). A schematic of their setup and an XRD pattern is shown in figure 4.2. With this setup, the amount of protein sample needed per trial was reduced to picoliters (from $\sim 1\mu\text{l}$ if prepared by hand, 10-100nl with a dispenser robot). The main limitation of this method is the size of capillaries, up to 10cm, limiting the number of experiments to ~ 100 .

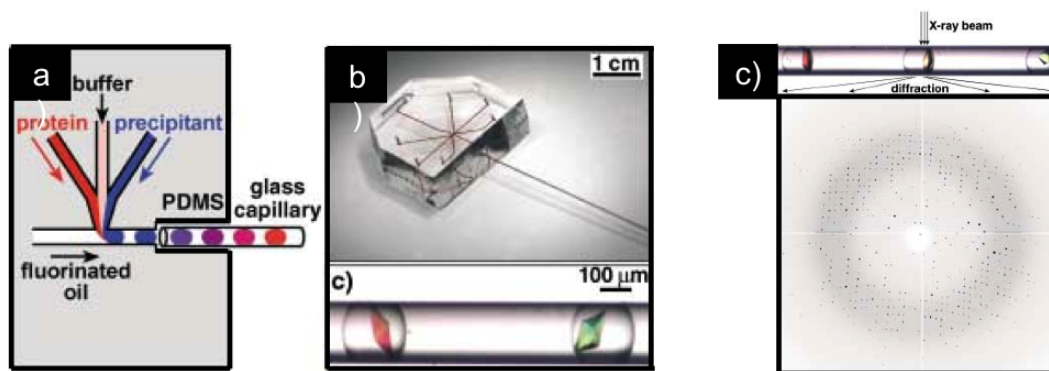


Figure 4.2: a) Schematic of protein crystallisation setup by Ismagilov and co-workers. b) Image of device. c) Capillary and diffraction pattern from protein crystal. Image from reference [23]

4.1.2 Self assembly under flow

One of the most important characteristics of soft matter is its ability to self assemble on the molecular and mesoscopic scales [25,26]. Microfluidics has been used extensively for this purpose. Micro devices have been coupled to both in house SAXS setups [35] and synchrotron sources [36,37].

Many biological processes, which involve self assembly under specific conditions, such as concentration gradients or under shear flow can be mimicked using microfluidic devices. For example Martel et al. studied the silk fiber aggregation triggered by an increase in pH [38] using a concentric flow microfluidic device, which reproduces the geometry of the silkworm spinning duct. A fibroin solution with $\text{pH} = 2$ is flowed through the central channel and a phosphate buffer through the outer one. SAXS measurements allowed the determination of R_g as aggregation took place while WAXS readings showed the formation of crystalline β -sheet domains within

the fiber. Pfohl and co-workers have carried out extensive studies on the dynamics of biological systems under shear flow in concentration gradients analogous to biological processes [39].

4.1.3 Soft Matter under flow

Soft matter systems are often highly flow responsive. Changes in the structure on the material resulting from an applied flow field can have a large impact on the system's rheological properties and even phase behaviour [40]. The study of complex fluids under flow using scattering has traditionally been carried out using flow-SAS [42–45, 75], using custom made flow devices, or rheo-SAS [46, 75], where a rheometer is integrated with a beam line. Microfluidics offers advantages over flow or rheo-SAS in that it allows to precisely design specific flow fields, and devices can be rapidly prototyped, within hours of the initial design.

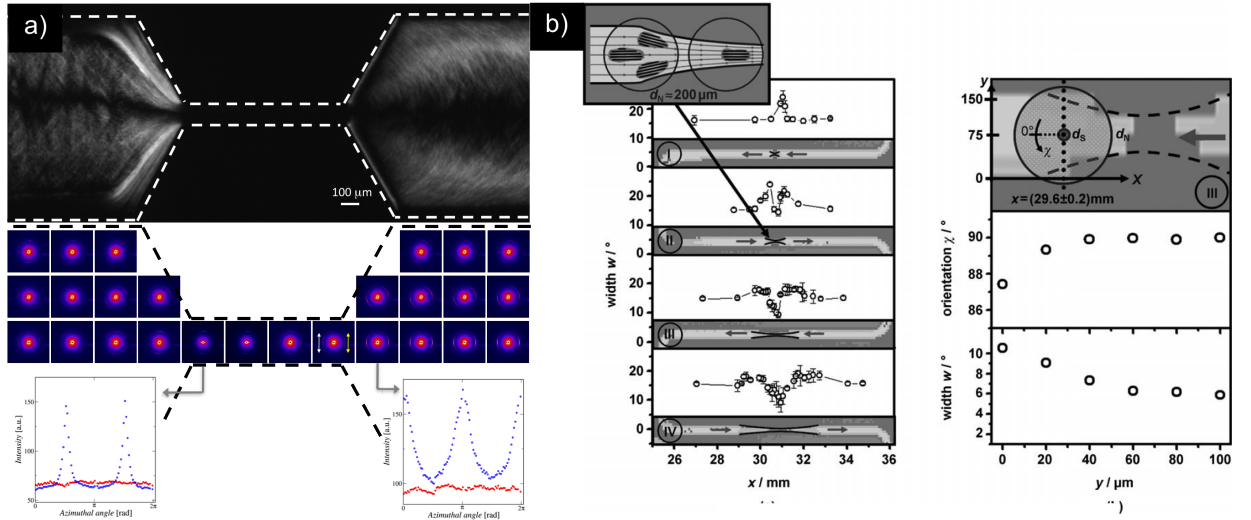


Figure 4.3: a) Optical microscopy image of chip with a solution of CTAC/Water/Pentanol, SAXS patterns for the corresponding positions in the channel. Image adapted from [40] b) Schematic and images of constriction geometries adapted from Pfohl et al. The schematics on the left show different sections of the chip, along with a transmission mapping of different constrictions. The graphs on the right show the orientation of the liquid crystal and width along the channel. Image from [49]

Microfluidic-SAXS has been employed to study the alignment of particle suspensions in different channel geometries [27, 40, 48, 49]. Figure 4.3a shows a schematic of an experiment performed by Martin et al [40], where a CTAC/Water/Pentanol mixture (17.4/62.6/20 wt%), was flowed through a series of contractions and expansions [40, 50]. An increase in the lamellar spacing, measured from the position of a peak was observed. This was attributed to water swelling of the

lamellae, which correlates well with rheology and optical microscopy data. The flow field applied in this device is similar to that of a tubular batch reactor, exemplifying how the combination of microfluidics with small angle scattering can lead to direct insight of ubiquitous industrial processes, and a mechanistic understanding of macroscopic properties such as viscosity which are essential to product performance. Figure 4.3b shows a device used to study the alignment of a liquid crystal (liquid crystal 8CB) under shear flow. As the fluid enters a constriction the degree of alignment along the direction of flow increases [49], showing similar behaviour to the CTAC system despite the different molecular architecture.

4.1.4 Rapid spatio temporal mapping of kinetics

The most popular application of combining microfluidics with small angle scattering has been to measure kinetic processes in proteins and other biomolecules in solution after a sudden change in solvent composition. The time resolution is typically about 1 ms, although measurements down to 50 μ s have been reported. This topic has been the subject of a number of reviews [37,39,51]. Here, we give a brief overview of some of the more significant experiments on protein collapse as well as of a number of improvements and alternative strategies that have not yet been implemented. Kinetic processes in protein solutions can be measured using a variety of techniques, ranging from pressure cells to stopped flow devices (see ref [52] for a review). Two types of microfluidic mixers have been used to study sub millisecond kinetics: flow focusing laminar mixers and turbulent mixers. The former has received far more use, its main advantage being the low sample volume required.

Flow focusing geometries, first developed by Brody [53] et al and further studied by Knight et al [54] showed the possibility of sub millisecond mixing. Reducing the distance two fluids have to diffuse through to less than a micron, mixing within less than a millisecond can be achieved (assuming diffusion coefficient $\sim 10^{-9}$ m²/s) [54]. A schematic of the flow focusing geometry is shown in figure 4.4a (ii), the fluid from the central channel (shown in red) is hydrodynamically focused into a $\simeq 1$ μ m wide stream. The fluid coming through the two side channels (shown in grey) quickly diffuses across, generating the mixed fluid (green). This setup was used by Pollack and co-workers to induce the collapse of cytochrome c after a pH jump [55]. A 200 by 150 μ m X-ray beam (which thus over illuminates the central stream) was used to map the central stream as a function of distance along the channel, which knowing the velocity of the fluids, can be transformed into time after mixing. Since, the collapse and unfolding of a number

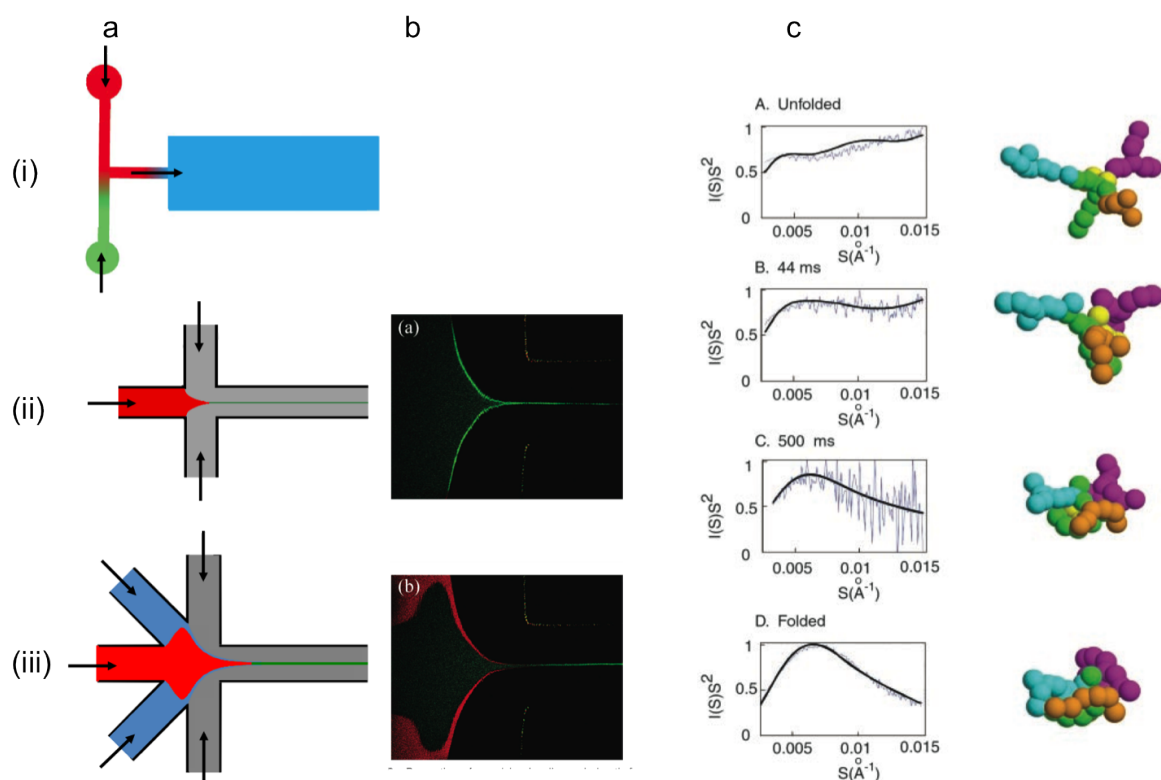


Figure 4.4: a) Schematics of (i): a turbulent mixer (ii) a flow focusing laminar mixer without side streams (iii) a flow focusing laminar mixer with side streams (see text for details) b) Fluorescence microscopy images of setups a(ii)-(iii). Green indicates mixing of the central stream with the side streams. Red indicates mixing of the central stream with the diagonal streams. c) Kratky plots of scattering intensities obtained at different positions along the channel corresponding to different times after mixing and images structure corresponding to the fit to the data (black lines). Image adapted from references [12, 51, 56]

of biomacromolecules has been studied [37, 51, 66]. Figure 4.4c shows the results obtained by Pollack and co-workers on the kinetics of collapse of RNA. The scattering profiles correspond to different points along the channel. The limit on the earliest time measurable in these devices does not usually come from the mixing time (i.e. the time taken for the side streams to diffuse into the central stream) or the beam size but from the dead time, that is, the time the two streams are in contact without being focused. This is shown in figure 4.4b (ii), the mixing between the central and side streams, indicated by the green colour, can be seen to occur as soon as the fluids come together, well before the central stream is focused. This results in effectively a dead time, typically of the order of 1ms.

An approach to overcome this was developed by Park et al. [56], who introduced diagonal streams (containing the same solvent as the central stream but no solute) to the previous setup to separate the central and side streams. With this setup, focusing is achieved before fluids come in contact: a comparison of mixing with and without the diagonal side streams is shown in figure 4.4a (ii)-(iii). The diagonal side streams in the bottom image prevent mixing prior to focusing. It can be seen (Fig 4.4b) that the green colour, indicating mixing of the side and central streams only appears in the focussing region and not before. Mixing times down to 200 μs with no dead time and a central stream size of 220 nm were reported. A shortcoming of these mixers is that the side stream component must be added in excess, it is not possible to accurately control the ratio of side streams to central stream. In fact, since the solute in the central stream will diffuse into the side streams as it travels along the channel, the central solution becomes more dilute. The diffusion coefficient of macromolecules such as cytochrome or RNA is an order of magnitude lower than that of a buffer, hence the dilution is limited. Pollack and coworkers report that their cytochrome solution is diluted by a factor of 2 at the end of the channel compared to the initial solution.

Other devices, for example serpentine mixers, have been developed for use with other techniques such as synchrotron radiation circular dichroism spectroscopy (SRDS) [57] or Fluorescence Resonance Energy Transfer (FRET) [58].

A second approach to generate fast mixing is to work at high Reynolds numbers (> 2300) where flow becomes turbulent and mixing is enhanced by the formation of eddies. Even in turbulent flow, the last step of mixing must happen by diffusion, with distances being reduced to $\sim 0.1 \mu\text{m}$, the mixing time goes down to $\sim 10 \mu\text{s}$ [39] for $D \simeq 10^{-9} \text{ m}^2/\text{s}$, which is typical of low molecular weight solvents. A schematic of a turbulent mixer is shown in figure 4.4a (i). The fluids pass through a nozzle, where they reach speeds of the order of several m/s. Mixing can be achieved within $\sim 100 \mu\text{m}$ down the observation channel. These mixers have been used in combination with SAXS to study the collapse of proteins [4, 60]. The main disadvantage of these mixers is the large flow rates required ($\sim 5 \text{ ml/min}$). In principle, due to the relatively large volumes exposed to the beam, they could be coupled with a high flux SANS beam line, however, unfeasibly large sample volumes would be needed if acquisition times remain high. As mentioned in the introduction, it is possible to achieve elastic turbulence at low Reynolds numbers, this may be used to promote mixing of complex fluids at lower flow rates than the mixers outlined.

4.2 Introduction to microfluidic SANS

As outlined in the previous section, microfluidic-SAXS has demonstrated great potential for the study of complex fluids. While synchrotron SAXS sources offer high brilliance ($\sim 10^{12-14}$ photons/s), contrast in multicomponent soft and biological systems, generally comprising low atomic number species, is fixed and somewhat limited. Small Angle Neutron Scattering (SANS) [61,70] contrast, on the other hand, arises from nuclear interaction which varies markedly for light elements and between isotopes, and significantly hydrogen and deuterium. Selective deuteration has enabled major advances in soft matter science, from the elucidation of polymer conformation in melts [71], the reptation mechanism [72] or exchange kinetics in micelles [73] to name a few. Neutrons also offer large material penetration [70,74] (approximately 90% for 1cm of aluminium). However, SANS suffers from considerably lower fluxes compared to SAXS and limited focussing and collimation, generally requiring longer acquisition times and larger beam sizes, typically 1-1000 s and 10 mm in diameter, respectively. While rheo-SANS is now a well-established technique [75], flow is generally limited to Couette or cone/plate-plate geometries, stopped flow for rapid mixing and kinetics [76], or custom made flow cells including Poiseuille [77], cross-flow [78] and screw-extruder geometries [79], with characteristic dimensions in the mm to cm range, which can now be relaxed in microfluids [80]. However, despite its great potential, the coupling of microfluidics and SANS appears challenging, due to the small scattering volumes associated with microchannel dimensions ($\approx 100 \mu\text{m}$) and unfavourable signal-background ratio by common microfluidic matrices (e.g. polydimethyl siloxane elastomers or other hydrogenated polymers, often thermoplastics). In this chapter, we tackle this challenge, benefitting from the sustained improvement of neutron sources and advances in rapid-prototyping of microdevices, and investigate the molecular reorganisation of model concentrated surfactant mixtures under flow.

