

DYNAMICS OF SURFACTANT-LADEN FLUIDS
SPREADING ON COMPLIANT SUBSTRATES
CONSTANTINOS SPYRIDONOS SPANDAGOS



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“τὰ πάντα ρεῖ, μηδέποτε κατὰ τ'αὐτὸ μένειν”

“everything flows, nothing remains the same”

Ἡράκλειτος ὁ Ἐφέσιος

(535-475 π.Χ)

Heraclitus of Ephesus

(535-475 BC)

DECLARATION OF ORIGINALITY

The work presented in this dissertation has been carried out in the Department of Chemical Engineering and Chemical Technology at Imperial College London between January 2008 and June 2011, under the supervision and guidance of Prof. Omar Matar and Prof. Paul Luckham. Except where acknowledged, the material presented is the original work of the author. No part of this work has been submitted for a degree at any other university.

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ABSTRACT

This work involves an experimental investigation of the spreading of liquids on gel layers in the presence of surfactants. Of primary interest is the instability that accompanies the cracking of gels through the deposition and subsequent spreading of a drop of surfactant solution on their surface. This instability, which has been reported recently in the literature, manifests itself via the shaping of crack-like spreading “arms”, in formations that resemble “starbursts”. The main aim of this study is to elucidate the complex interactions between spreading surfactants and underlying gels and to achieve fundamental understanding of the mechanism behind the observed phenomenon of the cracking pattern formation. This is hoped to be beneficial for improving a wide range of engineering, biological, biomedical and environmental settings where such systems are of central importance. Towards this aim, a parametric experimental work that involves the spreading of different types of surfactants on various types of gels was conducted, in order to explore the ways that system parameters such as the surfactant chemistry and concentration and the gel type and strength can affect the morphology and dynamics of the “starburst” patterns.

The surfactants used were SDS (sodium dodecyl sulphate) and Silwet L-77 (a trisiloxane ethoxylate); the former is one of the most common materials used in surfactant-related studies and the latter belongs to a certain class of surfactants, termed “superspreaders” which are known for exhibiting unique spreading behaviour. The different gel substrates were made of agar (a polysaccharide-based gel), and gelatine (a protein-based gel).

In terms of the spreading dynamics, the crack propagation was attempted to fit to a power-law by measuring the temporal evolution of the length of the spreading “arms” that form each one of the observed patterns. The values of the exponent of the power law are inside the predicted limits for Marangoni-driven spreading on thick layers. Therefore, Marangoni stresses induced

by surface tension gradients between the spreading surfactant and the underlying gel layer are identified to be the main driving force behind these phenomena, while gravitational forces were also found to play an important role. A mechanism that involves the “unzipping” of the gel in a manner perpendicular to the direction of the largest surface tension gradient is suggested. An attempt to quantify the stresses that form the cracks and a detailed rheological characterisation of the gels are also included.

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1: $S=22\text{mN/m}$, and $S/\Delta w =13.75 \text{ Pa}$. **2:** $S=27\text{mN/m}$, $S/\Delta w=12.2 \text{ Pa}$. **3:** $S= 28\text{mN/m}$, $S/\Delta w=12.7 \text{ Pa}$. All these are greater than, but very close to $G'=11\text{Pa}$. **4:** $S=27.5\text{mN/m}$, and $S/\Delta w =9.16 \text{ Pa}$. **5:** $S=32.5\text{mN/m}$, $S/\Delta w=8.78 \text{ Pa}$. **6:** $S= 33.5\text{mN/m}$, $S/\Delta w=12.8 \text{ Pa}$. All these are greater than $G'=1.38 \text{ Pa}$.

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LIST OF SYMBOLS

Symbol

Definition

Roman Symbols

b_{ch}	channel width in a Hele-Shaw cell
b	height of precursor film ahead of contact line
Bo	Bond number ($=\rho g H^2/S$)
D_s	surface diffusivity
D_b	bulk diffusivity
E	size of small perturbation to the contact line
F	force acting on the balance of Wilhelmy plate
g	gravitational acceleration
G	shear modulus
G'	storage modulus
G''	loss modulus
h	height of surfactant (when spreading in a vertical geometry)
h_{rel}	relative humidity
H	underlying layer/ film thickness
H_o	initial underlying layer/ film thickness
k	coefficient of spreading
k_a	adsorption coefficient of surfactant
k_d	desorption coefficient of surfactant
L	extent of surfactant spreading/ length of cracks
L_W	wetted length of Wilhelmy plate
L_f	length of fingers of fingering patterns

L_o	initial extent of surfactant spreading
$L_s(\delta)$	a numerical factor that is a function of Pe
M	mass
n	spreading exponent
Pe_s	surface Peclet number ($=SH_o/\mu D_s$)
Pe_b	bulk Peclet number ($=SH_o/\mu D_b$)
P_p	perimeter of Wilhelmy plate
R_{mic}	parameter that shows the preference of the surfactant to form micelles
R	radial extent of surfactant spreading
R_c	radius from the centre to the edge of the drop
R_f	radius from the centre of the drop to the tips of the fingers
R_o	radius from the centre of the drop to the leading surfactant edge
Re	Reynolds number ($=\rho UH_o/\mu$)
S	spreading coefficient/ spreading pressure/surface tension
S_o	initial surface tension/initial spreading pressure
t	time
t_a	adsorption time scale
t_d	desorption time scale
t_{Ds}	surface diffusion time scale
t_{Db}	bulk diffusion time scale
t_m	Marangoni time scale
$\tan\delta$	tangent of the phase angle

T	temperature
U	characteristic Marangoni velocity
U_{HS}	velocity of Hele-Shaw flow
u	tangential velocity
W_t	maximum force on the Wilhelmy plate when immersed in liquid
W_p	weight of Wilhelmy plate in air
w	width of cracks
X	concentration
x	number of ethylene oxide units in the headgroup of a polyoxyethylene surfactant

Greek Symbols

a_{sur}	surface activity
β	solubility parameter
Γ	surfactant concentration
γ	surface tension
$\dot{\gamma}$	shear rate
Δw	change of the width of the cracks
δ_{layer}	thickness of the viscous boundary layer
δ	phase angle
ε	ratio of H_o to L_o
θ	contact angle
μ	viscosity
ξ	“mesh” size
ρ	density of liquid substrate

σ	surface tension
σ_m	surface tension of surfactant covered liquid
σ_o	surface tension of surfactant free liquid film
σ_g	gel-air interfacial tension
σ_d	droplet-air interfacial tension
σ_{gd}	gel-droplet interfacial tension
Ω	volume of droplet

Chapter 1

Introduction

Synopsis

The aim of this Chapter is to reveal the motivation behind the work described in the present thesis and to highlight the need for fundamental understanding of the complex interactions between spreading surfactants and underlying gel-like materials. It also provides an outline of the structure of the thesis and a detailed description of the contents of each Chapter that follows.

1.1 Motivation

The spreading of fluids over various substrates has attracted the interest in many fields of science and technology such as environmental engineering, biomedicine, and the chemical and petrochemical industries (see Landt and Volmer 1926, Hoult 1972, for instance). The addition of surface active agents (surfactants) can have a tremendous effect on the rate and extent of the spreading process. Therefore, the ability to control these properties can be beneficial in many applications, including surfactant replacement therapy (Grotberg 1994 and 2001), lipid tear layers in the eye (McCuley and Shine 2004), coating processes (Weinstein and Ruschak 2004), spraying and herbicides (Knoche *et al.* 1991) among others. That is the reason why surfactant-enhanced spreading has been investigated by numerous experimental and theoretical studies and has been the subject of two major reviews by Lee *et al.* (2008), and Matar and Craster (2009). Such spreading processes have been shown to be accompanied by rich and interesting dynamics which owes its existence to the delicate interplay between the different mechanisms that play a role in the observed phenomena. These forces are operative over a large range of scales, thus complicating the understanding of the relative contribution of each one of them, the derivation of appropriate predictive models and the performance of simulations of the spreading process.

Although the spreading of thin films on liquids and rigid solids has been the subject of numerous studies, the majority of these studies have largely focused on the case of Newtonian fluids and materials having relatively simple rheology (an elastic, rigid solid or another Newtonian liquid, for instance). The dynamics of spreading on compliant substrates of complex rheology, however, has received less attention in the literature. A limited number of studies on the spreading on gel-like materials has been carried out (Szabó *et al.* 2000, Kanenko *et al.* 2005) and very few of these feature the spreading of surfactant-laden liquids. This is particularly surprising given the scientific and industrial interest that the nature of a

gel-like material can have, since it is possible to exhibit the full spectrum of solid-like to liquid-like behaviour, simply by changing the gel concentration. Furthermore, the complex interactions between spreading liquids and underlying gel-like materials is a problem that lies at the heart of a wide range of engineering, biological, biomedical and daily-life applications, which include:

- Drug delivery over compliant substrates, such as the spreading of bioadhesive or muco-adhesive liquids over tissue (Huang *et al.* 2000) or over mucus laden films (Khanvikar *et al.* 2001) in the lung (Halpern *et al.* 1998) or elsewhere in the body;
- The development of scaffolds in tissue engineering, which are porous, degradable structures that can be gels, designed to degrade within the patient, (Andersson and van den Berg 2004), however, it is sometimes required that drugs are administered through or over the scaffold without fracturing it;
- Understanding and improving the emplacement, fracturing and subsequent removal of gels in reservoirs in the oil industry which is a commonly used technique (Seright 2006 and 2008) to limit water production whilst retaining oil or gas production;
- Optimising the deposition of multilayers of gel-like materials in the manufacturing of photographic films;
- The spreading and subsequent breakup of particle rafts by surfactant (Vella *et al.* 2006), which is relevant to the collapse of particle shells encapsulating drugs for inhalation delivery (Tsapis *et al.* 2002).