4.3 Methods

Materials

Thick borosilicate microscope slides (Fisherbrand 1238-3118) and thin ($\approx 140 \mu\text{m}$) cover slides (6631 - 0146 thickness no. 1), ethanol (Absolute ACS Reagent Ph. Eur.) and acetone (ACS Reagent Ph. Eur.) were purchased from VWR. Quartz slides were purchased from H. Baumbach

& Co Ltd. Norland NOA-81 was purchased from Edmund Optics. Nanoports (N333) were purchased from Upchurch Scientific.

CTAC ($\geq 98.0\%$ (NT)), SDS (ACS reagent, $\geq 99.0\%$), Pentanol (puriss. p.a., ACS reagent, $\geq 99.0\%$ (GC)), Octanol (ACS reagent, $\geq 99\%$) and NaCl (puriss. p.a., $\geq 99.5\%$ (AT)) were purchased from Sigma Aldrich and used without further purification.

Sample preparation

For both systems, the surfactant was added to the D₂O or d-Brine and shaken until it dissolved. Mild heating ($\approx 50^\circ\text{C}$) was used to accelerate dissolution. The oil was added to the solution and shaken vigorously. Samples were prepared three days in advance of the experiment. Three different samples were prepared for each system and measured in 1mm Hellma cells with the full beam at both configurations. The peak position remain unchanged for all three samples. Additional samples, varying the composition for the two systems were prepared by adding the oil or aqueous phase to the previously prepared systems.

Microfabrication

Our approach follows a previously published method ⁽¹⁾ using NOA-81 as a negative photore-sist. 1mm glass slides have a neutron transmission of ≈ 0.37 , and therefore are unsuitable for microfluidic-SANS experiments. We use 0.14 mm cover slides, which have a transmission of ≈ 0.87 . We find that these are too brittle and break when drilling through them. We therefore reinforce the top slide of the device by gluing a 1mm thick slide with pre-drilled holes in the inlet and outlet positions as well as in the SANS observation window to it. NOA-81 is then sandwiched between the reinforced window and a thin cover slide using 0.54 mm silicon wafers as spacers. A negative mask is placed on top and the system is exposed to UV-A light at a power of 140 mW/cm^2 for 5 minutes, resulting in a total dose of 42 J/cm^2 . The device is placed on a hot plate at 65°C and the channels are flushed with 20 mL of ethanol. A small amount ($\leq 1\text{ml}$) of acetone is then flushed through the chip immediately followed by about 5-10ml of ethanol. This last step is repeated until we observe no more thiolene exiting the device. Excessive use of acetone leads to swelling of the channel walls and the definition worsens. Nanoports were sealed to the inlet and outlet positions using fast curing Araldite (Huntsman). We also carried out the above procedure with 0.5 mm quartz slides instead of thin borosilicate slides, no further modifications are required for this.

Microdevice cost and performance

Excluding the nano ports, tubing and connectors, which are reusable, the above devices can

be fabricated in about one hour at a cost of $\sim \pounds 22$ for quartz windows, while borosilicate chips can be manufactured at a cost of approximately $\pounds 2$ per device. The device performance is very similar, the only significant difference is the neutron transmission: 98% for quartz devices and 76% for borosilicate ones. The scattering from the cell is extremely low in both cases. Both Quartz and borosilicate give approximately flat scattering profiles in for $0.02 \leq q \leq 0.33 \text{ \AA}^{-1}$. Quartz gives $I \simeq 0.0025 \text{ cm}^{-1}$ while borosilicate gives $I \simeq 0.006 \text{ cm}^{-1}$. These are significantly lower than D_2O ($I \simeq 0.05 \text{ cm}^{-1}$), which is a relatively weak scatterer. For the chips used in this paper (depth = 0.54mm), we can compare the relative magnitudes of the scattering from our cells to those of a D_2O filled channel by multiplying the intensity in cm^{-1} by the relevant thickness. A quartz chip would scatter $\simeq 11$ times less than D_2O , while a borosilicate chip would scatter $\simeq 14$ times less than D_2O . Given that samples in the green and yellow regions of figure 4 in the main papers have scattering intensities greater than $\simeq 2 \text{ cm}^{-1}$ (40 times more than D_2O), the scattering from our cells will be negligible compared to the scattering from the sample. For comparison, a Hellma cell scatters approximately 5 times more than the borosilicate chips and 4 times more than a quartz chip.

SANS setup. The SANS experiments were carried out at the D22 spectrometer of the Institut Laue Langevin, Grenoble, France, with an incident wavelength of $6 \text{ \AA}$ sample-detector distances (SDD) of 2m and 5.6m, collimation 2.8 and 5.6m, yielding a wavenumber range of 0.025-0.33 and 0.01-0.13 $\text{\AA}^{-1}$ respectively. Circular cadmium diaphragms restricted the beam diameter to 500 or 1000 μm . The results were normalised and calibrated according to standard procedures (GRASP v6.89). The microdevices were mounted on an upright motorized pedestal with XYZ motion and Braintree BS-8000 and Harvard PHD2000 syringe pumps were controlled via LabVIEW.

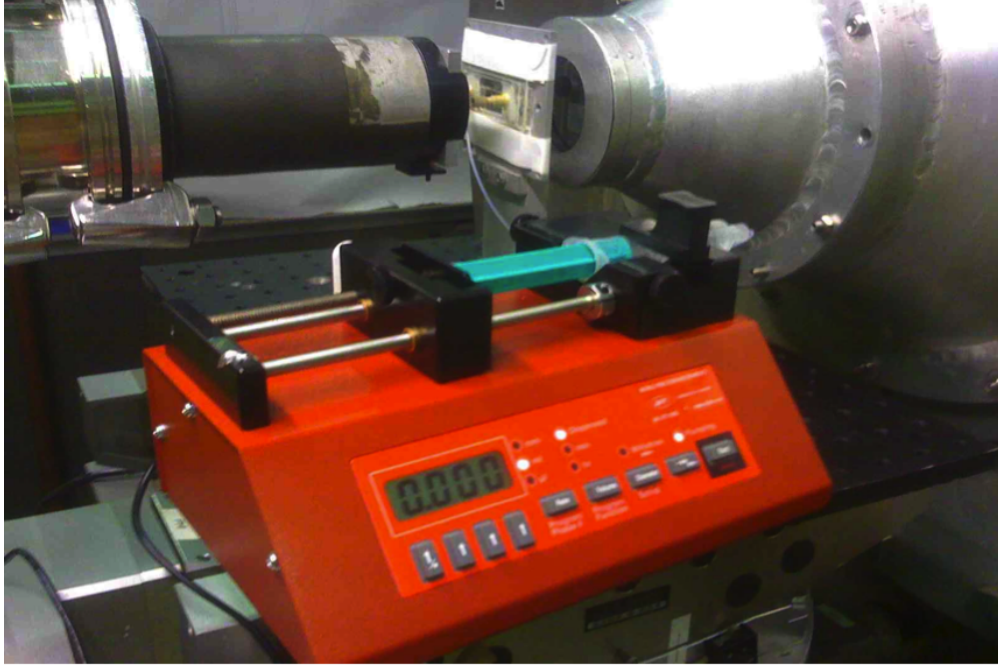


Figure 4.5: Microfluidic-SANS setup

The table below shows the different q -ranges, and fluxes for the different sample to detector distances (SDD). The flux is reduced by a factor of approximately 275 when reducing the beam diameter to 0.5mm from the full beam.

Table 4.1: Fluxes for different configurations and beam diameters

SDD	q -range $\text{\AA}^{-1}$	/	Flux - full beam	Flux - 1mm	Flux - 0.5 mm
2.8m	0.03-0.36		$2 \cdot 10^7$	$3 \cdot 10^5$	$7 \cdot 10^4$
5.6m	0.01-0.13		$7 \cdot 10^6$		$2.5 \cdot 10^4$

Neutron mapping of microdevices. The experimental setup is illustrated in figure 4.6a and an optical micrograph of a 6-constriction microdevice is shown in (c), with depth $d = 540 \mu\text{m}$, width of wide channel $W = 2000 \mu\text{m}$, and constriction widths $w \simeq 60 \mu\text{m}$. Microchannel mapping is achieved in two stages: a coarse grid map is first achieved by a red laser alignment along the main features, followed by neutron transmission scans of the empty chips along the x and y directions. Representative vertical (y) scans, across wide and narrow channels, are shown in 4.6d; an x -axis scan along the microchannel centreline is shown in 4.6b. The hydrogenous thiol-

ene matrix has a $6\text{\AA}$ neutron transmission $\simeq 74\%$, which is sufficient to locate microchannels with 5 s transmission measurements. The width of the constriction A-B in 4.6c was estimated to be $60\text{ }\mu\text{m}$ from a neutron transmission reading, in reasonable agreement with optical microscopy images. For subsequent data reduction and calibration, we use dimensions obtained directly from neutron transmissions.

Surfactant mixtures. We select two concentrated surfactant mixtures to evaluate the feasibility and potential of microfluidic-SANS. The first is a CTAC/pentanol/ D_2O mixture at ratios 17.4/62.6/20 wt%, which forms an L_α phase with excess water and interlamellar distance $\simeq 60\text{ }\text{\AA}$. The thermodynamics and flow response of these systems has been previously investigated by H. P. Martin [40,50], who is thanked for help in sample preparation. Different compositions were studied under quiescent conditions, the results are reported in section 4.6.1. Scattering profiles were acquired using a $500\text{ }\mu\text{m}$ diameter beam for 3 min for the positions in the wider channel and for 6 min in the $100\text{ }\mu\text{m}$ constriction. The beam footprint thus over illuminates the latter and the acquired signal comprises also device background scattering, yielding good statistics ($\sim 10^5$ counts) in the full q range. A 2 s acquisition suffices to resolve the peak position in the wider channel. The second system investigated is an SDS/octanol/d-brine multi-lamellar vesicle (MLV) forming mixture, which has been studied extensively by Roux and co-workers [15,16] by Small Angle Light Scattering and microscopy. As the interlamellar peak occurs at lower q , we use the 5.6m SDD to study this system. Scattering profiles were acquired using a 1mm diameter beam for 5 minutes (corresponding to $\sim 10^5$ counts) for the positions in the main channel and for 10 minutes in the constriction. A reading of 10 s in the main channel yields reasonable statistics for the full q range and permits azimuthal averaging (see the annex at the end of this chapter). Samples were loaded into the chip at 0.5 mL/hr and allowed to rest for 15 minutes. We refer to this as the ‘rest’ or initial case throughout the paper, although, the systems are not fully relaxed at this condition.

4.4 Results

A range of flow geometries including periodic contraction-expansion flows, cross-slots and channel height gradients are fabricated. 2-dimensional SANS acquisitions down to 1 s (see section 4.6.2) are able to resolve their flow response at the molecular level. The experimental setup is illustrated in figure 4.6a and an optical micrograph of a 6-constriction microdevice is shown in

(c). The SANS experiment starts by generating a spatial microchannel map by fine xy neutron transmission scans, illustrated in figure 4.6(b,d,e), followed by the spatio-temporal mapping at selected positions.

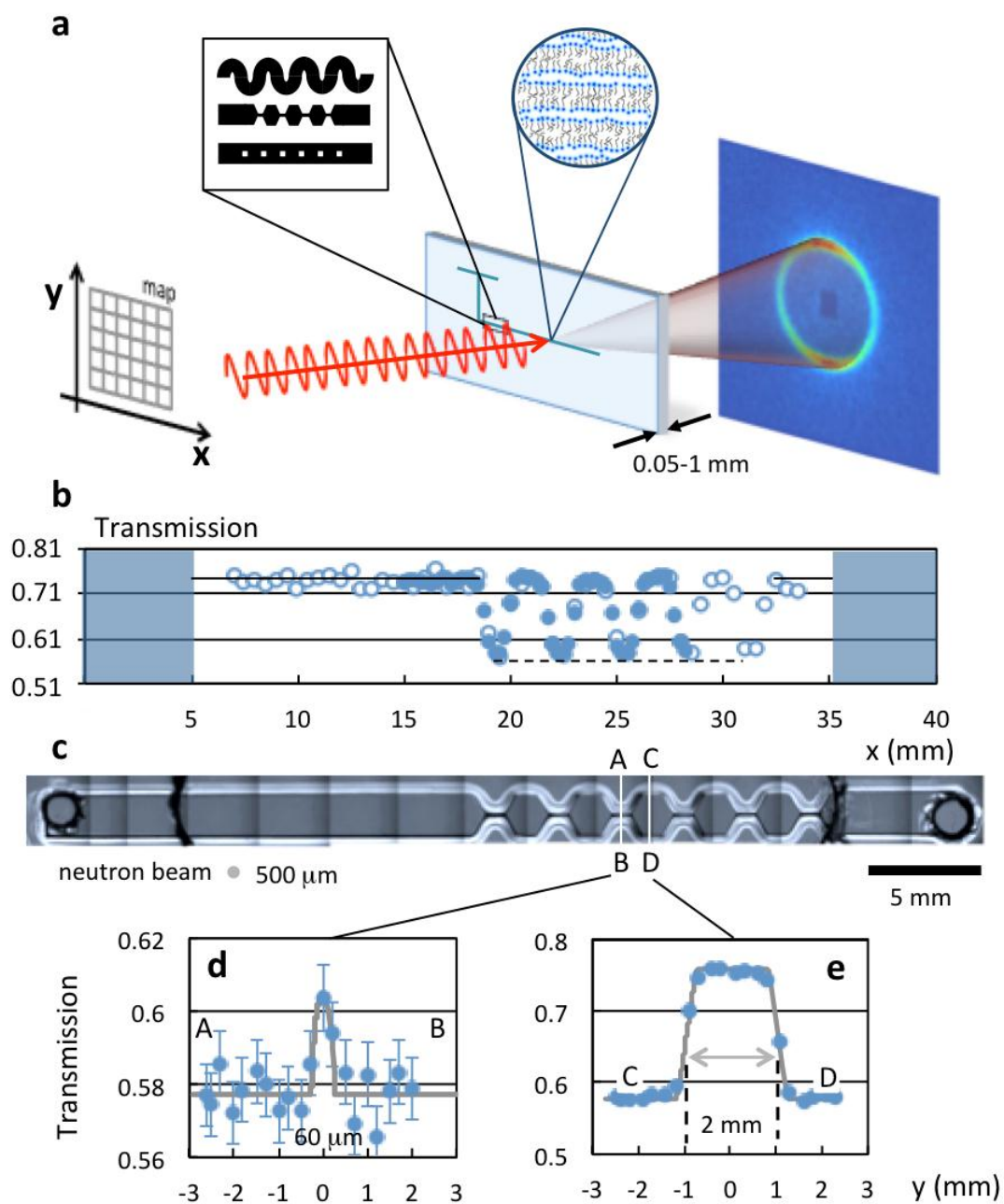


Figure 4.6: a) Schematic of a microfluidic-SANS experiment, depicting patterned microchannel geometries and an illustration of a lamellar system, microdevice mounted on a motorised xyz stage for spatio-temporal mapping, and 2D scattering pattern. b) Transmission mapping of the microfluidic device with a 500 μm diameter neutron beam along the microchannel length, with ($\circ$) 10 s and ($\bullet$) 60 s acquisition. c) Optical micrograph of the device. d) Lateral scans (y axis) along a wide (C-D) channel and (A-B) flow constriction. Grey line is the computed transmission from the beam and microchannel overlap.