It is expected that the interactions of the spreading liquid with the underlying gel-like material will lead to exceedingly complicated flow structures. This has been confirmed by a recent study by Daniels *et al.* (2005, 2007) which has shown that such systems can also exhibit flow instabilities and complex behaviour that are very poorly understood. This work considers the spreading of either pure silicon oil droplets or droplets of Triton X-305 dissolved in deionized

water on agar gels. These are polymeric materials that consist of galactose and undergo gelation over a certain threshold agar mass fraction, which depends on temperature. These investigators report that the droplets are observed to spread into “spreading arms” patterns, in formations which resemble a “starburst”.

The formation of these patterns can be considered as behaviour similar to the fingering instability that occurs on the surface of liquids and solids and has been reported in many experimental and theoretical studies, being mainly associated with the presence and the spreading of surfactants (see also Chapter 3). An example of the complex dynamics accompanying the spreading of a surfactant-laden droplet on a thin liquid film is provided by the work of Edmonstone *et al.* (2006), in which it was demonstrated how the presence of surfactants at concentrations beyond the critical micelle concentration gives rise to a fingering instability that exhibits highly nonlinear processes such as tip-splitting, merging and shielding. The isolation of the mechanism underlying these patterns had been a hotly disputed topic in the literature since 1981 when these patterns were first reported by Marmur and Lelah.

According to Daniels *et al.* (2007) the formation of the cracking patterns on the surface of gel layers is associated with the *Marangoni Effect*, however fundamental understanding of this new class of flow behaviour, has not yet been achieved, and the precise mechanism behind the intriguing observation of these patterns remains unclear. By experimentally examining important system parameters that can influence the instability, possible explanations can be investigated. Furthermore, it is possible that important contributions to the problem can be made by the use of a specific class of surfactants that are able to drastically reduce the surface tension of water and thus promote strikingly rapid spreading on very hydrophobic substrates, even in very small quantities. These surfactants are termed “superspreaders” and the phenomenon is called “superspreading”. Recently, a mechanism for superspreading was proposed by Karapetsas *et al.* (2011a) whereby surfactant adsorption at the contact line was

demonstrated to be primarily responsible for the rapid spreading observed for superspreaders. The contact line adsorption provides a mechanism for removal of surfactant from the contact line region and an impetus for sustained Marangoni-driven spreading.

This work is aimed at achieving fundamental understanding of this new class of flows that can be observed during the spreading of surfactants on the surface of gel layers. Through direct experimentation, the spreading of an anionic surfactant (SDS) and a non-ionic trisiloxane (Silwet L-77) on thick underlying agar and gelatine gel layers has been studied, in order to provide insight into the nature of the liquid-gel interactions and examine the effect of varying the chemistry of the surfactant and gel, among other parameters, on the observed pattern characteristics and spreading dynamics. Furthermore, this work represents the first attempt to take into consideration the presence of superspreading surfactants in the process.

1.2 Thesis Organisation

This thesis has been divided into 7 Chapters, and its structure is given as follows. Chapter 2 provides background information on the surfactant spreading process, and an overview of the different types of surfactants, of surfactant adsorption and Marangoni stresses. A literature review of spreading in the presence of non-superspreading and superspreading surfactants, but in the absence of any instabilities follows. Surfactant-induced Marangoni driven instabilities, such as fingering and dewetting are being reviewed separately in Chapter 3. Chapter 4 details the properties of the surfactants and the gels that are used, the experimental set-up and the visualization technique that is employed in order to capture images of the spreading process. A section presenting the results of the rheological characterization of the gels in full detail is also included. The results of the spreading experiments are presented in Chapter 5, together with illustrations of the different morphologies observed and of the spatio-temporal evolution of the patterns. Quantitative and qualitative comparisons between the results of different

surfactants and different gel layers are made as well as with varying the system parameters. This is followed by a determination of the relative strength of Marangoni forces over gravitational and diffusive forces. Chapter 6 provides a discussion of the various experimental results. Of main interest is the understanding of the spreading mechanism that is responsible for the observed phenomena, and of the factors that initiate or hinder the pattern formations in particular. Concluding remarks and recommendations for future work are given in Chapter 7.

Chapter 2

Background

Synopsis

Background knowledge that is necessary for the understanding of the surfactant-induced spreading over various substrates is provided in this Chapter. Information on the nature and the various applications of surfactants and polymer gels is presented, since these two types of materials are of central importance in this PhD thesis. A spreading effect that is highly associated with the presence of surfactants, the so-called *Marangoni Effect*, is also described. Marangoni spreading is further categorized into spreading over thin films and spreading over deep fluid layers and an overview of the significant relevant studies that exist in the literature is presented. In these studies, the efforts by various researchers to predict and determine the value of the spreading exponent, n , of the power law $L(t) \sim kt^n$ that describes how the spreading front advances with time are highlighted. A separate section of this Chapter focuses on an intriguing property of a certain class of surfactants that are termed “superspreaders” to promote very rapid spreading, even over very hydrophobic substrates.

2.1 Surfactants

The term “surfactants” stands for “SURFace ACTive AgeNTS”. These materials have the ability to lower the surface tension of substances, improving their wetting and spreading behaviour. They are amphiphilic compounds, since they contain both hydrophilic and hydrophobic groups. The hydrophilic part of a surfactant molecule is polar (shown schematically as a “head” in Figure 2.1), whilst the hydrophobic part is non-polar (shown schematically as a “tail” in Figure 2.1).

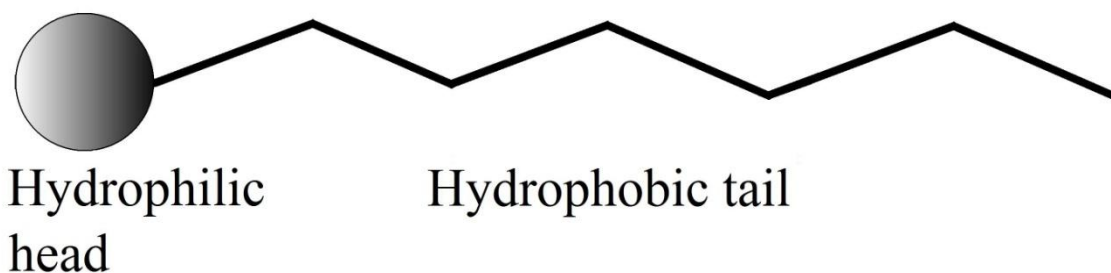


Figure 2.1: A surfactant molecule

Surfactants can be classified into various groups, depending on the character of their hydrophilic group, which can be either ionic or non-ionic, while their hydrophobic group is a hydrocarbon chain (either linear or branched). The various groups that surfactants can be categorised into are:

1. IONIC

Their hydrophilic group is charged, either negatively or positively.

- a) Anionic surfactants, where the hydrophilic group is negatively charged. A typical example is SDS (sodium dodecyl sulfate), which is commonly used as a detergent (Jönsson *et al.* 1999).

- b) Cationic surfactants, where the hydrophilic head is positively charged. They are used mainly for surface modification, and a typical example is DTAB (dodecyltrimethylammonium) (Porter 1994).
- c) Zwitterionic surfactants, which contain two oppositely-charged groups, and they are used mainly in shampoos and skin care products. Typical examples are dodecyl betaine and phospholipids.

2. NON-IONIC

Their hydrophilic group is not charged. Typical examples are sugar-based surfactants, and the polyoxyethylenes, which can be used to stabilise oil-in-water emulsions, or in detergents since they are resistant to hard water (Porter 1994).

The critical micelle concentration (cmc) is an important characteristic of a surfactant and is defined as the surfactant concentration at which micelles (surfactant molecule aggregates) are formed.

2.2 Surfactant Spreading over Condensed Phases

The spreading of uncontaminated and surfactant-laden liquids on the surface of condensed phases plays a key role over a wide range of industrial and daily-life applications. These applications include coating flow technology, micro-fluidics, film drainage in emulsions and foams, drying of semi-conductor wafers in micro-electronics, spreading of oils or spreading of herbicides, and ink-jet printing among others (Knoche *et al.* 1991, DeWitt *et al.* 1994, Schwartz *et al.* 1995, Patzer *et al.* 1995, Le 1998, Braun *et al.* 1999, Matar and Craster 2001, Weinstein and Ruschak 2004). In addition, one of the most important applications of surfactants in biology and biomedicine is Surfactant Replacement Therapy (Shapiro 1989, Grotberg 1994 and 2001), where surfactant is added into the lungs of prematurely-born infants who lack sufficient amounts that would normally protect them from any disturbances

in respiration. Therefore, it is not surprising that gaining exact knowledge of the surfactant-driven spreading mechanism and ability to control the parameters that can affect its nature, rate, and extent, has been the centre of attention of researchers worldwide.