Figure 4.7 examines the CTAC/pentanol/ D_2O lamellar system flowing through a contraction-

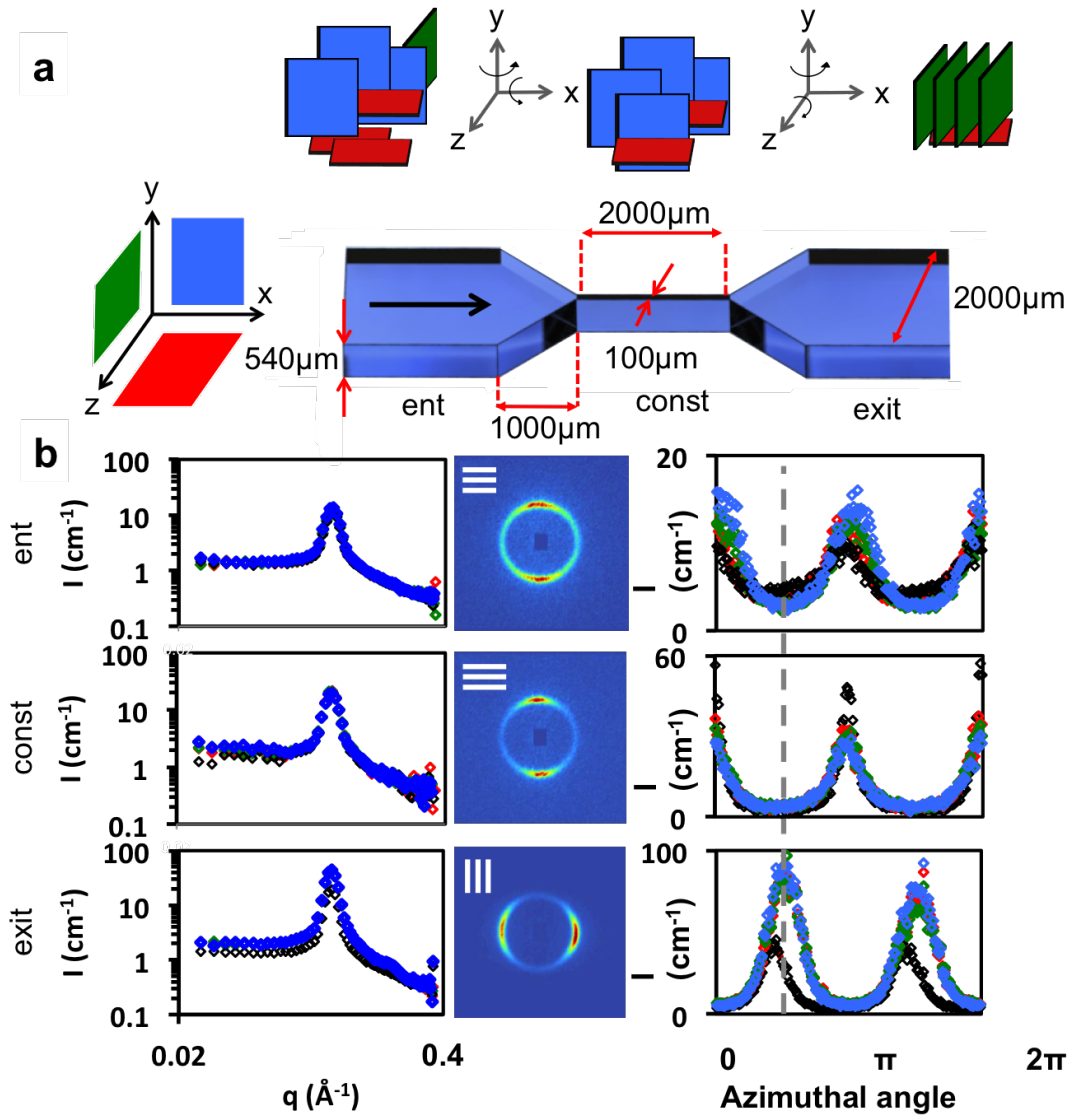


Figure 4.7: CTAC/pentanol/D₂O under microflow. a) Schematic of the chip. Dimensions are width = 2mm (main channel) and 100μm (constriction), depth = 540μm. Green, blue and red sheets represent lamellae orientations in the y-z, y-x and x-z planes as indicated. b) Radially (left) and azimuthally (right) averaged profiles for positions Ent, Const and Exit, indicated on the constriction schematic. Black symbols: rest, Red symbols: 2ml/hr, Green symbols: 5ml/hr, Blue symbols 10ml/hr. The 2D scattering profiles are shown in the middle column.

expansion geometry with flow rates between 0 and 10 mL/hr, corresponding average velocities of up to 50 mm s⁻¹. The schematic of the first constriction and selected reference points entry constriction and exit are indicated, along with corresponding 2D scattering profiles, radial and azimuthal averages. As reported earlier [40], we find that the fluid orients parallel to the flow

direction (blue lamellae on the schematic), within the input channel and the constriction, and then perpendicularly (green lamellae in the schematic) upon exiting the constriction as it decelerates and experiences orthogonal extension. This applies to all constrictions in series and at all flow rates examined including the ‘at rest’ condition, corresponding to a fluid introduced at low flow rate (0.5 mL/hr) and allowed to relax for 15 min. The scattering profiles are well modelled by a Lorentzian function $I(q) = A/(1 + (q - q_0)/S)^2 + B$, where A is the height of the peak, q_0 the peak position, S the full width half maximum (FWHM) and B the incoherent background, in the q -range 0.07-0.2 Å⁻¹.

The integrated scattering intensity and peak sharpness increase as the system flows along the channel. Specifically, the intensity increases by approximately 50% upon entering the constriction, and by an additional 60% upon exiting. As illustrated in Fig. 4.7, we interpret these results as arising from a lamellar sheet rotation from the xz to yz planes, thereby increasing the coherent scattering intensity, as well as from xy to the yz plane, thus flipping the angle of the structural peak. The radially averaged profiles at the entry and constriction remain unchanged with increasing flow rate. At the exit, however, the scattering intensity nearly doubles compared to the ‘rest’ reference and an additional peak/shoulder appears at $q \simeq 2q^*$, where q^* is the wavevector of the main peak, which is not present at other positions and indicates strong structural alignment.

At the constriction entrance, scattering anisotropy increases with flow rate as expected for lamellae aligning under flow, exhibiting higher alignment within the constriction. Unexpectedly, however, the azimuthal average corresponding to the system at ‘rest’ within the constriction indicates a larger alignment than that under flow which we interpret as related to the longer residence time associated with the ‘rest’ condition. At the exit the systems under flow show an even greater degree of anisotropy, but now *perpendicular* to the flow direction as the lamellae sheets decelerate and rotate upon exiting the constriction. The apparent tilt in the ‘rest’ pattern is due to inhomogeneity in the flow of this viscous systems.

Next we average the 2D scattering profile within the constriction at 10 mL/hr along 12 sectors to obtain $I(q)$ profiles as a function of angle and thus orientation under flow. The Lorentzian fit parameters are plotted as a function azimuthal angle in 4.8. Trivially, the sector intensity A follows the azimuthal profile in (a); we find that the peak position q_0 remains unchanged, as does the scattering background, within experimental uncertainty. However, along the flow direction, the peak height A increases and its width decreases, quantifying the lamellar alignment upon

lateral compression and acceleration within the constriction. At the exit position, at 10 ml/hr, approximately 50% of the scattering intensity lies between $\pm 10^\circ$ of the flow direction.

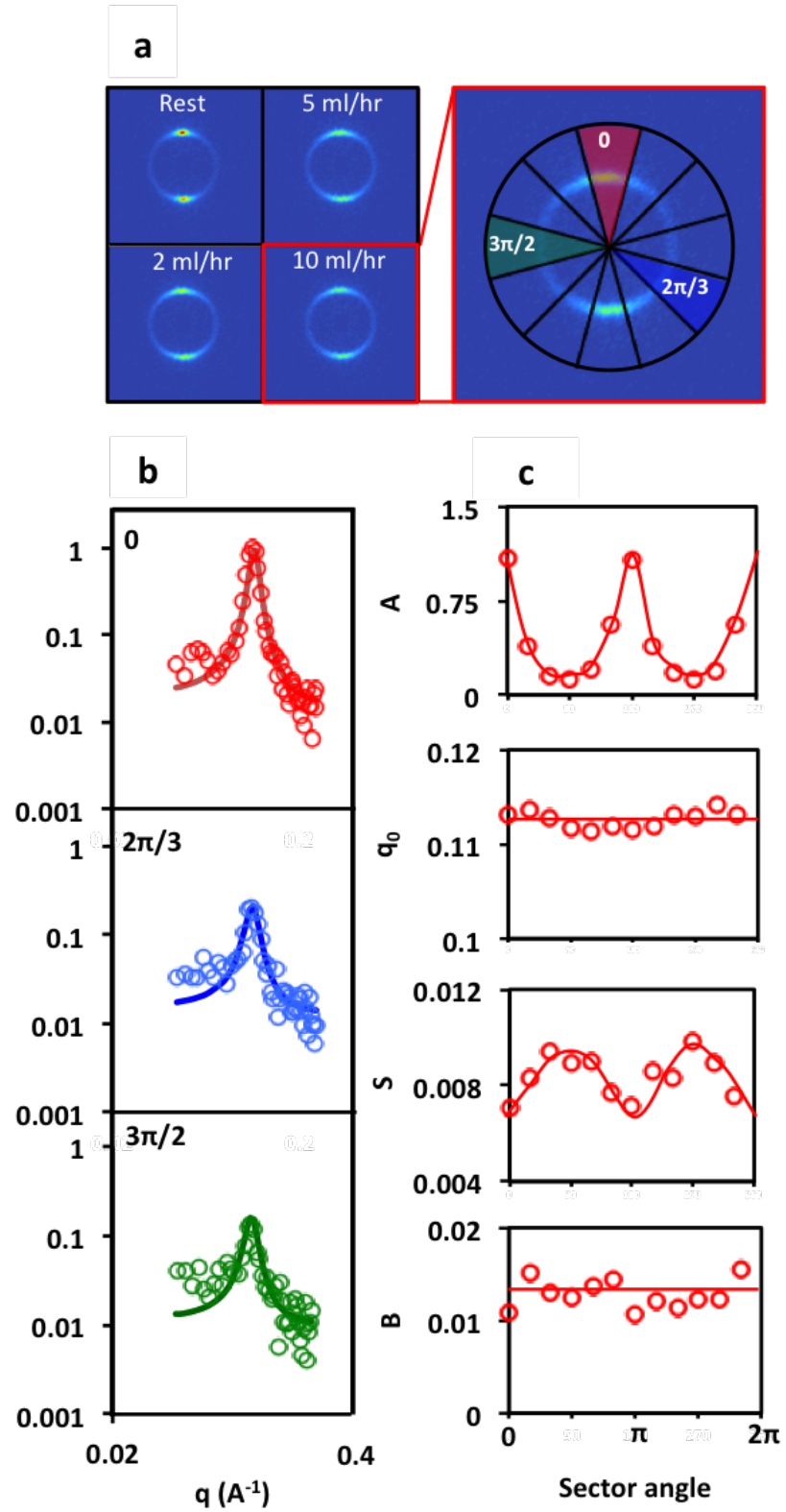


Figure 4.8: a) 2D scattering profiles at the constriction as a function of flow rate, and enlarged profile for 10 mL/hr, including azimuthal sectors, analysed in (b) and (c). b) Representative $I(q)$ profiles for sectors 0, $2\pi/3$, and $3\pi/2$; lines are fits to a Lorentzian profile $I(q) = A/(1 + (q - q_0)/S)^2 + B$. c) Fitting parameters A , B , q_0 , S as a function of azimuthal angle for 10 mL/hr.

Our FPP approach is also capable of patterning orthogonally to the microchannel direction [8, 24] and we next consider a wedge-shaped, or height gradient, microchannel, confined between two quartz windows, depicted in figure 4.9 (i). Sample injection occurred from the taller towards the thinner channel cross-section at constant flow rate 0.5 mL/hr, thus at increasing velocity. SANS measurements were carried out at 10mL/hr. Figure 4.9 (ii) shows the transmissions, measured at rest, of the empty and sample-filled channel. The former is found to be constant, at $T=0.98$, in good agreement with the estimation based on a single quartz plate with a full beam $T=0.99^2=0.98$, yielding an outstanding neutron cell. The sample transmission in the microchannel decreases exponentially with height h [mm], as expected, and following $T = 1.03e^{-0.463h}$; the result is validated for $h \rightarrow 0$ and from independent measurements on thickness standards ($T \approx 0.68$ within 1 mm Hellma cell). Figure 4.9 (iii) plots the peak angle in the azimuthal average corresponding to the main orientation of the lamellae contributing to coherent scattering (i.e. parallel to the neutron beam). A change from orthogonal alignment, with respect to the flow direction at the channel entrance, towards parallel at the thinner section is observed. The scattering intensity, after appropriate thickness normalisation, is found to decrease towards the thinner section of the microchannel wedge, along the velocity and extension gradient. The intensity ratio, referenced with respect to the thick cross-section, is plotted in figure 4.9 (iv). This decrease accompanies the flow alignment of the lamellae sheets along the velocity direction (and thus perpendicularly to the neutron beam, indicated by green to red lamellae in the schematic), in agreement with the flow alignment parallel to the narrower channel walls discussed above.

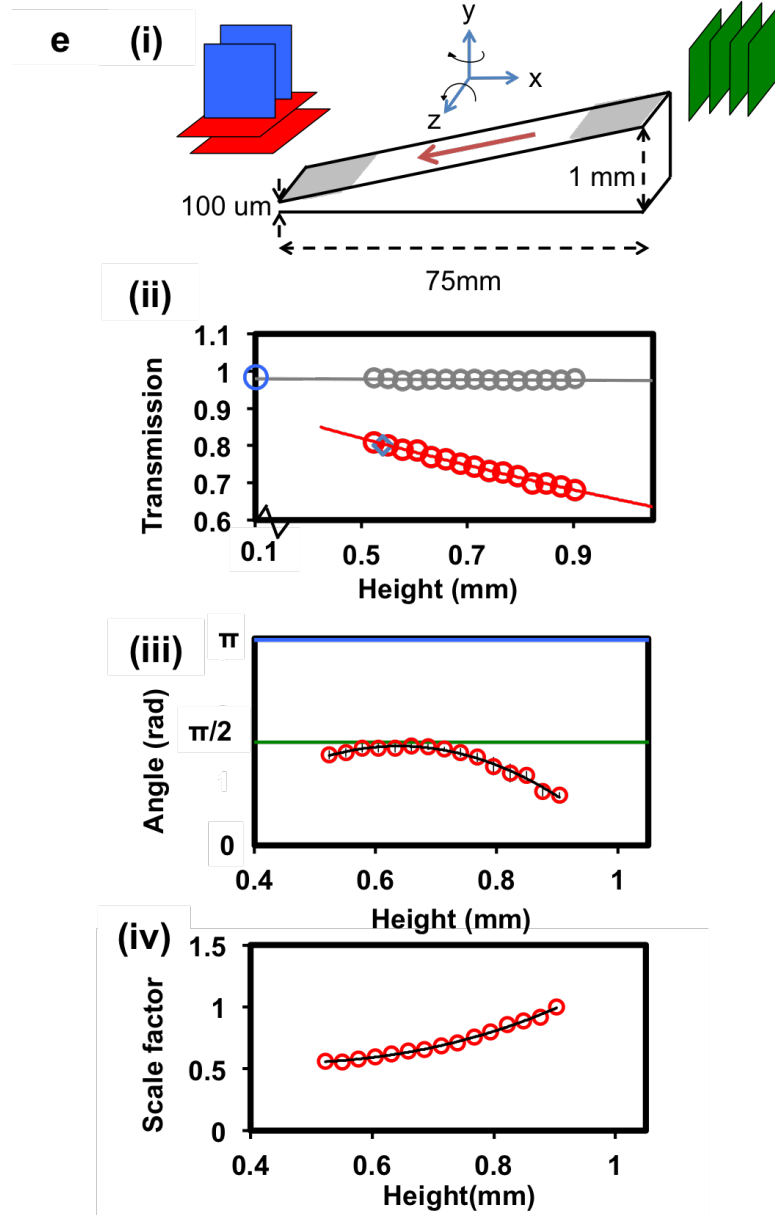


Figure 4.9: (i) schematic of a wedge device; (ii) transmission for the empty cell (grey $\circ$) and with sample (red $\circ$); lines are guides the eye; (iii) Angle of peak in the azimuthal average, signalling the main orientation of the lamellae perpendicular to the x-z plane. Blue line = π corresponding to lamellae oriented in the y-z plane (as does the x-axis), green line = $\pi/2$ corresponding to lamellae oriented in the y-z plane; (iv) Intensity ratio, referenced to the thickest cross section i.e. $(\sum_i I(q_i)/tT)/(\sum_i I_{thick}(q_i)t_{thick}T_{thick})$ where t is the thickness and T is the transmission and the subscript thick refers to the 0.9mm point. The scale factor is thus normalised to 1 at $t = 0.9\text{mm}$.

We now investigate an SDS/octanol/d-brine mixture, to evaluate whether similar lamellar rotations, as observed in the CTAC system, are present in multilamellar vesicle (MLV) forming systems. [15,16] The characteristic inter-lamellar spacing of MLVs is now $\simeq 150 \text{ \AA}$, scattering is generally isotropic, and we re-configure the spectrometer to a lower q range (and lower neutron flux). We first report on a cross slot geometry, depicted in fig. 4.10, generating an extensional flow around the stagnation point in the centre. A representative 2D scattering profile at flow rate 10mL/hr is shown and radially-averaged scattering and peak intensities as a function of flow rates (0.3-60 mL/hr) are computed. The decrease in scattering intensity with flow quantifies the disruption of lamellar ordering by flow, and the insensitivity of the peak position q^* with flow rate, within experimental uncertainty, indicates unchanged lamellar spacing.

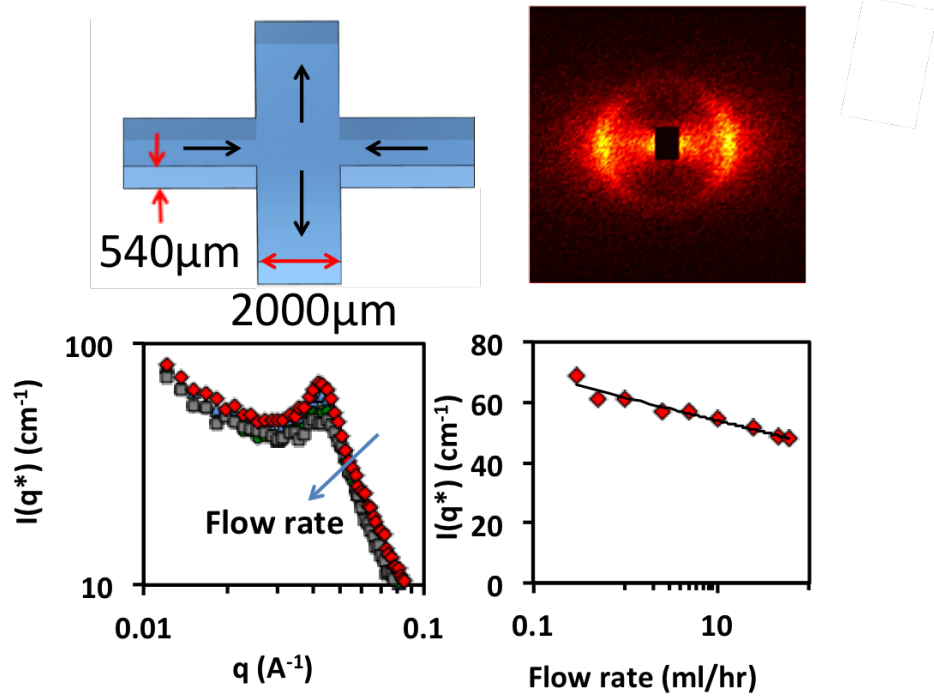


Figure 4.10: SDS/octanol/d-brine system under microflow. Top left: Cross slot device schematic (depth= $540 \mu\text{m}$, width = $2000\mu\text{m}$) Top right: 2D scattering profile for total flow rate of 10 mL/hr; bottom left shows representative radial averages as a function of flow rate, and bottom right plots peak intensity $I(q^*)$ as a function of flow rate.

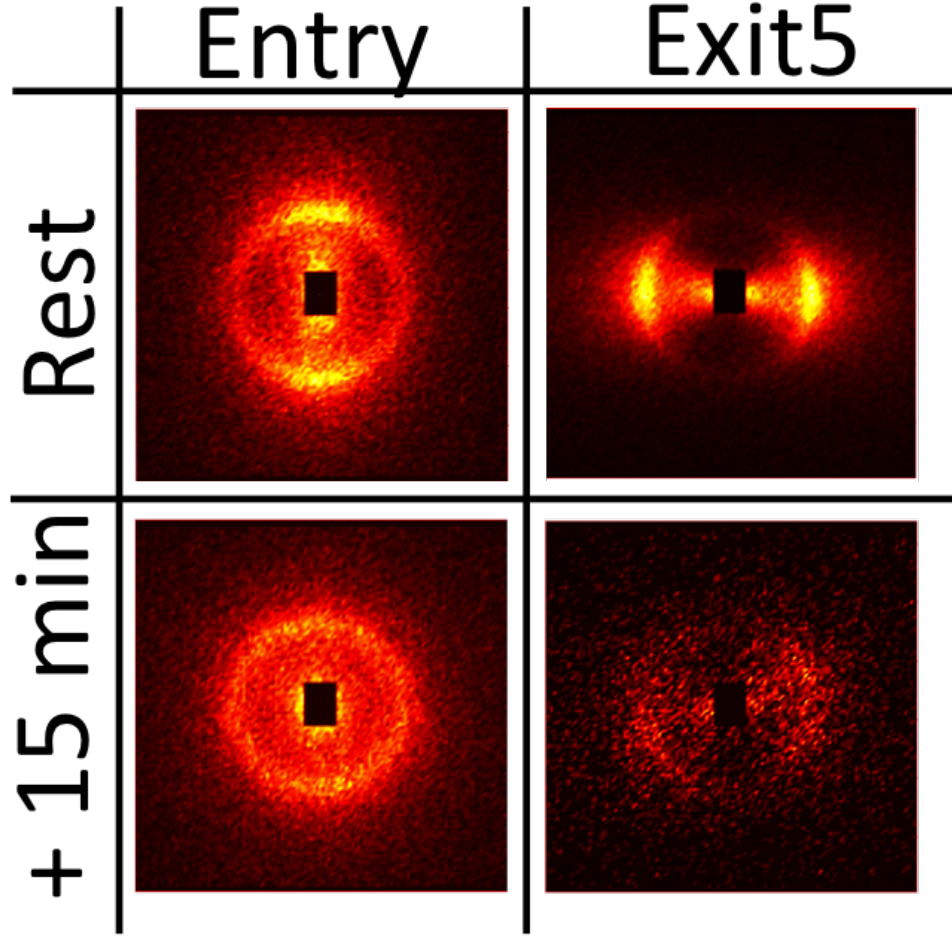


Figure 4.11: 2D scattering profiles at Entry and Exit5 after cessation of flow, following 0.5 mL/hr, for $\Delta t=15$ and 30 min.

Flow response through a series of constrictions is evaluated in figure 4.11, showing 2D scattering patterns (positions marked in the schematic) at flow rates of 1, 5 and 10 mL/hr and average flow velocities indicated. The system is aligned from the outset, following injection into the device. At the entry position, the system is least aligned at the lowest flow rate of 1 mL/hr. By contrast, upon expansion (Exit5), the least alignment is found at 10 mL/hr, indicating a correlation between alignment *residence time* within the device, rather than flow magnitude. An orientational flip at the constriction exit is observed, as found for the CTAC system. The peak positions q^* do not vary with flow rate, like in the cross slot geometry, indicating no change of lamellar spacing in this range of flow type and residence time. The overall intensities at 1mL/hr increase by a factor of 1.5 from the entry position to the constriction and by a further 40% from

the constriction to the fifth expansion. At the entry and constriction the intensities are not significantly affected by flow rate, while at the expansion they decrease by 30% when the flow rate is increased from 1 to 10 mL/hr.

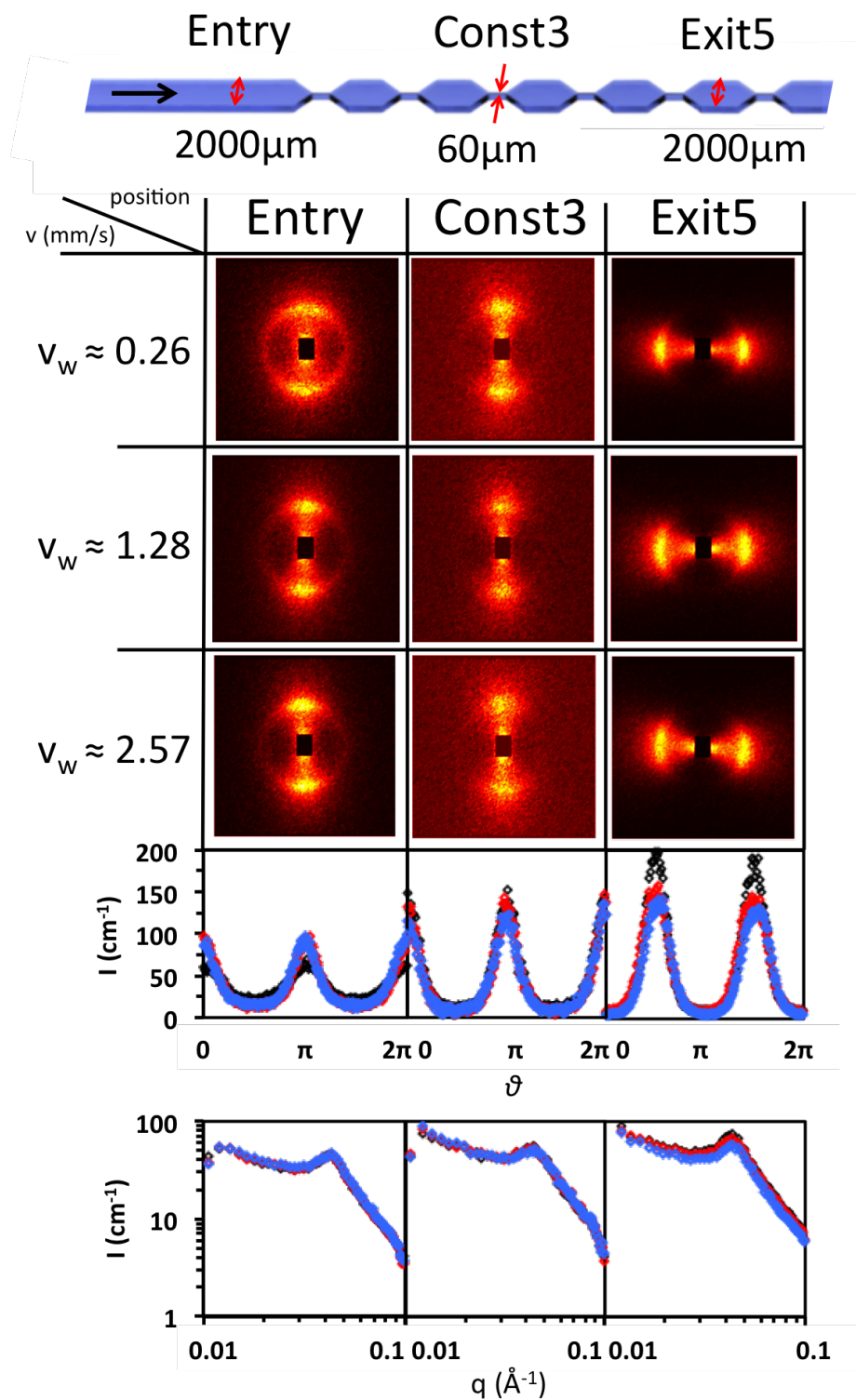


Figure 4.12: SDS/octanol/d-brine system under microflow. Contraction-expansion series schematic and 2D scattering patterns at flow rates 1, 5, 10 mL/hr ; the mean velocities are shown in the left column with corresponding azimuthal and radial averages.

Figure 4.12 considers the structural relaxation of the system over time following cessation of flow after steady state 0.5 mL/hr conditions. Two time points are shown: $\Delta t = 15$ and 30 min, enabling the quantification of the relaxation processes both in terms of lamellar orientation and structure.

We have thus resolved the lamellar rotations and alignment experienced by two distinct, representative lamellar-forming systems under different flow types and magnitudes. For the case of constriction-expansion, we find that both systems align parallel to the flow before and within the constriction and perpendicularly upon exit, which appear to be general phenomena for anisotropic particle suspensions [27, 49]. We also find that significant rotation of lamellae from the plane perpendicular to the neutron beam to the planes parallel to the neutron beam occur both from before to within the constriction and further upon exit. Thus, both types of rotations appear to be universal to systems with significantly different molecular structures. We demonstrate 2D SANS data acquisition times down to 2 s. Longer acquisition times of ≈ 5 min from 100 μm constrictions yield sufficient statistics for quantitative azimuthal sector analysis.

4.5 Discussion

In this work, we demonstrate for the first time the coupling of microfluidics and SANS, scattering from single microchannels $\gtrsim 60\mu\text{m}$ wide. We note that our microdevices are fabricated using a fast and inexpensive rapid prototyping FPP method, which permits both lateral and orthogonal patterning is achieved, as required for precise flow field control. Device fabrication takes less than 1h and does not require clean-room facilities, and is thus readily accessible.

We acknowledge that concentrated surfactant systems form highly scattering, ordered liquid crystalline phases, and that the general suitability of our approach must be further investigated. Based on current SANS instrumentation performance and typical scattering behaviour of model systems, we next establish a ‘capability map’ for microfluidic-SANS. We illustrate in Fig 4.13 the scattering features of representative soft matter systems, namely the relevant wavevector ranges, characteristic scattering intensities (in absolute units cm^{-1}), and typical corresponding neutron flux. We focus on the interplay of experimental parameters from a user perspective, and estimate the required acquisition times for a reference microfluidic channel of 500 μm depth and a 500 μm diameter neutron beam, viz. a volume of $\approx 0.1\ \mu\text{l}$ (acquisition times for 100 $\mu\text{m} \times 100\mu\text{m}$ channels would simply read $\times 25$). We populate the graph with systems ranging from

weakly scattering dilute polymer solution, which also require relatively low wavenumber measurements, to strongly-scattering microemulsion and crystalline systems, generally measured at high wavenumber for which neutron flux (in reactor sources) is highest. We consider systems requiring less than one minute acquisition times, to readily enable fine mapping with sub-mm beam sizes, as well as high-throughput experiments (shown in ‘green’). Other systems, while *compatible* with current SANS capabilities, are limited in the number of acquisitions possible during a SANS experiment, which have a typical duration 24-72hrs. Systems whose required acquisition times are greater than 100 min are considered as *unfeasible* at the moment (indicated ‘red’ in the graph), and higher flux neutron sources will be required to explore those systems using microfluidic-SANS. Salt free semidilute and concentrated NaCMC solutions, studied in the first two chapters, show $I(q^*) \sim 0.01\text{-}0.1\text{cm}^{-1}$, and are thus currently in the red region of the graph. Further increases in flux will make microSANS experiments on NaCMC feasible, which will allow us to better understand the chain dynamics in semidilute and concentrated solutions. For reference, the mounting and mapping of devices in this work was typically achieved within one hour, and measurement times per state point ranged from a few seconds to a few minutes. The time taken to acquire all data presented in this paper, including device mounting, mapping, equilibration times, etc was approximately 24 hrs establishing the feasibility of microfluidic-SANS experiments within a typical beam time allocation.