Whether a thin layer of a fluid “2” will spread over an underlying fluid “1” or not, is thermodynamically determined by the spreading coefficient, S , (Harkins 1952):

$$S = \sigma_{13} - (\sigma_{23} + \sigma_{12}), \quad (2.1)$$

where σ_{23} , σ_{13} , and σ_{12} indicate the surface tensions of fluid “2”, of the underlying film (fluid “1”), and of the interface between them (fluid “3”) , respectively. In all the studies mentioned herein, fluid “3” is air. In the same manner, for drop of surfactant placed over an underlying fluid substrate, S represents the difference between the surface tension of the uncontaminated (σ_{13}) and the contaminated ($\sigma_{23} + \sigma_{12}$) regions of the substrate. Spontaneous spreading occurs only when $S \geq 0$ (Suciu *et al.* 1970, Huh *et al.* 1975, DiPietro *et al.* 1978, Adamson and Gast 1997). In this case, the uncontaminated region of the underlying fluid film has a higher surface tension than the surfactant contaminated region, and the surfactant spreads spontaneously to a final contact angle of zero. For negative S , there is no spontaneous spreading, and only partial wetting of the substrate and non-zero contact angle can be achieved (de Gennes, 1985). The drop can remain situated over the substrate as a lens-shaped formation (Karapetsas *et al.* 2011b).

The presence of a surfactant can enhance the spreading process and promote spontaneous spreading, since it can lower σ_{23} and possibly σ_{12} , thus ensuring that S would be positive. By disturbing the surface tension of a previously uncontaminated region of an underlying fluid film, the presence of a surfactant-laden drop can generate surface tension gradients at the interfaces upon which is deposited. These surface tension gradients in turn give rise to shear stress at the air-film interface that force fluid (both the surfactant and the underlying film) to

move from regions of lower surface tensions towards regions of higher surface tensions, thus promoting rapid and spontaneous spreading (Edwards *et al.* 1991). This phenomenon is termed *Marangoni Effect*, (Marangoni 1872, Levich 1962, Edwards *et al.*, 1991), and the shear stresses associated with it are termed Marangoni stresses. Various studies on the Marangoni-driven spreading have demonstrated it to be accompanied by a thinning of the film near the area of surfactant deposition (see Gaver and Grotberg 1990 and 1992, Jensen and Grotberg 1992 and 1993, for instance) and by the formation of a thickened front at the surfactant leading edge (Jensen and Grotberg 1993). The studies mentioned here focus on surfactant-driven spreading on thin films (Section 2.2.1), where such height disturbances can be more obvious; however, similar phenomena can also be observed on spreading on thick substrates (Section 2.2.2), (Jensen 1995).

For a surfactant drop of length L_o , spreading over an underlying fluid film of height H_o , surface tension, S_o and viscosity μ (see Figure 2.2A), the characteristic Marangoni velocity, U , is given by equation (2.2):

$$U = \frac{H_o S_o}{\mu L_o} \quad (2.2)$$

During a spreading process, the spreading front advances with time following a power law of the form of $L(t) \sim kt^n$. Here, $L(t)$ denotes the radial extent of spreading (sometimes denoted by $R(t)$), k is the coefficient of the spreading, t is the spreading time and n is the spreading exponent (sometimes denoted by α). The importance of n is high due to the fact that it can provide a signature of the balance of the forces involved in the spreading phenomena. A prediction of the value of the spreading exponent can yield an insight into the mechanisms behind the spreading phenomena. Therefore, the determination of the value of the spreading exponent has been an essential part of the studies that have focused on spreading phenomena

of any type. For example, in the case of small drops spreading on a solid surface in the presence of capillary forces, $n = 1/10$, while in the presence of strong gravitational forces, $n = 1/8$ (Tanner, 1979). De Gennes (1985) proposed the following law:

$$R(t) = \left(\frac{\sigma}{\eta} \Omega^3 \right)^{1/10} \cdot t^{1/10} \quad (2.3)$$

where Ω denotes the droplet volume, and η and σ denote the viscosity and the surface tension of the spreading liquid, respectively.

Marangoni spreading can be categorized into spreading on thin fluid films and on spreading on thick fluid substrates (deep fluid support). For each of these cases, different scaling relationships were found to apply. In general, for a Marangoni-induced spreading process, the value of n has been found to depend on the nature of the underlying layer (either thin film or deep fluid), on the geometry of the problem (either circular or rectangular front, for instance) and on the rate at which the surfactant is being supplied to the underlying layer (infinite or non-infinite source, for instance). An overview of the most significant experimental and theoretical studies on Marangoni spreading on both thin and thick substrates is presented herein. Findings on the spreading exponent value for a wide range of different spreading processes are highlighted for each one of the two cases.

2.2.1 Spreading over Thin Films

For spreading on thin films, the lubrication approximation applies when the length of the surfactant drop is much greater than the height of the film, and thus the aspect ratio $H_o/L_o (= \varepsilon)$ is much less than 1. In addition, εRe , also needs to be less than 1, where Re is the *Reynolds* number which determines the ratio of the inertial forces of a fluid to its drag forces. Borgas and Grotberg (1988) conducted the first theoretical study on the spreading of an insoluble

surfactant monolayer on a thin viscous film. By considering the lubrication approximation, it was predicted that due to Marangoni spreading, the region beneath the advancing drop of surfactant becomes twice as thick as the original height of the film. Gaver and Grotberg (1990) further showed that there is a thinning in the region ahead of the surfactant-contaminated area in order to balance the thickening of the film beneath it. This thinning of the region ahead of the spreading front has been experimentally confirmed by many researchers (see Ahmad and Hansen 1972, Starov *et al.* 1997 and Dussaud *et al.* 1998, for instance). Further ahead of the surfactant leading edge, a thickened front is formed (Jensen and Grotberg 1993). Considering these Marangoni-driven height disturbances, the film height profile can be assumed to have the form illustrated in Figure 2.2B.

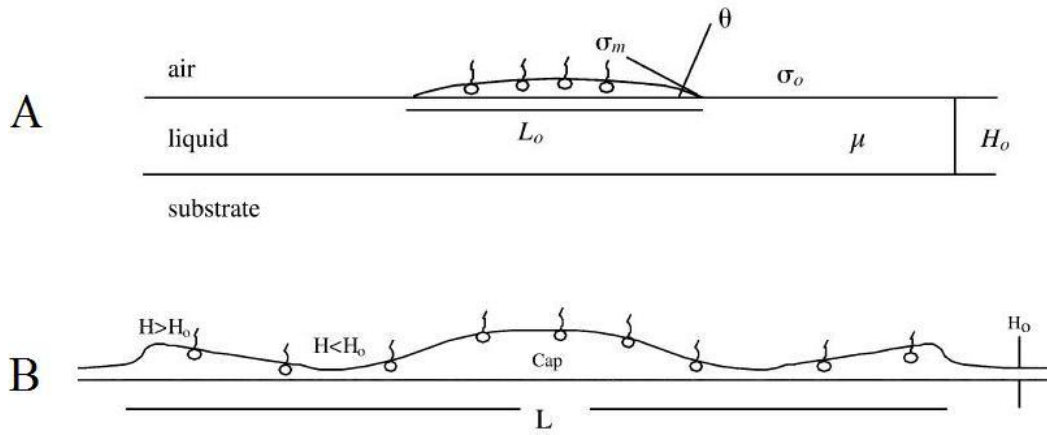


Figure 2.2: (A) A drop of surfactant with surface tension, σ_m , extending a length, L_o , and contact angle θ , on a liquid film of height, H_o , surface tension, σ_o and viscosity, μ .

(B) The spreading profile, H , for a surfactant-driven spreading over a thin liquid film: H_o is the undisturbed film thickness and L is the extent of surfactant spreading. The area labelled “cap” is the area of the original surfactant drop (from Afsar-Siddiqui *et al.* 2003).

An early effort to determine the value of the spreading exponent, n , of the power law of $L(t) \sim kt^n$ for spreading on thin films was made by Ahmad and Hansen (1972), who suggested that radial extent of an insoluble, non-volatile surfactant monolayer provided from an infinite source in 2D rectilinear geometry follows the relation:

$$L \cong \left(\frac{2H_o}{\mu} \right) St^{1/2} \quad (2.4)$$

where H_o is the film thickness, S is the surface tension and μ is the viscosity. The researchers confirmed this experimentally by using oleic acid on thin glycerol films. Borgas and Grotberg (1988) predicted that the advance of a quasi-steady 2D insoluble surfactant front supplied with surfactant in rectilinear geometry follows the relation:

$$L = \left[\frac{2SH_o L_\varepsilon(\delta)}{\mu} \right]^{1/2} t^{1/2} \quad (2.5)$$

where $L_\varepsilon(\delta)$ denotes a numerical factor that is determined a function of Pe .

The theoretical analysis by Gaver and Grotberg (1990) that followed predicts that for an insoluble surfactant monolayer spreading from a finite source in axisymmetric geometry, and in the absence of any gravitational and diffusion forces, the spreading front advances with time with an exponent equal to $1/4$. The $t^{1/4}$ time dependence was confirmed by the experimental works of Gaver & Grotberg (1992) who studied the spreading of an oleic acid monolayer on glycerol films of thicknesses ranging from 0.4 mm to 2 mm.