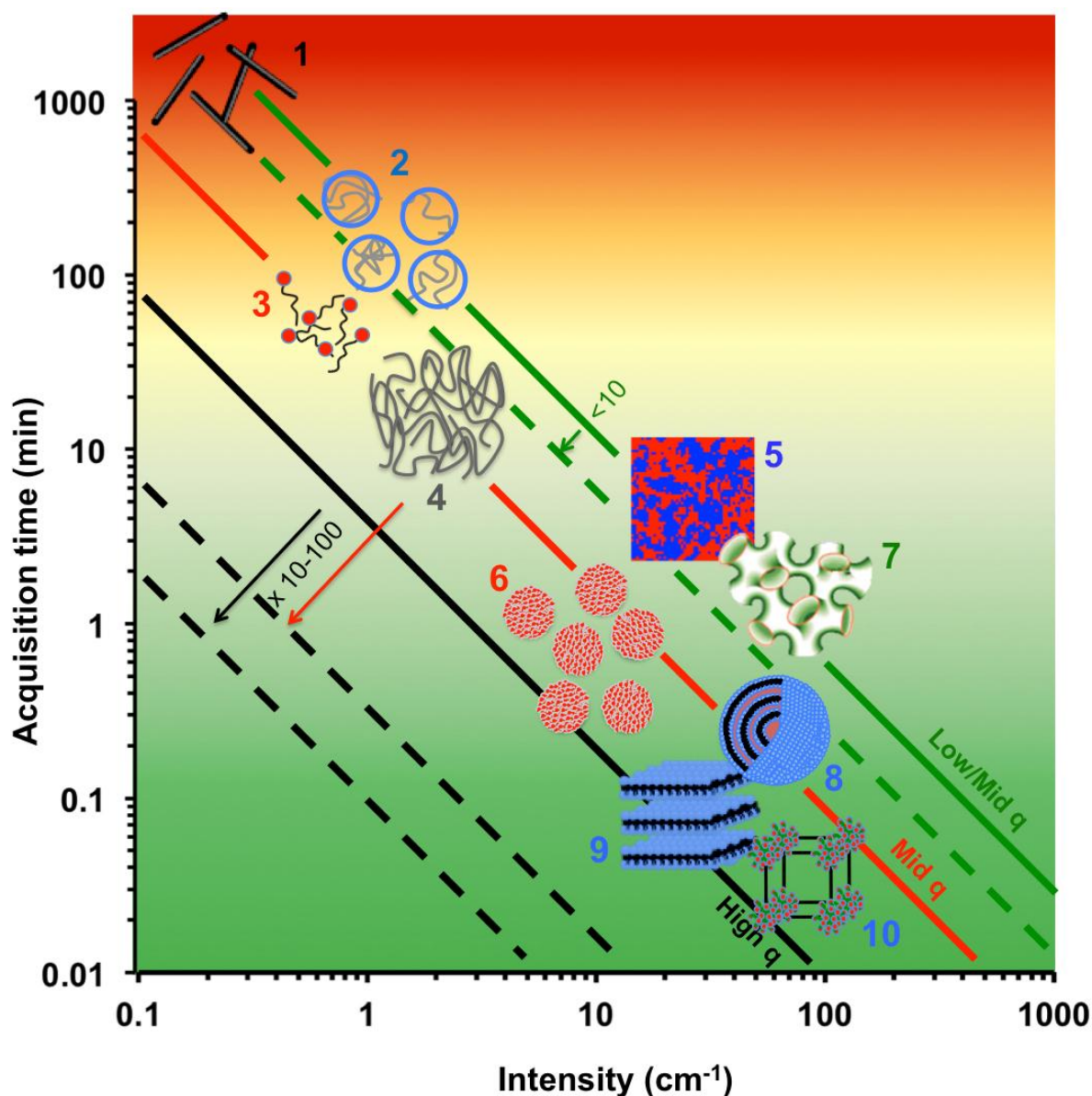


Figure 4.13: Microfluidic-SANS roadmap, illustrating acquisition times for representative soft matter systems, characterised by a typical absolute intensity (cm^{-1}), q -range and configuration, referenced for a volume of $0.1\mu\text{l}$. Solid lines correspond to different SANS configurations and fluxes for different q ranges: high q ($0.05\text{-}0.5\text{\AA}^{-1}$), mid q ($0.01\text{-}0.2\text{\AA}^{-1}$), mid/low q ($0.005\text{-}0.05\text{\AA}^{-1}$); dashed lines indicate the expected neutron flux increases over the next decade. 1: Dilute carbon nanotube dispersion, 2: Dilute polymer solution, 3: Dilute surfactant solution, 4: Semidilute/concentrated polymer solution, 5: Polymer solution or simple liquid mixture near phase boundary, 6: Concentrated surfactant solution, 7: L_3 phase micro emulsion, 8: Multilamellar vesicle emulsion e.g. the SDS system studied in this paper, 9: L_α phase e.g. the CTAC system studied in this paper, 10: Cubic surfactant phase. We colour code the background from readily feasible experiments (green) to currently unfeasible microfluidic-SANS experiments (red).

Continued neutron flux improvements will enlarge the range of systems amenable to microfluidic-SANS studies within feasible timescales, indicated by the dashed lines in Fig. 4. The prospect of third generation sources (including the ESS in Sweden [83]) and high performance time-of-flight SANS spectrometers will contribute to further expand the feasibility of microfluidic-SANS. Predicted gains of a factor of 10-100 in flux and wider wavevector ranges (q_{max}/q_{min}) of 3-4 orders of magnitude will allow the interrogation of increasingly small sample volumes and lower sample contrasts. Smaller beam diameters, down to 10 μm , as well as non circular geometries may thus be employed for finer spatial mapping. Throughout this experiment only one (of 3 possible) scattering planes was investigated; through multilevel patterning and device rocking all flow directions may be accessible. Further to rheological studies of flow-responsive systems, the high-throughput screening of mixtures, in continuous and droplet flows, is expected to become a reality within the near future.

4.6 Annex

4.6.1 Sample formulation

We have studied, using the standard (full beam) configurations, the effect of changing composition on our systems.

Figure 4.14 shows the scattering profiles for the CTAC and SDS systems used in this experiment and the effect of increasing the aqueous or oil content. The exact sample composition, along with the value of the peak position q^* is given in Table 4.2.

	CTAC (wt%)	D2O (wt%)	Pentanol (wt%)	q^* ($\text{\AA}^{-1}$)		SDS (wt%)	Brine (wt%)	Octanol (wt%)	q^* ($\text{\AA}^{-1}$)
CTAC1	17.40	62.60	20.00	0.112	SDS1	6.50	85.60	7.90	0.0425
CTAC2	16.37	64.80	18.82	0.105	SDS2	5.99	86.74	7.28	0.0387
CTAC3	15.46	66.76	17.77	0.099	SDS3	5.55	87.70	6.75	0.0357
CTAC4	13.25	71.52	15.23	0.086	SDS4	4.55	89.92	5.53	0.0268
CTAC5	10.70	77.00	12.30	0.076	SDS5	3.50	92.24	4.26	
CTAC6	17.06	61.37	21.57	0.116	SDS6	6.45	84.93	8.62	0.0320
CTAC7	16.42	59.06	24.53	0.112					
CTAC8	14.50	52.17	33.33	0.059					

Table 4.2: Compositions of the different systems studied.

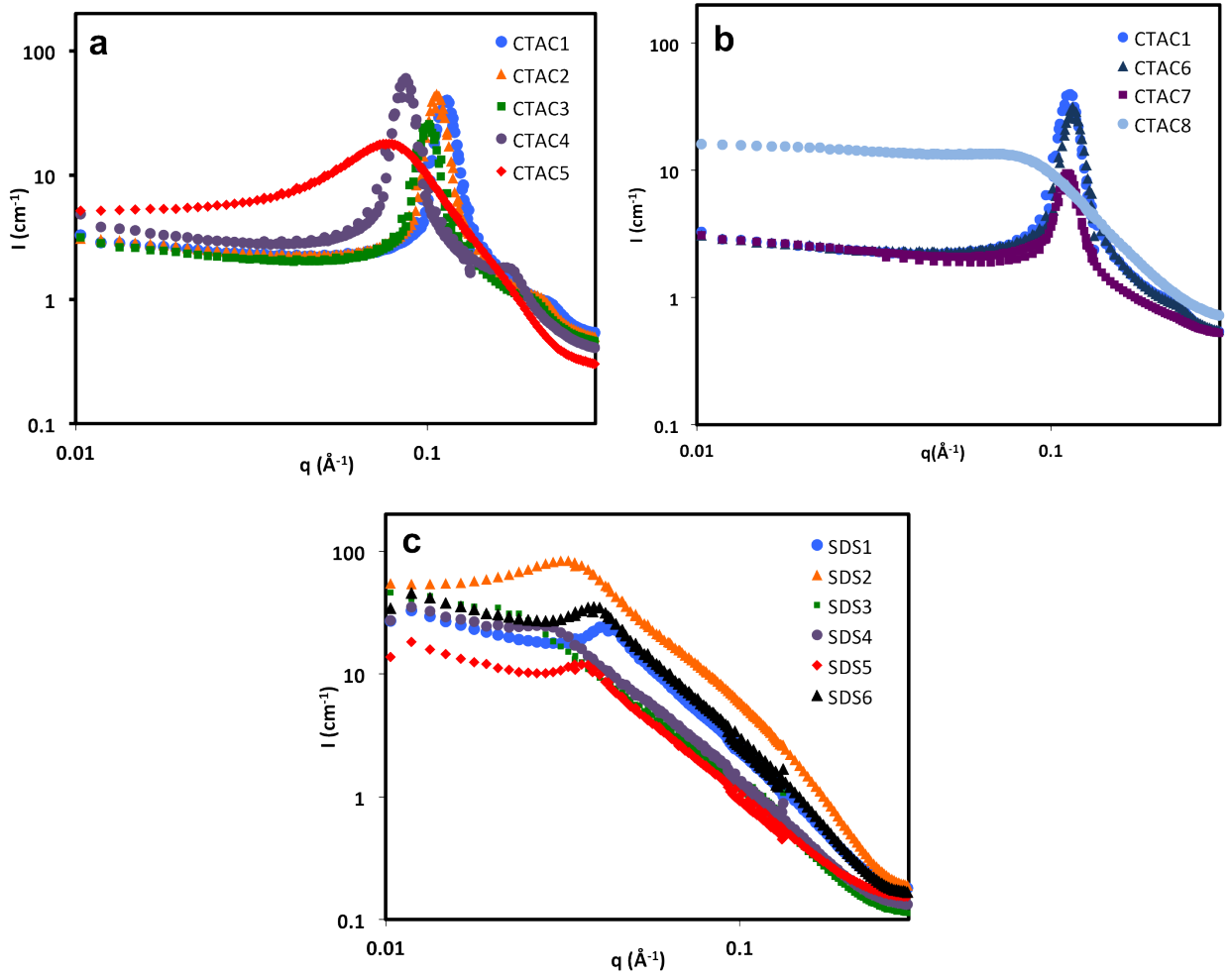


Figure 4.14: Top left: Effect of addition of D₂O to the CTAC system. Top right: effect of adding Pentanol to the CTAC system. Bottom: Effect of adding Octanol or d-Brine to the SDS system.

Figure 4.15 shows the peak position as a function of the aqueous phase for both systems. It can be seen that adding either water or oil increases the lamellar spacing.

4.6.2 Acquisition times

Acquisition times are critical for designing a microfluidic-SANS experiment. Due to the flux reduction resulting from chopping of the beam, acquisition times are increased by two orders of magnitude. The data presented in this paper mostly consist of 3 minute acquisitions for the main channels for the CTAC system and 5 minutes for the SDS one corresponding to approximately 10^5 total counts.

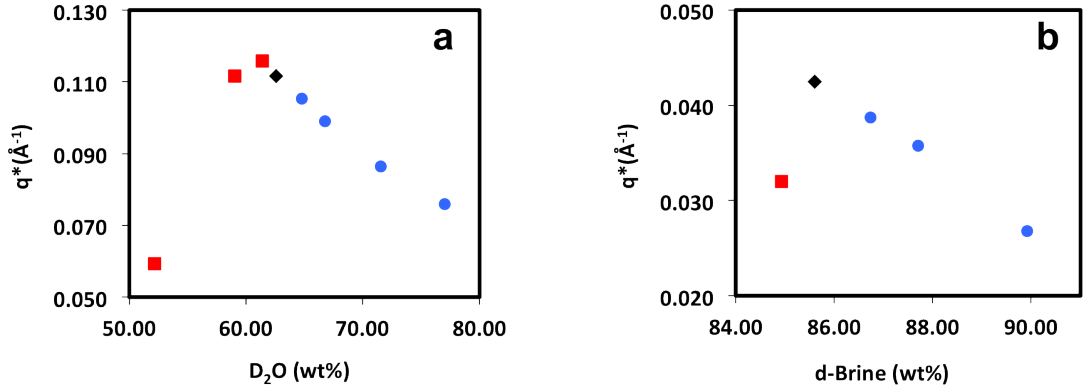


Figure 4.15: Left: Effect of composition on the CTAC system. Black diamond corresponds to sample CTAC1, used throughout the paper. Blue circles correspond to adding D₂O to the system. Red squares to adding pentanol. Right: Effect of composition on the SDS system. Black diamond corresponds to sample SDS, used throughout the paper. Blue circles correspond to adding d-Brine to the system. Red square to adding octanol.

Figure 4.16a shows the scattering profiles for an SDS system, acquired for 5 min (blue) and 10 s (red). These two readings correspond to figure 4.11 position Exit5 for $t = 15$ min (blue) and $t = 30$ min (red). It can be seen that even a short acquisition yields reasonably good statistics, and it is possible to obtain both the peak position and a high q power law with good accuracy: fitting the high q ($q \geq 0.05$) slope with $I = Kq^{-n}$ yields $K = 0.0135 \pm 0.0024$ and $n = 2.73 \pm 0.07$ for the 10s acquisition and $K = 0.0112 \pm 0.0004$ and $n = 2.82 \pm 0.01$ for the 5 min one.

Figure 4.16b shows a CTAC profile for a 3 min acquisition (blue) and for a ≈ 1 s acquisition (red). The peak position and shape can be extracted with accuracy from the second one. Data outside of the peak region, $q \leq 0.07 \text{ \AA}^{-1}$ and $q \geq 0.2 \text{ \AA}^{-1}$ is significantly more noisy, thus, parameters such as the background cannot be obtained accurately. An azimuthal average around the peak region for the same two data sets are shown in figure 4.16d. The statistics are sufficient for the one second acquisition to resolve alignment.

Figure 4.16c shows, on a linear scale, a blow up of the high q part of the 5 min acquisition shown in figure 4.16b. This shows that a small shoulder ($\Delta I \approx 0.3 \text{ cm}^{-1}$) appearing at $q \approx 0.2 \text{ \AA}^{-1}$ can be resolved with a 5 min acquisition.

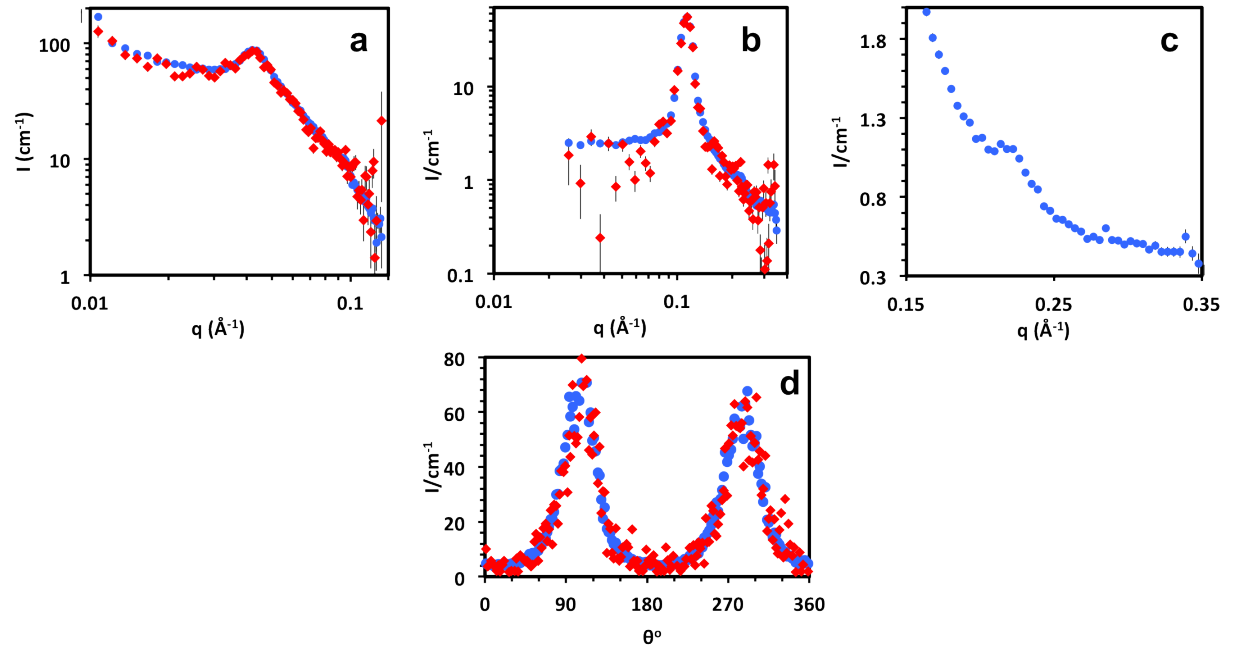


Figure 4.16: Top left: Radial averages for SDS system at position Exit 5 as shown in Fig. 4.11 in the main paper. Red symbols: 10s acquisition, Blue symbols 300s acquisition. Top middle: Radial averages for CTAC system at exit as shown in Fig. 4.7 in the main paper Red symbols: 1s acquisition, Blue symbols 180s acquisition. Top right: zoom into high q region of top middle graph (without red symbols), a small feature at $q^{**} \simeq 2q^* = 0.22 \text{\AA}^{-1}$ can be seen. Bottom: Azimuthal average of the same profiles as top middle graph.

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5 Microfabrication for small angle scattering

5.1 Abstract

We evaluate the compatibility of a number of materials and micro fabrication techniques for microfluidic-SAS experiments. Representative materials are characterised in terms of their transmission and background scattering. Based on this, we are able to identify suitable techniques and materials. A method for microfluidic fabrication based on photolithography of a thiol-ene resin is further evaluated and compared with other methods. This method is limited to dimensions $\geq 60\mu\text{m}$ laterally. If smaller dimensions are needed, PDMS devices where the resolution limit goes down to $1\mu\text{m}$, can be coupled to an observation window fabricated using the photolithographic method.

5.2 Introduction

In this chapter, we evaluate different approaches for manufacturing devices compatible with SANS and SAXS, with emphasis on the former. The chapter is organised as follows: We first briefly discuss the aspects to be considered when designing a microfluidic-SANS/SAXS experiment. We then review the different materials and techniques commonly employed in microfluidic fabrication. We characterise the compatibility of different materials and micro fabrication techniques for producing micro devices with neutrons, in terms of their transmission and background signal. We identify a number of micro fabrication methods from the literature which yield SANS compatible devices. Two rapid prototyping methods of microfabrication, the first of which, was implemented in the previous chapter are proposed. While the focus of this chapter is on SANS, the two types of devices discussed in depth are also compatible with X-rays.

5.2.1 Microfluidic-SAS, general considerations

Two aspects of a microfluidic-SAS experiment differ significantly from a standard experiment. First the increased acquisition times that result from smaller beam sizes and second the cell used: a microfluidic chip instead of a standard cell or capillary. We briefly consider these two aspects in this section.

Acquisition times

The scattered intensity is proportional to the sample volume, the contrast factor, the transmission and the radiation flux impinging upon the sample. The flux is of course dependent on the instrument, but also on the sample to detector distance (STD), which sets the accessible q -range, and determines the collimation. In the case of synchrotron X-rays, where fluxes at sample are typically of the order of 10^{10} - 10^{14} photons/s for a 0.01 mm^2 beam, acquisition times remain relatively short even for low contrast samples at low angles. For neutrons the fluxes are typically three to four orders of magnitude lower (10^8 neutrons/s/cm²) even with large ($\approx 1 \text{ cm}^2$) beams, readings of weakly scattering samples at low angles can take several hours. Light scattering measurements can usually be achieved in a few seconds or minutes and the quality of the data is not limited by the acquisition time but rather by the signal to noise ratio, and the presence of dust (the latter is usually not a problem when using X-rays or neutrons as smaller length scales are probed). Acquisition times can often be the limiting factor when combining scattering from a microfluidic device as the sample volume and the beam size are smaller than in a normal cell. As seen in the previous chapter, the flux of a neutron beam is reduced by over two orders of magnitude when working on a microfocus configuration.

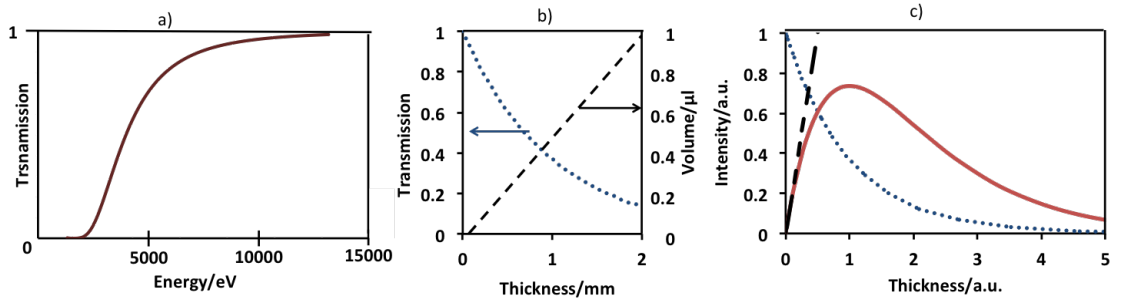


Figure 5.1: a: Transmission of borosilicate slab thickness $140 \mu\text{m}$ as a function of X-ray energy, values obtained from [1] b: Transmission and volume as a function of thickness. c: red : Scattered intensity from a sample, i.e. the product of transmission (blue dashed line) and sample volume (black dashed line).

Transmission and background

In our previous discussion we have not considered absorption of radiation by the cell. Depending on the material and the type of radiation used, the flux at the sample can be reduced significantly. For example, a 1mm layer of PDMS, which is fairly thin by microfluidic fabrication standards would absorb 90% of incoming X rays of energy 12 keV. The absorption of radiation by matter can be described by a Beer-Lambert law

$$I = I(0)e^{-\mu t}$$

where I is the transmitted radiation intensity, $I(0)$ is the incident intensity, μ is an absorption coefficient, specific to each material and radiation energy and t is the thickness of the sample. Figure 5.1 shows how X ray transmission varies as a function of photon energy for 140 μm borosilicate slab (a) and the transmission as a function of thickness (b). The transmission of the sample must also be considered, here there is a compromise, the scattered intensity is proportional to the sample thickness, but inversely proportional to the absorption. To calculate the optimum sample thickness, the product of the two must be considered. This is shown in figure 5.1c. The quality of a cell, comes not only from its transmission, but also its scattering profile. If both the sample and cell make a similar contribution to the total signal, deconvolution can be difficult. This is discussed in more detail in the following sections.

5.3 Microdevices for scattering: design and material considerations

A number of ways to fabricate chips compatible with neutrons (see previous chapter), X-rays [2–4] and light [5–7] have been developed recently. The preferred method of fabrication depends on the channel dimensions and resolution needed, the type of radiation, solvent compatibility, q range to be studied and performance of the chip. For example, if samples have a large structural feature such as a sharp peak at high q , background contribution and absorption from the window materials may not be an issue. On the other hand for weakly scattering samples such as protein solutions, high transmission and low background are essential. Figure 5.2 shows an idealised scattering spectrum of a solution of hard spheres before and after subtracting the cell contribution. Part c) shows the deconvolution of the total signal (black line) into intramolecular

scattering, i.e. arising from individual particles, the form factor (green line) and the contribution from inter particle interactions, the structure factor $S(q)$, blue line. Schematics of microdevices

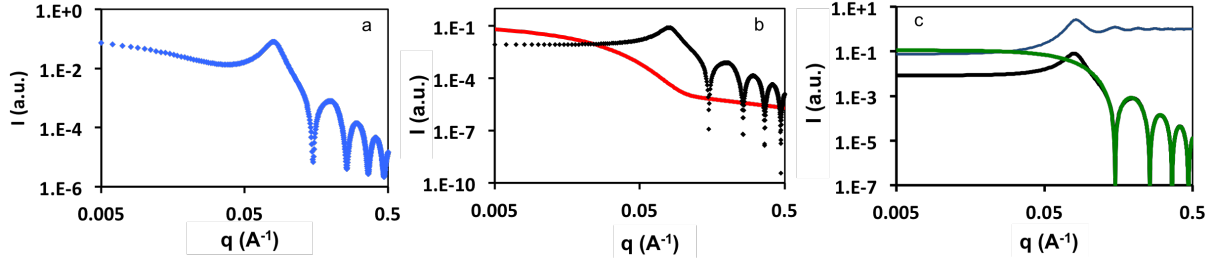


Figure 5.2: Left: signal from the cell and solution. centre: deconvolution of the sample and cell, red line indicates contribution from the cell, black diamonds correspond to the solution of spheres. Right: deconvolution of the intra (green line) and intermolecular (blue) contributions to the total scattered signal (black).

fabricated using different techniques that have been used in scattering experiments are shown figure 5.3. The method used in the previous chapter falls under category b). In general, micro fabrication using negative lithography allows for rapid prototyping (within one hour) and suffers from limited lateral resolution. PDMS replication allows devices to be fabricated in a short time once a mould has been produced, but gives low transmission and high background for both neutron and X-rays. Method c), overcomes the limitations of b) in terms of lateral resolution, bringing the minimum feature size to $\simeq 1\mu\text{m}$.

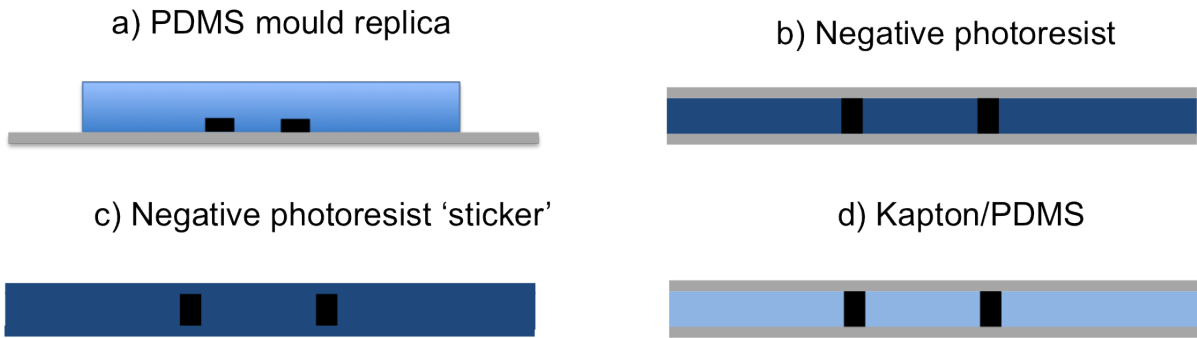


Figure 5.3: Schematics of microdevices using rapid prototyping techniques, black represents the channels, blue and grey stand for different materials. See following references for a detailed discussion of microfabrication techniques: a) PDMS mould replication [13], b) negative photoresist device by photolithography [8] c) Negative photoresist sticker method, [9, 10], d) PDMS sandwiched between two thin Kapton sheets [2].

5.4 Materials for microfabrication

Micro fabrication techniques and materials suitable for microfluidic SAXS experiments have been reviewed elsewhere [2, 3, 11–14]. Here we give a brief review of different materials and techniques commonly used in micro fabrication, the feasibility of using these in a microfluidic neutron scattering experiment is assessed in section 5.6.

5.4.1 Inorganic materials

The first microfluidic devices were made of inorganic materials such as silicon and glass [15–17]. Channels on glass and silicon devices are often fabricated by a variety of etching techniques, depending on the features required and cost/time limitations [17, 18]. Glass and silicon have excellent chemical resistance to most common solvents as well as good thermal stability, optical properties (glass) and a Young’s modulus in the range of tens of GPa. Quartz is a standard material for neutron cells, (e.g. Hellma QS series), and it therefore seems like an obvious choice for the fabrication of neutron compatible microdevices. The cost of these devices and the fabrication time is however much higher than those of microdevices made of polymers, which are considered next.

5.4.2 Polymers

Polymer based micro devices offer a number of advantages over silicon or glass devices. Polymers are generally inexpensive compared to glass and silicon, offering the possibility of tailoring surface properties (e.g. they can be physically patterned or chemically modified) and crucially, depending on the method of fabrication, they allow for rapid prototyping, that is, the possibility of fabricating a device within hours of the initial design [19]. Generally, we may divide polymers into three categories: elastomers and thermosets and thermoplastics [18–20].

Elastomers

Elastomers refer to polymers with rubber-like behaviour, that is, high elasticity (low Young’s modulus) and high failure strain. The most commonly used elastomer in microfluidics is Poly(dimethylsiloxane) (PDMS) [15, 20]. PDMS devices are typically fabricated by imprinting PDMS using a mould, often made of SU-8 [21] (see also section 2.3 for more details). Small feature sizes [21] can be generated with high accuracy both in planar and 3D geometries. PDMS also offers good biocompatibility [22] and is permeable to certain gasses, which is highly advan-

tageous in the field of biology. On the other hand, PDMS suffers from poor solvent compatibility as it is swollen by a number of common organic solvents [23]. Due to its elastomeric nature, PDMS deforms under pressure, which poses a problem in a scattering experiment, as the irradiated volume must be known for absolute calibration. Due to its large hydrogen content, and the relatively large thicknesses of PDMS devices required for mechanical integrity, a PDMS device would give a neutron absorption and background scattering too high for a neutron experiment.

Thermosets

These are polymers which irreversibly cross link. Cross linking may be achieved by high temperatures, under the exposure of light or other radiation or upon mixing with a cross linking agent. Once a cross linked network has been formed, the polymer retains its shape when reheated. Materials of this class include SU-8 [18], the most common photoresist, as well as NOA-81 [8, 24].

Thermosets are often used for master fabrication (e.g. SU-8), may also be used as positive or negative photoresists [18, 24]. NOA-81 has been used in both closed face and open face lithography [9, 24]. NOA-81 offers good solvent compatibility compared to PDMS, except for chlorinated solvents. Depending on the technique used, the minimum feature size is of the order of $50\mu\text{m}$ [24] to a few μm [9]. Window materials for micro devices made with photoresists must meet two criteria: they must be transparent to the type of radiation used for photo curing (at least one side), typically UV radiation; and the photoresist must adhere to the window material. Given the good optical qualities of quartz and fused silica, and their high neutron transmission, combining them with photolithography seem like an obvious way to manufacture SANS compatible microfluidic devices.

Thermoplastics

Polymers which show a significant softening above their glass transition temperature (T_g) are referred as thermoplastics. These include polystyrene (PS), poly methyl methacrylate (PMMA) or polycarbonate (PC). They can be heated above T_g and moulded into an specific shape, and then cooled to the solid state. Alternatively, these materials as well as some thermosets can be shaped by other techniques such as laser ablation, which yields high resolution features.

PMMA and cyclo-olefin-copolymer (COC) devices with thickness of $250\mu\text{m}$ and Polyimide (Kapton) with thickness of $150\mu\text{m}$ have been fabricated by hot embossing and laser ablation respectively and used in SAXS experiments [25, 26]. A disadvantage of polymers such as PMMA is their incompatibility with a number of organic solvents. Kapton on the other hand offers

excellent solvent compatibility. Kapton devices have been fabricated by a different procedure [2, 14, 27] which yields a Kapton/PDMS/Kapton sandwich, with windows down to $\approx 2 \times 5 - 50$ μm thin [2, 14] and the resolution is similar to that of SU-8 photolithography. As well as the mentioned examples, which have been implemented with SAXS, a number of techniques exist to manufacture 'lab-on-a-foil' devices [28, 29], see reference [28] for a review which allow for polymer devices with windows down to 25 μm .

Polymers will generally yield higher incoherent signals than inorganic materials such as quartz or silicon due to their high hydrogen content, decreasing the quality of the cell. These may however reach an acceptable level if the windows are thin enough. It is also possible to use deuterated polymers to reduce incoherent scattering and absorption, however the cost of these materials may make this unfeasible.

5.4.3 Metals

Metals offer high thermal and electric conductivity compared to polymer and inorganic materials (thermal conductivity ~ 2 -3 orders of magnitude higher). Metals generally have high Young's modulus and tensile strength as well as high melting points. Additionally, some metals or alloys have magnetic properties, which may be useful in microfluidic-SANS experiments. Gold, Nickel and Copper are the most commonly used metals in micro fabrication [18, 30, 31]. Devices made out of other metals have also been reported [31–34]. Interestingly, these devices can have extremely thin channels, for example, Nickel devices with 10 μm thick channels [30] have been reported.

Other materials used in micro fabrication such as paper, hydrogels and ceramics, are not considered here since these do not tolerate high flow resistance (relevant for complex fluids) and/or are expected to yield high scattering background.

5.5 Methods

In order to evaluate the performance of microfluidic devices in SANS, selected materials and methods were employed and tested under typical measurement conditions. Neutron scattering measurements were performed at the D22 beamline at ILL (Grenoble, France). The wavelength was fixed at $\lambda = 6$ Å. Two sample to detector distances were used: 2.8 and 5.6m. These yield a q -range of $0.01 \text{ Å}^{-1} \geq q \geq 0.3 \text{ Å}^{-1}$. The acquisition times were 2 minutes for the high q configuration

and 7 minutes for the low q one. The data was reduced using GRASP, calibrating against empty beam. The materials for microfabrication in section 5.7 are detailed in the previous chapter.

5.6 Window materials for SANS

As discussed previously, suitable cell materials for SANS should exhibit a combination of (i) high transmission and (ii) low scattering in the relevant q -range, at (iii) the thickness required to impart mechanical integrity to operate a SANS flow cell.

5.6.1 Transmission

	T/mm	Device thickness/mm	T_d
Aluminium	0.99	5.00	0.95
Copper*	0.90		
Nickel*	0.81	0.02	1.00
Polyethylene ^a	0.45	0.40	0.73
Polystyrene	0.62	0.40	0.83
PMMA*	0.61	0.40	0.82
Polycarbonate*	0.70	0.40	0.87
Thiolene	0.57	0.40	0.80
Kapton*	0.79	0.10	0.98
d-PS*	0.93	0.40	0.97
d-PMMA	0.92	0.40	0.97
Borosilicate glass	0.41	0.28	0.78
Quartz	0.98	0.88	0.98
Fused silica	0.98	2.30	0.95
Silicon	1.00		≈ 1
Hellma			0.96

Figure 5.4: Neutrons transmissions for a number of materials studied. The second column shows the transmission (T) of a 1mm window of the material, the third column shows the typical thickness of a device made out a given material, and the fourth column shows the estimated transmission for a micro device made of such material (T_d), see text for thicknesses assumed. * Calculated transmission. ^a from reference [35].