Jensen and Grotberg (1992) found that in cases where the surfactant monolayer is supplied by an infinite source, the scaling is $t^{1/4}$ to $t^{1/2}$ depending on the geometry of the surfactant drop: for an axisymmetric monolayer drop the scaling is $t^{1/4}$, for a planar strip the scaling is $t^{1/3}$ and for a planar front the scaling is $t^{1/2}$. The $t^{1/2}$ scaling confirms the early findings of Ahmad and Hansen (1972). In cases where the surfactant is provided by a finite source and gravitational

effects are present, Gaver and Grotberg (1990) found that for a radially spreading drop from a finite source, the scaling is $t^{0.2}$, but can increase to $t^{1/2}$ if diffusion effects are also considered. Many other major studies that followed have confirmed the $t^{1/4}$ scaling prediction made by Gaver and Grotberg (1990). The studies of Afsar-Siddiqui *et al.* (2003) on SDS and AOT solutions spreading on very thin water films, of Dussaud and Matar (2005) that considered the spreading of oleic acid on 250 μ m thick glycerol films, and of Fallest *et al.* (2010) on the spreading of the surfactant NBD-PC on thin glycerol films, all find results in good agreement with the predicted $n= 1/4$ values.

Jensen and Grotberg (1993) suggest that solubility does not significantly affect the value of the spreading exponent, however this is questioned by Lee and Starov (2007, 2009). In the latter set of studies, the spreading of surfactant solutions on thin water films is found to proceed in two stages, each one of which is associated with different spreading exponent values that seem to depend on surfactant solubility; the lower the solubility, the higher the value of the spreading exponent, especially in the second stage. The spreading of SDS and highly soluble DTAB shows that for the first stage, which is faster, n is approximately equal to 0.5 for both surfactants, therefore the role of solubility is not very significant. For the second slower stage, the spreading exponent values seem to depend more on solubility, since n is near 0.21 for SDS and near 0.03 for DTAB (Lee and Starov 2009). However, for Tween[®] 20, a surfactant less soluble than both SDS and DTAB, the spreading exponent is much higher in the first stage, namely near 0.75 (Lee and Starov 2007).

2.2.2 Spreading over Thick Substrates

DiPitero *et al.* (1978) provided one of the first studies on surfactant spreading on thick liquid substrate and reported the presence of a unsteady viscous boundary layer beneath the area of surfactant deposition, which is termed Blasius boundary layer (Blasius 1908). The presence of

the latter has been experimentally confirmed by Dussaud and Troian (1998) and Dussaud *et al.* (1998). In most of the relevant studies that exist in the literature, it is assumed that the surface tension gradient is balanced by the Blasius boundary layer (see Dagan 1984, Camp and Berg 1987 and Jensen 1995, for instance).

According to Fay (1969), the advance of a Marangoni-driven, non-volatile and immiscible thin film from a constant concentration source spreading on a deep liquid underlying layer follows the following relation:

$$L(t) = k \frac{S^{1/2}}{(\mu\rho)^{1/4}} t^{3/4} \quad (2.6)$$

Jensen (1995) studied the spreading of an insoluble surfactant monolayer from a finite source. The author reported disturbances in the height of the air/liquid interface that are identified by elevation of the fluid near the contact line and thinning near the spot of surfactant deposition. These height disturbances can be levelled by capillary forces and, at later times, by gravitational effects that can overwhelm Marangoni stresses that dominate initially. The leading edge of the monolayer advances with time according to the following relation:

$$L(t) \sim \left(\frac{\alpha^2 M^2 t^3}{\mu\rho} \right)^{\frac{1}{2(n+2)}} \quad (2.7)$$

where α denotes the surface activity ($\alpha = -d\sigma/d\Gamma$, where Γ is the concentration of the surfactant) and M the total mass of spreading material. For a uniform front of an infinite transverse extent, $n=0$, and (2.7) gives an exponent of 3/4, as predicted before. For a rectilinear strip, $n=1$, and (2.7) gives an exponent of 1/2. For an axisymmetric drop $n=2$, and (2.7) gives an exponent of 3/8. This was experimentally confirmed by de Ryck (1997).

These predictions are highly significant for the work of the present PhD thesis, since the spreading of surfactants on thick underlying gel layers is examined. Therefore, the theoretical arguments behind the derivation of (2.6) are presented in detail in section 6.1 of Chapter 6.

The $t^{3/4}$ scaling prediction has been confirmed by numerous other theoretical studies (Joos and Pintens 1977, Foda and Cox 1980, Jensen, 1995). The same time dependence is also reported in many experimental studies, for instance in the case of PDMS and Triton X-305 spreading on agar gels (Daniels *et al.* 2005, 2007), on the surfactant-induced fracture of a particle raft (Vella *et al.* 2006), on silicon oil spreading on surfactants (Bergeron and Langevin 1996) and on oil spreading on water (Hoult 1972, Camp and Berg 1987). A recent study by Berg (2009) on the spreading kinetics of surfactants that spread along the interface of thick layers of water and decane also confirms the $t^{3/4}$ law. For oil spreading on water, three spreading stages exist, with each one being dominated by different forces (Fay 1969, Hoult 1972). In the first and second stages spreading is mainly driven by gravitational effects and resisted by viscous drag. In the last stage, spreading is promoted by Marangoni forces and surface tension gradients (Frenkel 1946), and it is this exact similarity of the behaviour of oil with that of a surfactant monolayer that has been responsible for motivating original research to be conducted on surfactant spreading on thick fluid support.

2.3 Relative Strength of Marangoni Forces to other Effects

Surfactant-induced height profile disturbances mentioned in Section 2.2.1 have been found to depend on the relative strength of Marangoni forces to other effects which can be present during a spreading process, and in particular to gravitation and to surface and bulk diffusion. The Bond number, Bo , determines the relative strength of Marangoni forces and gravitational effects (Gaver and Grotberg, 1990):

$$Bo \equiv \frac{\rho H^2 g}{S} \quad (2.8)$$

where ρ is the density of the underlying fluid and g denotes the gravitational acceleration. If the value of Bo is much smaller than 1, then gravitational effects are negligible and Marangoni forces dominate the spreading process. If Bo is much greater than 1, then gravity can be significant. This is more likely to happen on thicker films, or on the thickest region of a thin film. Gaver and Grotberg (1990 and 1992) demonstrated that flow reversal can occur when gravitational forces exceed Marangoni stresses, and this can lead the move of fluid from the thickened regions towards the thinned regions of the underlying film, thus levelling the original height profile disturbances.

The *Peclet* number, Pe , determines the relative strength of Marangoni forces over surface and bulk diffusion effects:

$$Pe = \frac{SH_o}{\mu D_x} \quad (2.9)$$

where D_x denotes either the surface diffusivity, D_s , or the bulk diffusivity, D_b . In the former case one may refer to a surface Peclet number, Pe_s , and in the latter to a bulk Peclet number, Pe_b . For focusing either on the surface or in the bulk, if Pe is found to be much greater than 1, then Marangoni stresses dominate. If Pe is much less than 1, surface diffusion effects dominate. However, even when surface diffusion does not seem to be as significant as Marangoni stresses, it still can affect the spreading process by diminishing surface tension gradients and thus relaxing the original disturbances of the film (Afsar-Siddiqui *et al.* 2003). Gaver and Grotberg (1990) showed that with decreasing Pe there is a decrease in film deformations and in the speed of spreading. In addition, when Pe increases, the deformations increase significantly and there large surfactant concentration gradients can be maintained

rather than decreased. This could be surprising if one considers that Marangoni spreading normally reduces the surfactant concentration gradients, but can be explained by the fact that surfactant can be ‘trapped’ and accumulated between regions of the film where significant deformations occur (Afsar-Siddiqui *et al.* 2003).

Jensen and Grotberg (1992) found that capillary forces can also have an effect on the height profile, by levelling the height disturbances in the beginning of the spreading process, where interfacial curvature effects are present in the uncontaminated area, in front of the surfactant spreading edge. Such diminishing of the height disturbances can be also observed in cases where an endogenous surfactant is present prior to external addition of a surfactant drop (Espinosa *et al.* 1993, Jensen 1994, Grotberg *et al.* 1995).

2.4 Superspreading

A particular type of surfactants has attracted the interest of many researchers due to its unique property to reduce significantly the surface tension of water and to promote very rapid spreading on very low energy (hydrophobic) substrates, even in very small quantities. These surfactants are called “superspreaders” and the phenomenon is called “superspreading” (Hill 1998 and 2002). Superspreading has been the centre of attention of many experimental and theoretical studies for the last 20 years, and even though very significant contributions have been recorded, the mechanism responsible for it is not completely understood up to date. However, it has been suggested that a necessary condition for surfactant to be able to superspread is to have a silicon molecule in its structure (He *et al.* 1993). In fact, Silicone-based surfactants and especially trisiloxanes (Halverson *et al.* 2009) have been greatly associated with such superspreading behaviour. A droplet of aqueous trisiloxane surfactant solution leads to spreading that occurs in an area that can be 25 times greater than for non-superspreading surfactants, and 50 times greater than of pure water (Nikolov *et al.* 2002). An

example of the strikingly fast spreading speed of a superspreading trisiloxane surfactant, compared to a non-superspreading surfactant is shown on Figure 2.3.

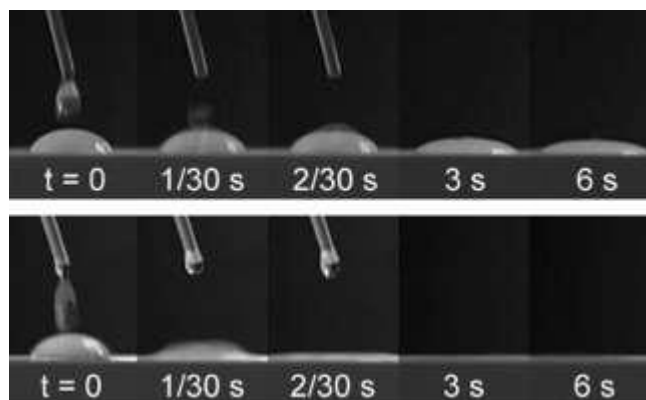


Figure 2.3: The addition of a drop of a non-superspreading surfactant to a sessile water drop does not lead to complete wetting of the moderately hydrophobic surface (top). The addition of a trisiloxane surfactant drop results in more rapid spreading and in complete wetting of the surface (bottom).

An early comparison of the wetting properties of a group of different silicon surfactants on hydrophobic surfaces (Parafilm) was presented by Ananthapadmanabhan *et al.* (1990). Their experiments showed that trisiloxane surfactants exhibited the most complete wetting behaviour. However, fluorocarbon surfactants, which are also able to drastically reduce the surface tension of water, did not appear to be as efficient in wetting as trisiloxane surfactants. Hence, it was concluded that the superspreading behaviour cannot be completely explained by taking in to consideration the surface tension only.

Zhu *et al.* (1994) found that another condition for superspreading is the presence of water vapour, since they observed that trisiloxane surfactants do not spread in dry air. In addition, these researchers state that the formation and presence of vesicle type aggregates is also a requirement for superspreading. This is also confirmed by other researchers (Stoebe *et al.* 1997, Hill 1998). Stoebe *et al.* (1997) explains that these vesicles and other aggregates contribute very effectively to the transfer of surfactant molecules to the contact surfaces.

However this has been questioned by Nikolov *et al.* (2002), where such aggregates are not considered to play such an important role. The latter study focuses more on the role the *Marangoni Effect* on superspreading, by examining the spreading of aqueous Silwet L-77 solution drops on hydrophobic substrates. Silwet L-77 is a highly-popular trisiloxane ethoxylate that is used mainly in agriculture where it exhibits superior spreading behaviour (see also Chapter 4) and has been the subject of numerous studies (Zhu *et al.* 1994, Wagner *et al.* 1999, Tang *et al.* 2008, Radulovic *et al.* 2010). Nikolov *et al.* (2002) demonstrated that the spontaneous spreading of Silwet L-77 is driven by surface tension gradients in the air-liquid interface, thus suggesting the dominant presence of Marangoni stresses. The same group of researchers provided new evidence in support of that view, by conducting two sets of experiments: the one involving the spreading of Silwet L-77 solution on a polystyrene surface, and the other involving the displacement of decalin from the polystyrene, by the same surfactant solution (Chengara *et al.* 2002). In both cases, it was shown once again that the rate of spreading is determined by Marangoni stresses. They also examined an interesting alternative in a more recent study (Chengara *et al.* 2007), where a drop of Silwet L-77 was brought in contact with a drop of water resting on a hydrophobic substrate, thus creating an “imposed” surface tension gradient that caused the latter drop to spread very rapidly. It was found that the spreading of the drop was characterized by an inertial rather than a viscous response and the spreading velocity was consistent with a balance of kinetic energy imparted to the substrate drop and the decrease in its surface energy.

Even though the important contribution of Marangoni stresses to superspreading is well-proven (Nikolov *et al.* 2002, Chengara *et al.* 2002, Chengara *et al.* 2007), an additional feature that enhances the surfactant-driven spreading is the ability of superspreading surfactants to significantly adsorb onto the solid surface, and ahead of the contact line. This ability leads to a significant decrease of surfactant concentration at the air-liquid interface,

which in turn generates a very large surface tension gradient, and has been acknowledged as a key factor by many researchers (Rafai *et al.* 2002, Kumar *et al.* 2003, Clay and Miksis 2004, Kim *et al.* 2006, Karapetsas *et al.* 2011a). Karapetsas *et al.* (2011a) state that such adsorption/desorption of surfactant monomers at the substrate can be achieved in two ways, either free transport from the bulk to the substrate, or transport through the contact line. The superspreading properties of trisiloxanes are usually attributed to the interesting “T”-shaped (often called “hammer-shaped”) structure of the trisiloxane molecule and the large cross-sectional area of the hydrophobic trisiloxane head (Radulovic *et al.* 2010). It is possible that such structure allows these surfactants to adsorb significantly onto the substrate, as suggested by Karapetsas *et al.* (2011a).

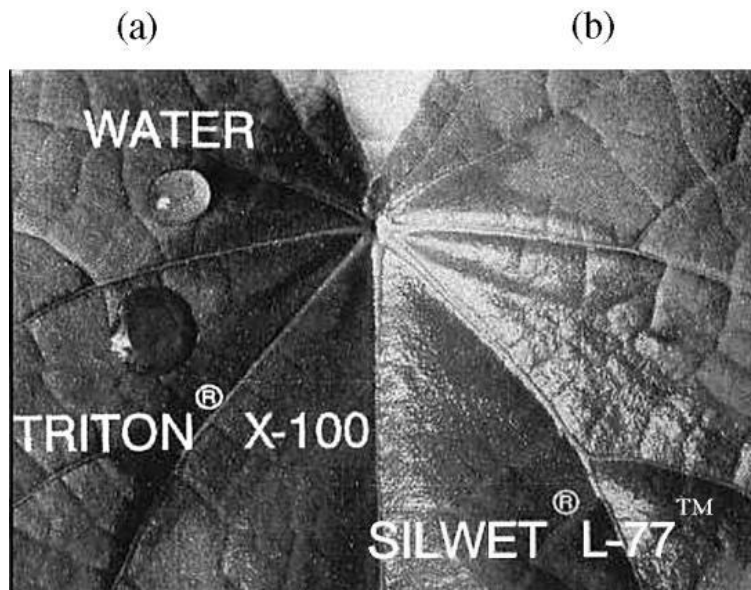


Figure 2.4: Comparison between spreading of (a) a drop of water and a drop of Triton X-100 solution and (b) of Silwet L-77 solution on a velvetleaf surface (from Nikolov *et al.* 2002).

Radulovic *et al.* (2010) suggests that hydrophobicity of the substrate can have a tremendous effect on superspreading of trisiloxanes. The importance of substrate hydrophobicity is highlighted by the fact that many efforts to determine the value of the spreading exponent, n ,

of the power law $L(t) \sim kt^n$, which describes how the radial extent of the drop can advance in time, have shown very different results, even though they same superspreading conditions were used (Rosen *et al.* 1996, Rafai *et al.* 2002, Nikolov *et al.* 2002, Zhang *et al.* 2006, Lee *et al.* 2008, Ivanova *et al.* 2009). What differentiates the above experimental settings, however, are the various degrees of hydrophobicity of the substrates tested. Figure 2.5 illustrates an overview of the different values of the spreading exponents found in the literature, as a function of the hydrophobicity of the surface.

Svitova *et al.* (1998, 1999 and 2001) proposed that the wetting abilities of a trisiloxane surfactant can be characterized by the critical wetting concentration (cwc), which is described as the concentration above which the surfactant exhibits complete wetting behaviour on moderate hydrophobic substrates. It is demonstrated that the value of cwc is independent of the hydrophobicity of the substrate (Ivanova *et al.* 2009), however it does increase while the length of the ethoxy chain increases.

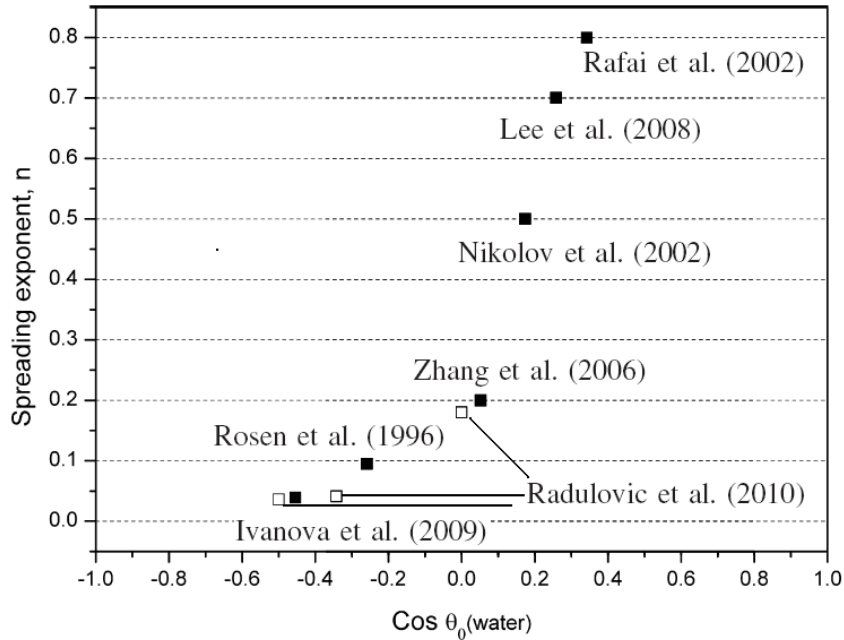


Figure 2.5: Values of the spreading exponent, n , of the power law $L(t) \sim kt^n$, for the spreading of drops of 0.1 wt% trisiloxane solutions, as a function of the substrate hydrophobicity, characterized by the equilibrium contact angle of pure water (from Radulovic *et al.* 2010).