Table 5.4 shows the transmission for several materials used in the fabrication of micro devices.

For comparison, a Hellma cell, commonly employed in neutron experiments is included. The transmission is of course a function of thickness and therefore, not just the quality of the material, but also the thickness required for microfluidic fabrication must be considered. We therefore calculate on the third column, the transmission of a micro device from each material. For quartz, borosilicate glass and fused silica, we use the device thickness of our fabricated devices described in section 5.7. For polymers such as PS, polycarbonate (PC) and PMMA, we assume two windows of $200\mu\text{m}$ each. For thiol-ene, we use $t = 250\mu\text{m}$, taken from reference [10]. For certain materials such as silicon, the absorption is so small that even very thick devices, on the order of say 1 cm, would remain virtually transparent to neutrons, and therefore we assume a transmission of 1 for a device. Inorganic materials generally show good transmission, except borosilicate glass, for which it is not an issue as thin windows can be used as shown in section 5.7. Polymers show a transmission of $\approx 0.6 \pm 0.1$ /mm which is acceptable for microfluidic SANS devices. Kapton devices, owing to the thin walls, have a cell transmission similar to a Hellma cell. The use of deuterated polymers, would also yield high transmissions for a typical thickness of $200\mu\text{m}$. Aluminium shows the largest transmission of any of the metals considered, meaning that even thick devices ($\approx 0.5 - 1$ mm) would yield acceptable transmissions. Nickel, while a relatively strong absorber can be used to fabricate extremely thin devices ($2 \times 10\mu\text{m}$) thus giving a transmission ≈ 1 . In conclusion, while significant differences exist in the transmission of materials for microfabrication, they do not seem to be a limiting factor for SANS compatibility.

5.6.2 Scattering

Inorganic materials

Figure 5.5a shows the scattering profiles for the several inorganic materials. The data is presented in two fashions, first, the reduced data in cm^{-1} is shown in the top graph. This can be somewhat misleading as we are interested on the scattering of the cell compared to that of a sample of the thickness equal to the channel depth. Figure 5.5 b shows the same data but with each curve multiplied by the thickness in cm required to make a device of each material, see above for specific values. We include for reference, the scattering of D_2O , a relatively weak scatterer, ($I \approx 0.05\text{cm}^{-1}$) of $500\mu\text{m}$ depth (which we take as a reference channel depth). The scattering for all materials considered is extremely weak, at least three times lower than D_2O . Given the increased acquisition times required for microSANS, samples must scatter above $\approx 1\text{cm}^{-1}$ (see

figure 4.13 of the previous chapter) and the scattering from cells of these materials may thus be considered negligible compared to the sample (~ 2 orders of magnitude smaller). The only significant differences between the materials is therefore, transmission and cost. Borosilicate slides are significantly cheaper than quartz or fused silica but offer a device transmission $\approx 25\%$ lower. While we do not consider the scattering of a silicon device in the bottom graph, it suffices to say that the scattering is extremely weak in the q range studied and thus even thick devices ($\sim \text{cm}$) would be highly compatible with neutrons provided that any crystalline peaks lie outside the region of interest for scattering, the metals illustrated here would provide suitable SANS cells.

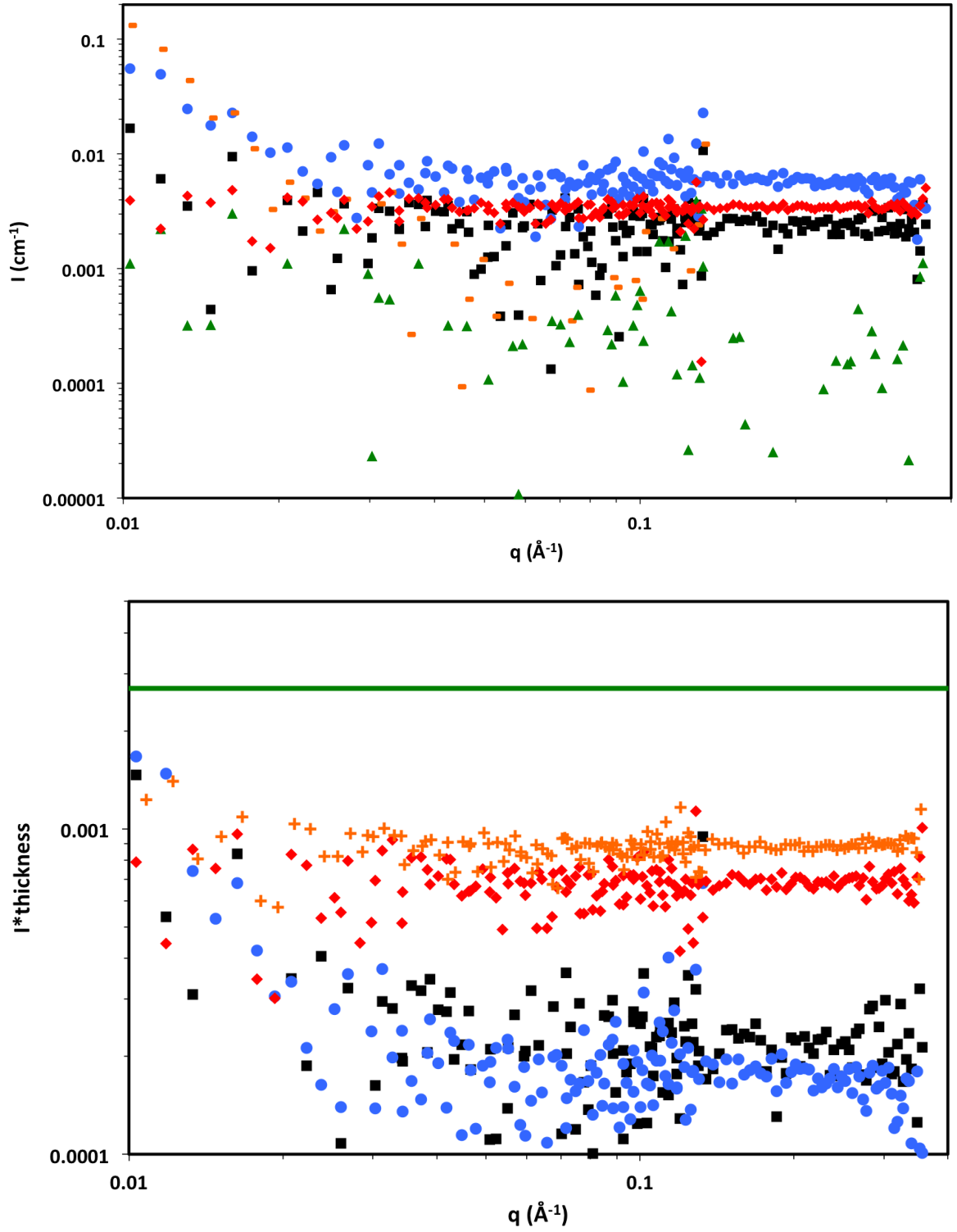


Figure 5.5: Scattering profiles for different inorganic materials discussed in section 5.4.1. Top graph: data in absolute units of cm^{-1} . Bottom graph: Same as top graph, but I is multiplied by the thickness in cm required to make a device of the given material. The approximate scattering of D_2O of $500 \mu\text{m}$ depth is included for reference as a green line.

Polymers

Polymers, due their relatively large hydrogen content, have large incoherent cross section, typically $\simeq 0.5\text{--}0.7\text{ cm}^{-1}$. Amorphous polymers typically show nearly flat profiles in the q range considered in this chapter, highly structured polymers (for example ordered diblock copolymers) can scatter strongly in this region and are therefore not recommended. Figure 5.6 shows the scattering of four selected polymer systems: hydrogenated polystyrene, deuterated polystyrene, PMMA and (cross linked) thiolene. Polypropylene, represented by the incoherent background given in reference [35] is also added for reference. Compared to the inorganic materials, or metals (see below), polymers perform poorly as materials for SANS cells. Taking the depth of the scattering channel to be $500\text{ }\mu\text{m}$, wall thicknesses $\simeq 20\text{--}25\text{ }\mu\text{m}$ would be needed for the channels to scatter similarly to D_2O . Most microfluidic fabrication methods, as outlined in section 5.4 require significantly thicker walls ($\simeq 150\text{--}250\text{ }\mu\text{m}$), while a few [2, 14, 28] may allow thin enough walls to yield SANS compatible devices. Deuterating the polymer yields an incoherent cross section $\simeq 30$ times lower, which, would make polymers excellent window materials for neutron cells. Deuteration is however expensive and many materials, such as photoresists, are unavailable in deuterated form.

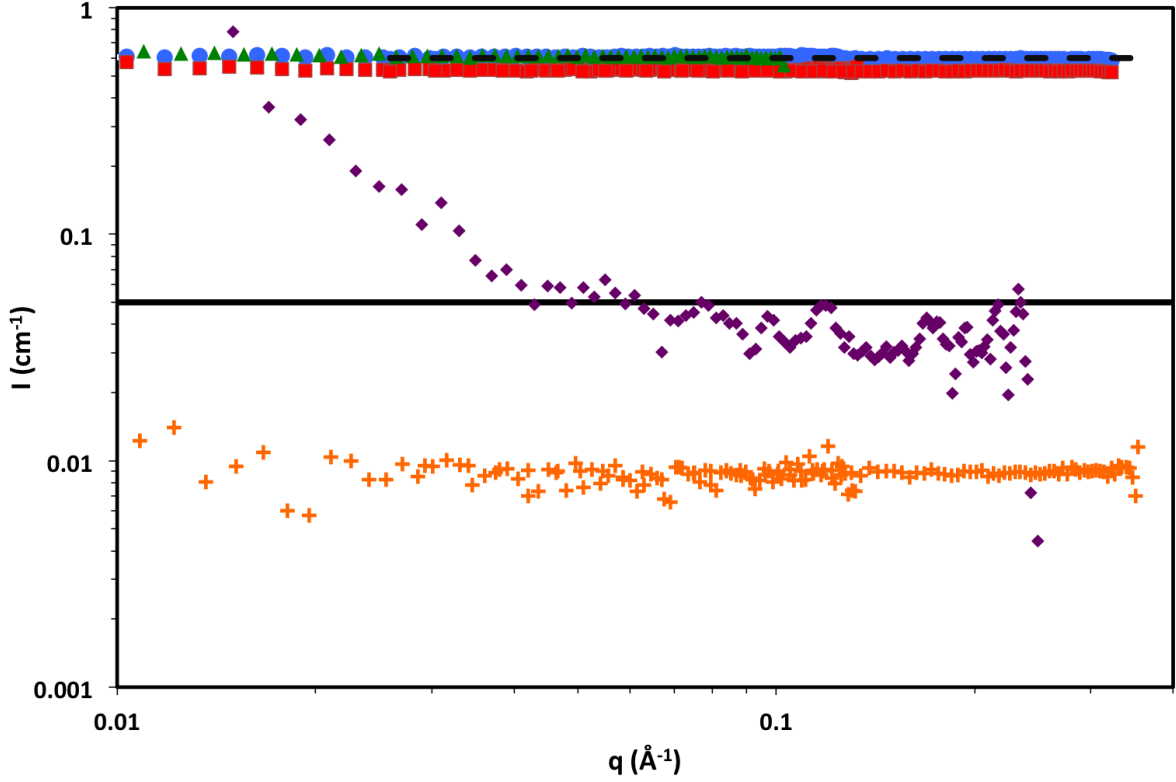


Figure 5.6: Scatering profiles for different polymers. Data in absolute units of cm^{-1} : hydrogenated polystyrene (blue circles), deuterated polystyrene (purple diamonds) thiolene (red squares), free triangles (PMMA), polypropylene (dashed line) taken from reference [35]. Hellma cell is shown as orange crosses, and $\text{D}_2\text{O} = 0.05 \text{ cm}^{-1}$ as a black line.

Metals

Figure 5.7 shows the scattering profiles for nickel, aluminium and steel in the same representations used in figure 5.5. We take the value for the nickel device as $10 \mu\text{m}$ per channel wall, as described in reference [30]. As can be seen on the bottom graph of figure 5.7, such a device would yield an outstanding neutron cell in the q range studied. Steel scatters significantly more than nickel, specially in the low q region. We lack a reference for the channel thickness needed for microfabrication. We select a value of $50 \mu\text{m}$ for figure 5.7b. Such a device would provide Hellma like quality for $q \geq 0.05 \text{ \AA}^{-1}$. Aluminium is the weakest scatterer of the metals tested. In the high q region ($q \geq 0.1 \text{ \AA}^{-1}$, it compares favourably even to quartz or fused silica, it decreases at lower q values, reaching the value of D_2O at $q \simeq 0.02 \text{ \AA}^{-1}$. Again we lack a reference for the thickness of an aluminium channel, so we arbitrarily choose 2.5mm , which should be enough to

maintain the mechanical integrity of a device.

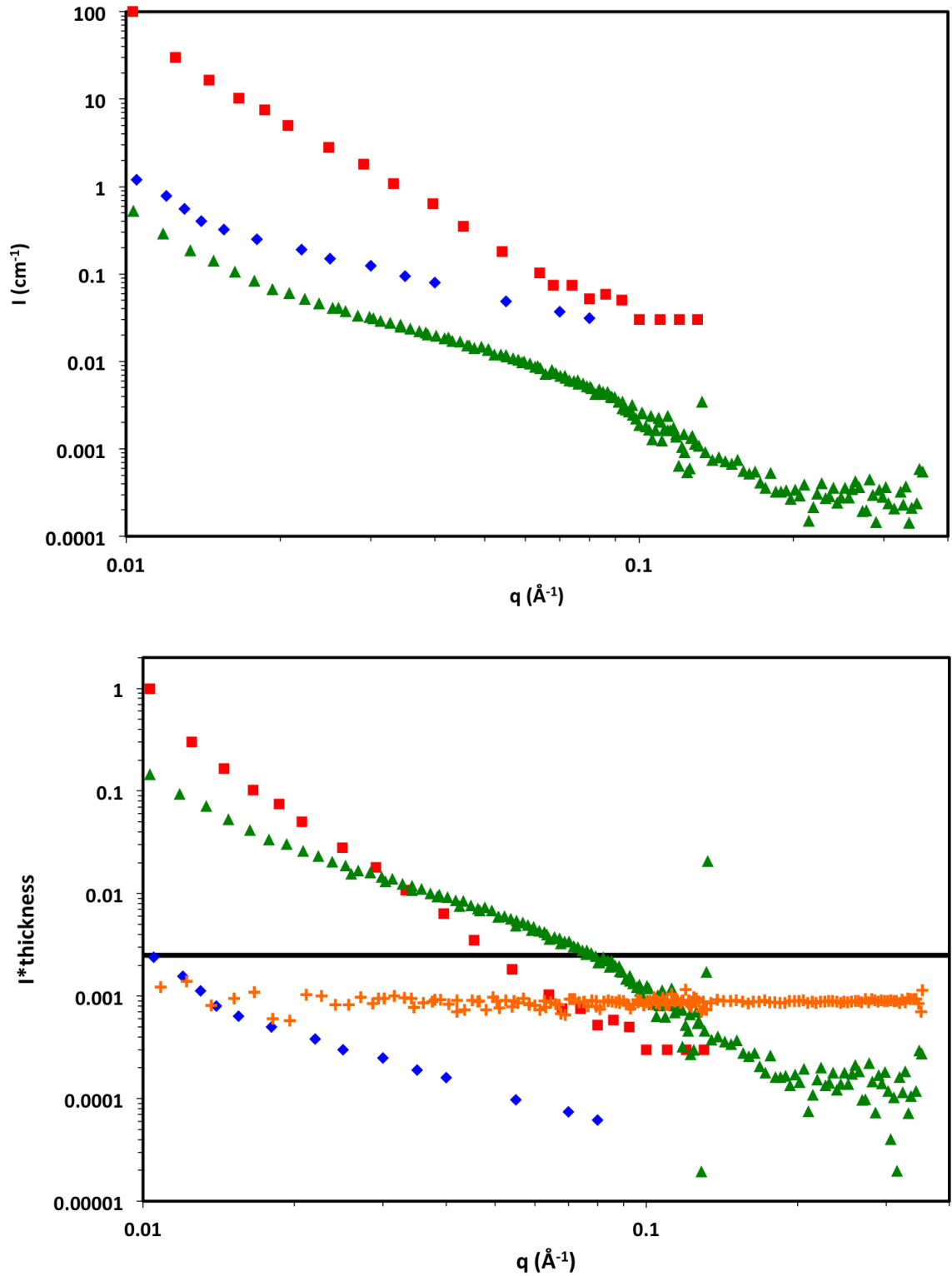


Figure 5.7: Scattering profiles for different metals discussed in section 5.4.3. Top graph: data in absolute units of cm^{-1} : steel [36] (red squares) nickel [37] (blue diamonds) aluminium, our data (green triangles). Bottom graph: Same as top graph, but I is multiplied by the thickness in cm required to make a device of the given material. The approximate scattering of D_2O of 500 μm depth is included for reference.