2.6 Gels

Gels can be formed by free radical polymerisation of monomers in the presence of a difunctional cross-linking agent (Dusek 1982, Hu *et al.* 2000, Fernández *et al.* 2005). They are unique formations that are often said to be an intermediate between solids and liquids. This is due to the fact that in certain conditions they can exhibit characteristics of liquid behaviour, like diffusion of small molecules and incompressibility, and at the same time they can behave like solids, i.e. have elastic properties and the ability to retain their shape (Szabó *et al.*, 2000). These observations can be attributed to the structure of polymer gels, that consists of a cross-linked three-dimensional network and of a fluid that fills the space between the network chains. The formation of such networks can be different in different types of gels. For example, an agar gel consists of a network of chains in a double-helix structure, while the corresponding network for a gelatine gel has a triple-helix formation. The network structure provides the solid-like characteristics of a gel, and the fluid between the chains is responsible for its resemblance with liquids (Kanenko *et al.* 2004). Gels of which the dispersion medium is water, are usually termed “hydrogels” (Fernández *et al.* 2005, Matsunaga and Shibayama 2007, Kanai *et al.* 2010).

Both temperature and long storage times can affect the concentration of a gel, by changing its physiochemical properties. This phenomenon is called aging and it is very common among polymers (Wang *et al.* 2003, Tosh *et al.* 2003). It has been demonstrated that the physical structure of a gel can continue to be subject to rearrangements, even for weeks after the original gelation time (Tosh *et al.* 2003). This is due to the fact that increased storage times can increase the formation of the helix structures of the polymer network of a gel (Tosh *et al.* 2003).

Aging effects have been reported for a wide range of gels; Soloukhin *et al.* (2003) studied the aging of polycarbonate of bisphenol-A for 30 months and reported an increase in its storage

modulus and stiffness. Mellema *et al.* (2000) reported changes in the structure and in the pore size of aged casein gels. Aging-induced changes in the rheological and mechanical properties of different silica and doped silica gels have also been reported (Hunt and Ayers 2001).

A very common observation regarding aging is the increase in the viscosity of the material with time. This has been reported for both agar (Craig *et al.* 1962) and gelatine samples (Peng *et al.* 2007) that were stored and allowed to age for more than 30 days. Peng *et al.* (2007) suggest that this increase in viscosity of the gel is the result of a viscoelastic separation mode. For aqueous gel solutions, evaporation can also alter the concentration of the polymer and therefore the strength of the gel. In our work, gels are used during a period of up to 72 after gelation, therefore ageing effects are limited, apart from changes in their storage (G') and loss moduli (G'') during the first few hours after gelation. For instance, the storage modulus of a 0.14 wt% agar gel solution was found to have a value of 7 Pa, 7 hours after gelation, and a value of 17.5 Pa, 28 hours after gelation. After that period of time, the value of the storage modulus was found to remain practically constant (see also section 4.6.2 and Figure 4.7 in Chapter 4).

Gels are used in many biomedical applications, since they can simulate biological tissues (Peppas and Langer 1994). In the oil industry, gels have been used for many years in order to control the conformance of oil production in wells. It has been demonstrated that larger gel volumes can result in incremental oil production (Sydansk and Moore 1992, Ricks and Portwood 2000). A process that is termed “gel treatment” and is described as the emplacement, fracturing and subsequent removal of gels in reservoirs, is used to limit water production whilst retaining oil or gas production. This is based on the ability of certain pore-filling gels to reduce permeability to water much more than to oil (Seright 2006 and 2008).

The interaction between surfactants and gels apply widely in biochemistry, where polyacrylamide gels are used in the so-called “SDS-PAGE electrophoresis” technique, to

separate proteins according to their molecular weights in the presence of SDS (Weber *et al.* 1972, Hartinger *et al.* 1996, Hatch *et al.* 2006). In addition, it has been demonstrated that the presence of surfactants can alter properties of gels such as viscosity, and gelling and melting temperatures (Prasad *et al.* 2005).

2.7 Spreading over Gel Layers

Even though numerous studies on fluid spreading over liquids and solids exist in the literature, very few of them up to date consider the spreading over gel-like materials. Szabó *et al.* (2000) studied the spreading of a film-forming liquid on polymer gels. Droplets of ethanol or tetrahydrofuran (THF) were spread on poly (2-acrylamido-2-methyl-propanesulfonic acid) (PAMS) gels. It was found that the mechanism, and hence the kinetics, of spreading on a gel surface is significantly different from that on a liquid or solid surface. Circular spreading was observed, with rates intermediate between those shown on liquid and solid substrates. The way that the spreading front advances with time was interpreted by the following power law:

$$R(t) = Kt^{1/2} \quad (2.10)$$

where K denotes the spreading prefactor which can be related to the “mesh” size (ξ) of the gel network. Figure 2.6 shows snapshots taken at different moments from the spreading of ethanol on water, gel and glass, with the time being measured in 1/30 s units. It is observed that the spreading process on a gel surface proceeds approximately four times slower than on water, and eight times faster than on a glass surface.

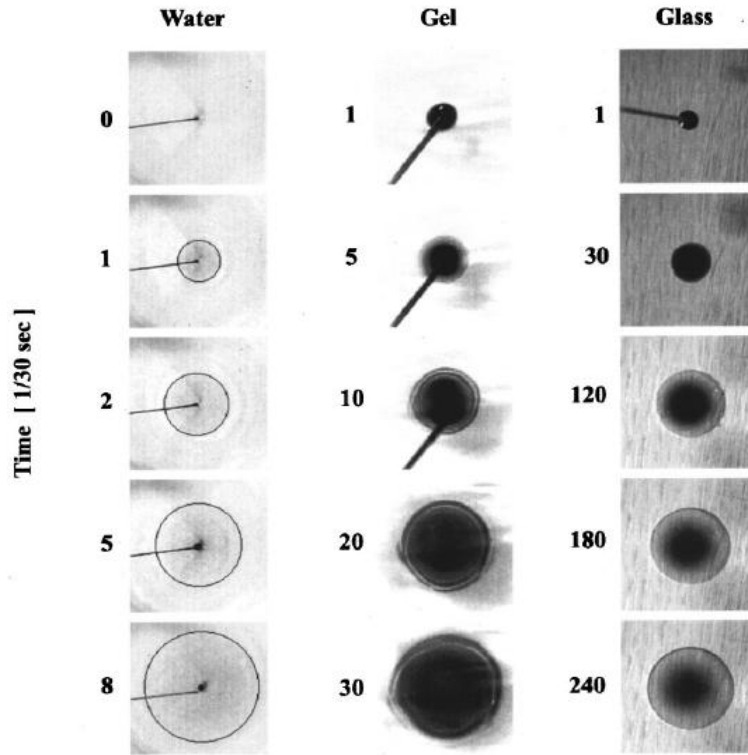


Fig. 2.6: Spreading of ethanol on water, gel and glass (from Szabó *et al.* 2000).

Kaneko *et al.* (2004), conducted similar experiments. A comparable study of the spreading kinetics of polymer solutions and gels of the same polymer concentration was performed, in order to clarify whether the spreading of a liquid on a gel substrate shows an intermediate behaviour between those on solid and liquid substrates. The spreading liquids were ethanol and a mixture of silicon oils and diethyl ether spreading, and the gels were once again poly(2-acrylamido-2-methyl-propanesulfonic acid) (PAMS) gels. The researchers focused mainly on the comparison of the exponent, n (which characterizes the underlying surface), of the spreading front, on the different materials that their behaviour was studied. For the spreading kinetics of liquids on different surfaces, it was shown that the leading edge (L) advances with time according to the following power-law:

$$L = K (t + c)^n \quad (2.11)$$

where K is the spreading factor and c is a constant considering the initial condition of the spreading liquids. For a liquid surface, n is $3/4$ (in agreement with equation 2.6) and for a solid surface is $1/10$ (in agreement with equation 2.3). The general conclusion of this study is that the spreading kinetics of hard, soft and intermediate surfaces can be characterized by power-law dependence. Concerning the polymer solutions, their spreading kinetics were found to be very sensitive to the polymer concentration. The more the polymer concentration increases, the value of n of the polymer solutions decreases between the upper ($3/4$) and the lower ($1/10$) theoretical limits for viscous liquids and solids, respectively. When the polymer concentration reaches a value at which a transient network is formed (1.3 wt %), the dependence on concentration is no longer observed. Concerning the polymer gels, it was observed that the values of n did not change by changing the polymer concentration, hence the spreading on an elastic gel surface is almost similar to the spreading on a solid surface. Universal values of n were identified and expressed as 0.45 and 0.3 for miscible and non-miscible spreading liquids, respectively. The difference of behaviour between spreading on polymer gels and on polymer solutions can be credited to the elastic nature of the gels.

Summary

When a surfactant is deposited on an underlying film, the surface tension is lowered and spreading is enhanced. The surface tension gradient between the surfactant-contaminated and the uncontaminated regions of the film, generate Marangoni stresses, which cause fluid to move towards regions of higher surface tension. Historically, most of the studies on surfactant-driven spreading have been focused either on spreading over thin films, or spreading over deep fluid layers. For each one of these categories, the spreading front has been found to advance with time following different scaling relationships. Some surfactants are called “superspreaders” since they can promote even more rapid spreading, on very

hydrophobic surfaces. Such “superspreading” behaviour is usually attributed to trisiloxanes. Marangoni spreading has been shown to be accompanied by disturbances in the height profile of the underlying fluid. These disturbances are identified by thinning or thickening of various regions of the substrate. They can occur on both thin and thick films, even though they are more obvious in the former case. The presence of such disturbances, however, is not the only instability that can be observed during a surfactant-induced spreading process. A more intriguing instability that is associated with the forming of protruding “fingers” on the underlying surface has been reported over a wide range of different experimental settings that include non-superspreading and superspreading surfactants. “Fingering” instabilities have received great attention by numerous researchers worldwide; therefore, it is necessary to dedicate the following Chapter of the present thesis to view its features separately.

Chapter 3

Surfactant-Driven Instabilities: Fingering, cracking and dewetting

Synopsis

The previous Chapter presented an overview of the existing literature on surfactant-driven spreading in the absence of any disturbances apart from changes in the height profile. However, it has been observed that the spreading of surfactant-laden fluids on condensed phases can also be accompanied by different types of more intriguing instabilities. The most common of such instabilities is called “fingering” due to its long protruding nature. Surfactant-driven fingering instabilities have been the subject of various experimental and theoretical studies, for the last 30 years, since they were reported for the first time. Although the origin of the fingers has been discussed thoroughly, no conclusive argument has yet appeared and the mechanism behind this behaviour remains a hot topic among researchers. Recently, a different form of this instability has been observed, via the formation of disturbances that look more like growing cracks rather than fingers, after the spreading of surfactants on gels and on particle rafts. In other cases, specific types of surfactants exhibit autophobing and dewetting behaviour. This Chapter presents the most significant published studies where all the above types of instabilities have been reported.

3.1 Fingering

3.1. Experimental Studies

Fingering instabilities have been observed with a variety of surfactants and over a wide range of experimental conditions, including vertical and horizontal substrate orientation, finite and infinite surfactant supply, rectilinear and axisymmetric geometry. Such instabilities were reported for the first time by Marmur and Lelah in 1981, during their study of the spreading of various aqueous surfactant solutions on the surface of horizontal glass slides. The surfactants they used were the anionic AOT (sodium bis [2-ethyl-hexyl] sulfosuccinate) and SDBS, (sodium dodecyl benzene sulfonate) and the non-ionic Triton X-100, Span 20 and Brij 35. All the above surfactants showed stable spreading for concentrations below the cmc. On the contrary, above the cmc, the formation of spreading fingers was reported, for both anionic and non-anionic surfactants. Especially for the spreading of SDBS, there was very obvious branching. The authors suggested that the formation and development of these fingers can be explained in terms of the adsorption of surfactant molecules onto the solid surface that subsequently turns from hydrophilic to hydrophobic. These surfactant molecules were moved ahead of the bulk of the drop due to the spreading of the primary film. The formation of fingers above the cmc is linked with the high degree of heterogeneities in the surface that is caused by the combination of horizontal and vertical orientations of the adsorbed surfactant molecules.

Troian *et al.* (1989a) conducted similar experiments observing the spreading of AOT on horizontal glass substrates pre-wetted with water films of thicknesses between 0.1 μm to 1 μm . Contrary to Marmur and Lelah (1981), fingering was observed (see Figure 3.1) at surfactant concentrations both above and below the cmc. The nature of the fingering patterns was linked for the first time with the thickness of the underlying film. For a 0.1 μm water film the fingers were narrower, sharp-tipped and more branched; for a 1 μm water film, the fingers were more

broad and straight. The width of the fingers also seemed to depend on the thickness of the film. The fingers were found to grow in time as $t^{0.7}$ for the $1\mu\text{m}$ films and $t^{0.66}$ for the $0.1\mu\text{m}$ films; a difference attributed to experimental error. However, the authors suggested that different experimental conditions such as using either very highly or very lowly concentrated surfactant solutions, or using dry substrates or substrates pre-coated with surfactant may result in absence of such fingering instability (see also Frank and Garoff, 1995a). They concluded that fingering can be generated due to the Marangoni Effect, and if a sufficient concentration gradient exists between an appropriate surfactant solution and an appropriate underlying film.

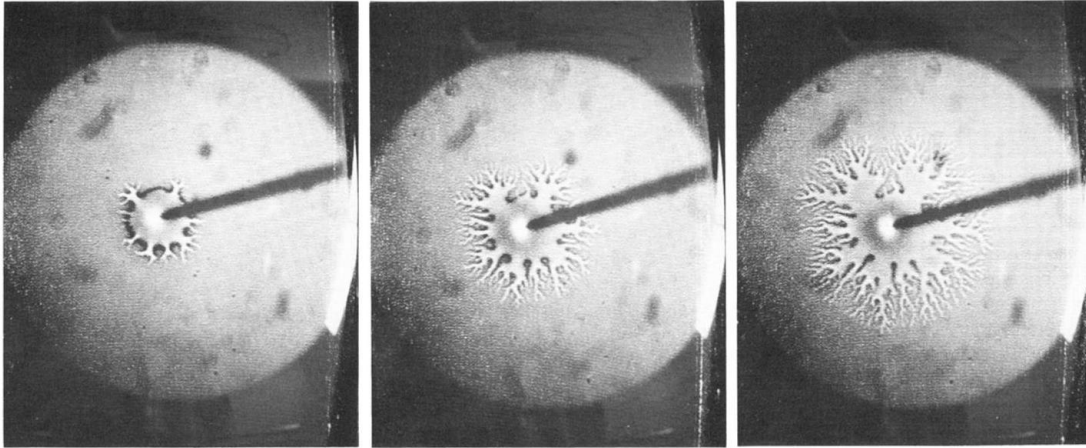


Fig. 3.1: Fingering patterns formed 0.1sec, 0.5 sec and 1 sec after the spreading of a $2\mu\text{l}$ drop 0.4 cmc AOT on a $1\mu\text{m}$ water film (from Troian et al. 1989a).

Frank and Garoff (1995a, 1996) suggested that a repulsive force between the surfactant polar head and the underlying substrate is necessary for the development of fingering. In addition, the spreading behaviour of a specific surfactant is not the same in all cases and on any underlying substrate, but it depends on the interaction between the surfactant head group and the substrate. In this study, “dendrites” were observed after the spreading of cationic CTAB (cetyltrimethylammonium bromide) and anionic SDS (sodium dodecyl sulphate) surfactants on negatively charged silicon wafers and on positively charged sapphire discs. The

experiments were run at ambient humidity and the amount of water absorbed onto their solid substrate was of the order of a monolayer. The results showed that, when spreading on the silicon wafer, CTAB exhibits autophobing and SDS promotes the formation of fingering patterns. However, when the sapphire disks are used, SDS autophobes while the spreading of CTAB is accompanied by fingering. It was then concluded that the spreading behaviour of a specific surfactant is not the same in all cases and on any underlying substrate, but depends on the interaction between the surfactant polar head and the underlying substrate. It was also demonstrated that fingering can occur even on very thin water films. The latter was confirmed by Birch *et al.* (1995).

Studies of the fingering behaviour that followed were focused on the effect of properties such as solvent viscosity and relative humidity, h_{rel} , on the formation of fingers (Bardon *et al.* 1996; Cachile and Cazabat, 1999; Cachile *et al.* 1999). This was examined by spreading the polyoxyethylene surfactants $C_{12}E_4$ (a solid) and $C_{12}E_{10}$ (a liquid) in ethylene and diethylene glycol, on horizontal, uncoated silicon wafers (Figure 3.2a). For h_{rel} smaller than 30%, no instabilities were observed and the spreading front was found to advance with time $t^{1/10}$, confirming the prediction made by Tanner (1979) for the spreading of small drops under capillary effects only. Fingers were formed as h_{rel} increased.