5.7 Microdevice fabrication

We have fabricated two types of microfluidic devices for SANS. The first type is based on a method previously published by Cabral et al. [8] later modified to increase neutron compatibility as outlined in the previous chapter. The second method is a modification which consists in coupling a PDMS device to a high quality SANS observation window.

5.7.1 Method 1: Photolithography

A schematic of a chip made by the FPP method is shown in figure 5.8. In order to maximise transmission and minimise the background signal, we use $140\mu\text{m}$ borosilicate cover slides. Due to the fragile nature of these slides, we could not drill through them. We therefore use a thick glass slide with holes drilled in the inlet, outlet and observation window as a reinforcement. We have also carried out the same procedure with $500\mu\text{m}$ quartz slides and 1.1mm fused silica slides. In principle, any UV transparent material with good adhesion to the resist can be used for this method.

The procedure is as follows: **a:** two small holes are drilled on a thick glass slide which serve as inlet and outlet, additionally a large hole is drilled around the region for observation with neutrons. We find that drilling the inlet and outlet holes before the large central one significantly reduced the breakage of the slide while drilling. This slide will act as a 'reinforcement' for the thinner glass slides. **b:** A few drops of thiol-ene are poured and spread on a thin cover slide, and the reinforcement is placed on top. Both are placed under UV to seal them. Any excess thiolene is removed using a razor. **c:** Holes are drilled through the thin cover slide on the inlet and outlet positions. **d:** Spacers are placed on top of a thin cover slide, thiol-ene is poured on top and the reinforced slide is used sandwich the thiol-ene. **e:** The device is flipped, a negative mask is placed on top and the whole structure is exposed to a dose of UV calculated from reference [8], for a $540\mu\text{m}$ deep channel, the device is exposed for 5 min to a UV light of $0.14\text{J}/\text{cm}^2$. **f:** the liquid thiolene that remains under the dark places in the mask is flushed out using ethanol, acetone and compressed air. **g:** The device is post cured by exposure to high intensity UV for at least 30 minutes (with no relevant upper bound). **h:** Nanoports are sealed to the device using fast curing Araldite glue, the device is ready for operation.

Feature size

The minimum feature size obtainable with this method is $\sim 100\mu\text{m}$, smaller features can be

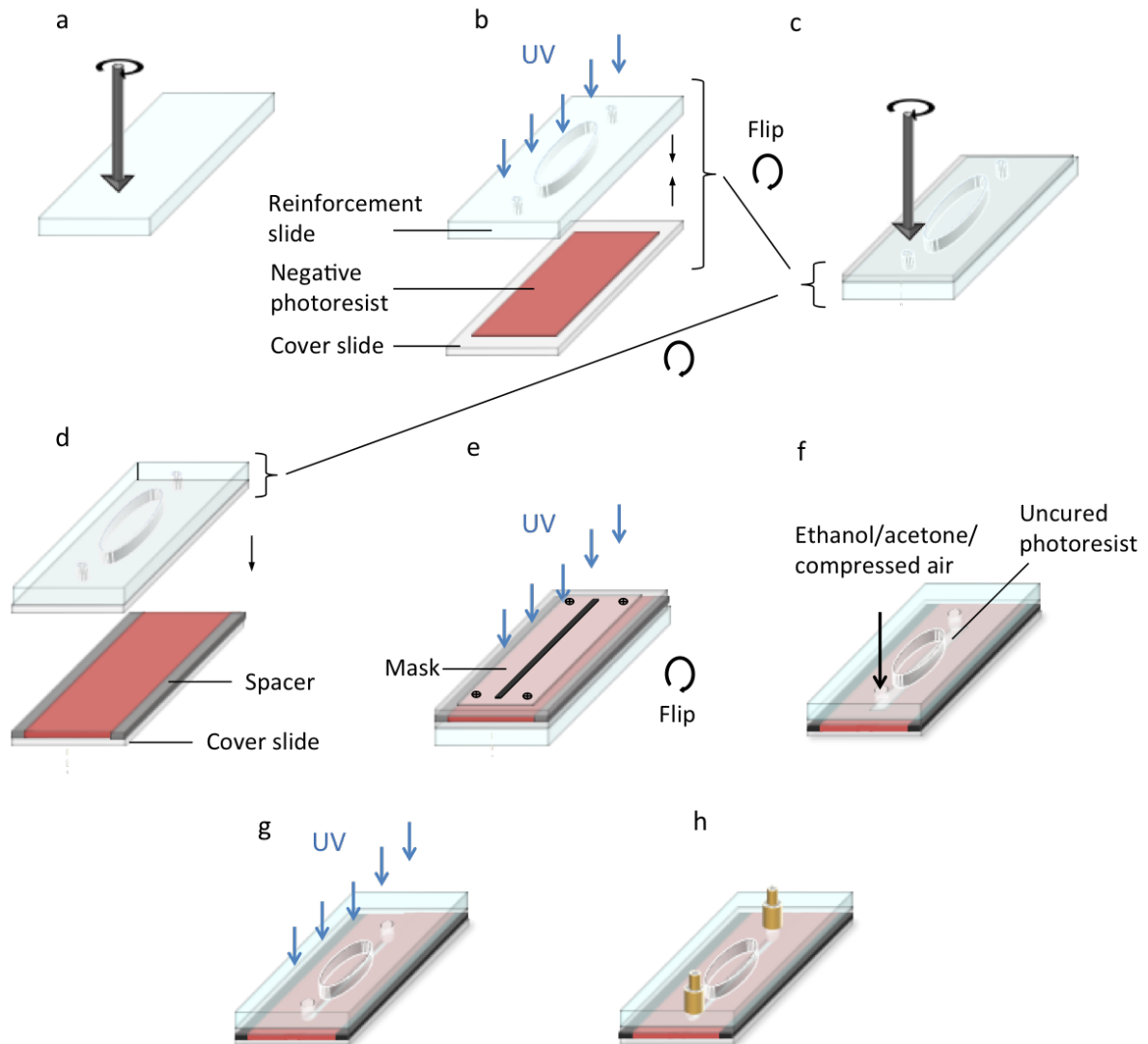


Figure 5.8: Schematic of micro fabrication procedure based on a method developed by Cabral et al [8]. a: Two holes are drilled on a thick ($\approx 1-1.2$ mm) borosilicate cover slide at the inlet and outlet positions. An additional large hole is drilled in the SANS observation window. b: Sealing of a thin cover slide to a reinforcement slide. c: Holes are drilled through the glued cover slide at the inlet and outlet positions. d: Spacers are placed on a thin cover slide and thiolene is poured on top and the reinforced slide is placed on top. e: The device is flipped 180° , a negative mask is placed on top of the device and UV light is shone. f: After UV curing, channels are washed with ethanol, acetone and compressed air. g: The device is post cured with UV to further crosslink the negative photoresist. h: Connectors are attached using an epoxy resin to the inlet and outlet position.

fabricated but at the expense of reproducibility as the feature size can largely deviate from the mask size depending on development, exposure time, compressed air pressure, age of thiolene, time between steps, etc. In general it is easy to make small features on thinner channels. A way to improve the minimum feature size was proposed by Bartolo and co-workers [9], who used thiolene stickers to achieve high definition solvent resistant structures. Their method can easily be adapted by simply replacing glass slides with quartz or with reinforced borosilicate slides. The resulting chips are then of the same structure as the previous method but with a minimum feature size of a few microns. While neutrons are the main focus of this chapter, the devices fabricated by this method using this borosilicate slides are also compatible with SAXS. Borosilicate capillaries (wall thickness $\approx 50 \mu\text{m}$) are commonly used as SAXS cells. Our devices have only ≈ 3 times the wall thickness and can thus be considered suitable SAXS cells.

5.7.2 Method 2: Hybrid devices

Another way of overcoming the limitations of our first method is to combine it with the widely used method of PDMS mould replication. In brief, a PDMS device can be sealed on top of an observation window fabricated by the first method. The small feature size available from PDMS can then be used for say, fast mixing or flow processing of a complex fluid, which is then transported to a high quality observation window. With this method it is not possible to carry out truly 'in situ' SANS/SAXS under flow, as the fluid has to go from the PDMS part into the window, which typically has a dead volume of 1-5 μl . A schematic of the device is shown in figure 5.9. Stages a-b follow the previous method but instead of having the observation window in the middle of the chip, we opt to reinforce only one side of the chip. Further details of this procedure can be found in a previous publication [38]. Stage c simply consists of sealing the PDMS unit, fabricated according to reference [21] to the thiol-ene unit using a plasma oven. The resulting cell has the same neutron/X-ray quality as the above chips.

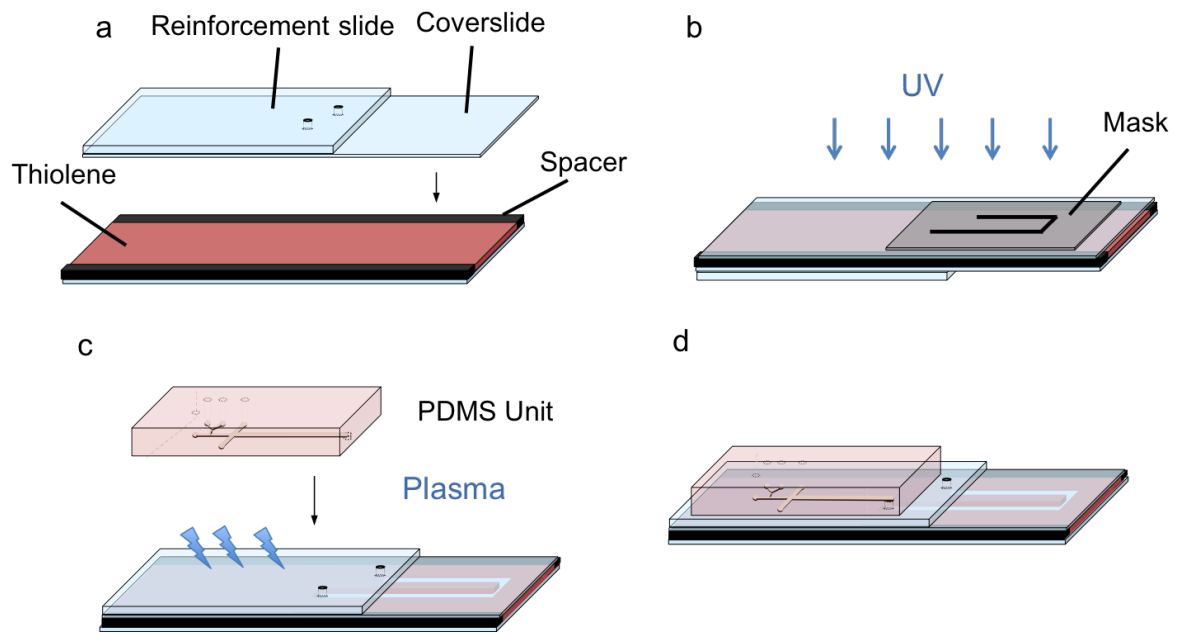


Figure 5.9: Schematic of PDMS thiolene hybrid microdevice. a: a thick glass slide with two holes for the inlet and outlet is glued to a thin coverslide. Spacers are placed on a second coverslide and thiolene (red) is poured on top. b: A negative mask is placed on top of the device and UV is shone. c: Channels are flushed and cleaned. A PDMS device, fabricated previously as described on the text is prepared. The two units are sealed using a plasma oven. d: Resulting device.

5.8 Conclusions

We have assessed the quality of a number of materials for fabrication of microfluidic devices compatible with SANS. Quartz, fused silica and silicon show excellent neutron compatibility. Devices made out of these materials will yield transmissions and backgrounds superior to a standard neutron cell. Borosilicate glass has a similarly low background but much lower transmission, devices must therefore have thin walls ($\approx 2 * 140 \mu\text{m}$ for 80 % transmission). We have implemented a simple, rapid, photolithographic technique, which yields solvent resistant, hard devices transmission up to $\approx 98\%$ when using quartz. FPP of thiol-ene has a limitation on the minimum feature size of about $50 \mu\text{m}$. If smaller dimensions are needed, for example for fast mixing or to apply high shear rates, a PDMS mould may be coupled to a high quality observation window with a dead volume of $1\text{-}5 \mu\text{l}$. A technique based on open face lithography of NOA-81, developed by Bartolo and co-workers [9], should yield similar devices to our photolithographic method but with a higher resolution (feature size down to microns). A large number of other techniques exist for fabricating microdevices out of these materials, which can overcome some of the limitations of our approach; e.g. resolution, greater solvent compatibility high pressures/temperatures. Polymers, which are a common materials in microfabrication are largely unsuitable for micro-SANS devices. Given their large incoherent cross section and absorption, the walls need to be either extremely thin ($\approx 25\text{-}50 \mu\text{m}$) or the polymer needs to be deuterated. We have only examined a small selection of metals. While nickel and steel scatter more strongly overall than the quartz, fused silica, borosilicate glass or silicon, the possibility of fabricating devices with extremely thin walls ($\approx 10 \mu\text{m}$) makes them good candidates for microfluidic-SANS devices. Aluminium has excellent transmission and scatters weakly at high q ($q \geq 0.1$), to the point that even thick devices ($\sim \text{cm}$) would scatter weakly at high q . Our devices are also compatible with SAXS, and add to the large number of microfabrication techniques developed for this purpose. These results may be useful for the study of soft matter under flow and for high throughput SANS/SAXS experiments.

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Conclusions

We have studied cellulose derivative polyelectrolyte carboxymethyl cellulose (NaCMC) in aqueous solutions, a semiflexible polymer with intrinsic persistence length $L_0 \simeq 55 \text{ \AA}$. In salt free solutions, the scattering and rheological behaviour is found to be similar to that of other synthetic, flexible polyelectrolytes. The scattering and rheological properties are qualitatively described by scaling theory for flexible polyelectrolytes. A near Fuoss dependence of the specific viscosity with concentration is found in the semidilute unentangled regime, followed by a semidilute entangled and concentrated regimes where the viscosity behaves similarly to that of neutral polymers. The correlation length is found to scale as $\xi \propto c^{-1/2}$, where c is the polymer concentration, throughout the whole concentration range. We find that the crossover from semidilute to concentrated happens at a much lower value than for flexible polyelectrolytes. Analysis of literature data indicates that $c_D \simeq L_0^{-3}$. Our data suggests the concept of thermal blobs does not apply to semiflexible polyelectrolytes. As salt is added to solutions of NaCMC, the viscosity decreases and neutral polymer in good solvent behaviour is found. The variation of the viscosity with salt is not well described by current scaling theories, especially at high salt concentration c_s , where the viscosity becomes approximately independent of c_s . The scaling theory for semiflexible polyelectrolytes developed by Odijk is modified to include a more accurate expression for the excluded volume, which is found empirically, by analysing data from the literature. This yields reasonable agreement with the data, up to a prefactor of order unity. Overall, we have characterised relevant static and dynamic properties of NaCMC in aqueous solutions, which emerges as a model semiflexible polyelectrolyte system.

Probing the structure of complex fluids under flow is useful for understanding their dynamics and, for this purpose, we explored a method to fabricate microfluidic devices that are compatible with SANS. Microfluidic SANS experiments are illustrated by measuring two previously investigated liquid crystalline systems, and successfully monitoring lamella re-orientation through a constriction. Additionally, the total scattering intensity is examined to evaluate the relative

population of lamellar sheets in the different scattering planes. Scattering from aqueous NaCMC was not possible due to flux limitations. We thus establish a roadmap for microfluidic SANS, focusing on soft matter systems, and how these may be studied in the future as improvements on SANS instrumentation takes place. Further, we evaluate the feasibility of a number of materials and techniques for the fabrication of SANS compatible microfluidic devices. We find that a number of methods published in the literature provide suitable devices for microfluidic SANS.