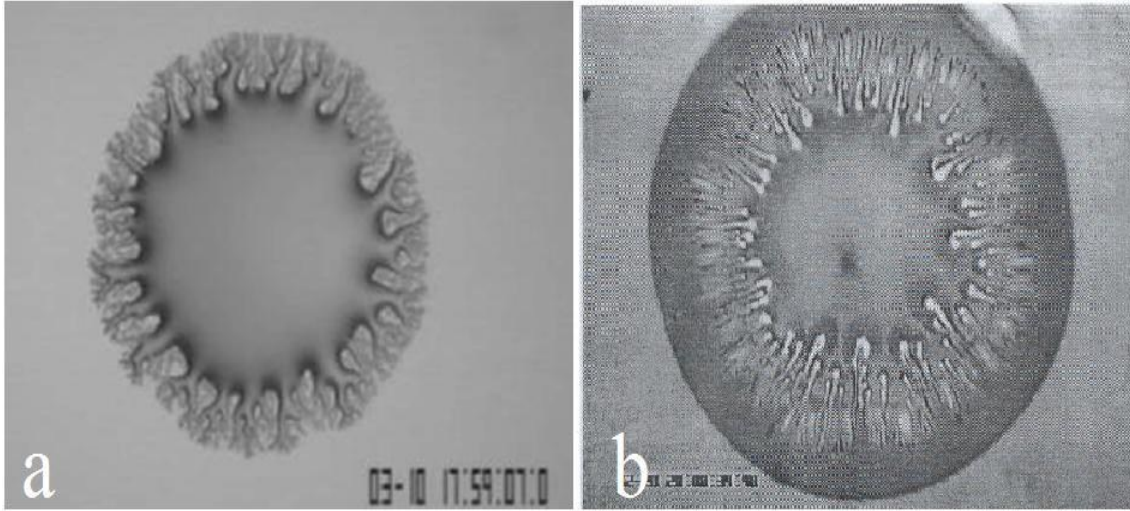


Figure 3.2: Fingering that accompanies the spreading of a droplet of $C_{12}E_{10}$ on (a) a bare oxidised silicon wafer (from Cachile et al. 1999), (b) on a surface pre-coated with ethylene glycol (from Cachile et al. 2002).

The width of the fingers seems to be affected by the surfactant concentration, with thinner fingers being reported for increasing concentration. The presence of $C_{12}E_4$, or of ethylene glycol as a solvent, can give rise to the formation of wider arms. Mobility measurements for the surfactants showed that both become more mobile when the relative humidity is high, and that between them $C_{12}E_4$ is more mobile. The existence of a precursor film ahead of the region of drop deposition was reported. Near the contact line, adsorption of the surfactant onto the substrate generates a surface tension gradient at the liquid-air interface and provokes the formation of a hydrophobic barrier at the solid surface. While the mobility of the surfactant increases, less surfactant adsorbs onto the solid substrate and this results in the forming of thicker fingers. For the specific set-up, the spreading kinetics (see Figure 3.3) show that the radius from the centre of the drop to the leading surfactant edge, R_o , advances in time as $t^{1/2}$ and the radius from the centre to the edge of the drop, R_c , advances in time as $t^{0.25-0.3}$. There is no evident trend for the evolution of the length of the fingers, L_f , thus it is assumed by the

researchers that the fingers originate from a minimum in thickness at the edge of the spreading drop.

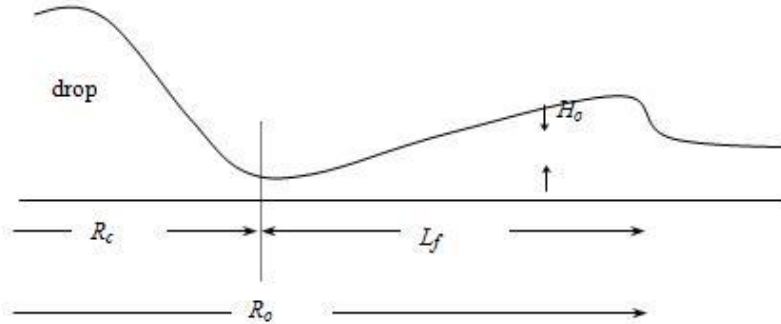


Figure 3.3: Schematic diagram of the thickness profile for a drop of spreading surfactant solution. R_c is the radius from the centre to the edge of the drop, L_f is the length of the fingers and R_o is the radius from the centre of the drop to the leading surfactant edge. The dotted line shows the region of the minimum film thickness (from Cachile *et al.* 1999).

The formation of fingering patterns was also observed after the spreading of the same surfactants on pre-coated silicon wafers (Cachile *et al.* 2002). However, these fingering patterns were different morphologically to those observed in the spreading on an uncoated surface, as Figure 3.2 shows. In this case, the surfactant leading edge is more obvious, and a mark of the original position of the fingers remains visible inside the spreading drop. The fingers are now straighter and less branched. Since fingering patterns are observed even though the solvent used in this study initially wetted the underlying substrate perfectly, the researchers clearly rule out van der Waals forces as being a significant ingredient of such instabilities. The minimum film thickness is now located at the tips of the fingers and not at the edge of the central drop as before (Figure 3.4). The spreading kinetics show that the surfactant leading edge, R_o , the radial extent of the fingers, R_f , and the distance from the minimum thickness to the leading edge, L_e , grow with time as $t^{1/2}$. Once again it was demonstrated that the film thickness can affect the spreading dynamics, since the values of the

spreading exponent of the drop was found to increase from 0.3 – 0.45 with increasing H_o . The researchers also suggest that the fingering instability could be the result of the magnification of perturbations at the contact line, as it was also proposed by Bertozzi and Brenner (1997). According to this, a small perturbation of size, E , to a thin precursor film of thickness, b , ahead of the spreading front can be amplified by a factor of E/b as the front travels over it, thus breaking the front up and generating the formation of the fingers.

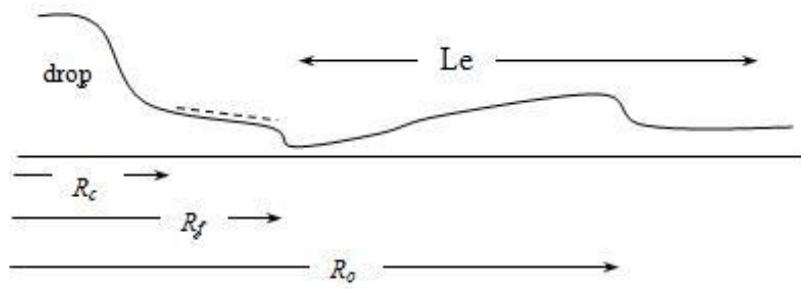


Figure 3.4: Schematic diagram of the thickness profile for a droplet of surfactant spreading over a thin liquid film. The dotted line shows the location behind the minimum film thickness region, R_o is the surfactant leading edge, R_f is the radial extent of the fingers and L_e is the distance from the minimum thickness to the leading edge. (from Cachile et al. 2002).

He and Ketterson (1995) reported narrow branching fingers after the spreading of a monolayer of valinomycin (an insoluble, ring-shaped surfactant) on a $1\mu\text{m}$ water film on a vertical glass slide. It was demonstrated that initially the surfactant front spreads upwards, while promoting fingering (Figure 3.5a). The spreading, which was found to initially advance with time as $t^{1/2}$ (confirming the experimental findings) gradually slows and stops advancing after approximately 5 minutes from the time of the spreading. It was suggested that hindering of further growth could not be caused by gravitational forces, since an estimation of the Bond number showed that gravitational effects are not significant, and should be attributed instead to the branching of the fingers. Fischer *et al.* (2001) also observed highly branching fingers, in

the thin region ahead of an oleic acid drop spread on a 10 μ m layer of glycerol on a silicon wafer. These patterns were described as “streamlets” (Figure 3.5b). What is important in this study is that it was demonstrated that undissolved surfactants can also exhibit fingering instability behaviour.

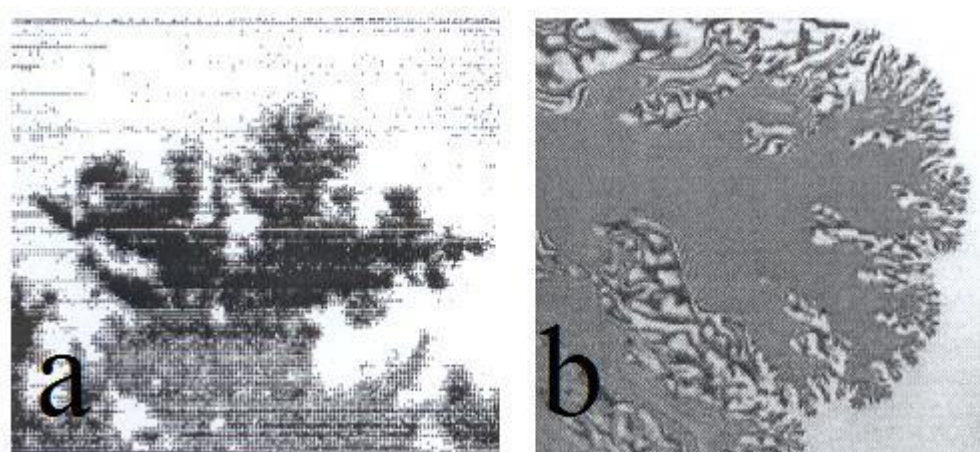


Figure 3.5: (a) Formation of fingering patterns during the spreading of valinomycin on a water film with $S = 5$ mN/m (from He and Ketterson 1995), (b) Fingering patterns observed during the spreading of oleic acid on a thin glycerol film (from Fischer et al. 2001).

A study was also conducted by Afsar-Siddiqui *et al.* (2003) on the spreading of surfactants on thin water films resting on glass substrates. Two types of surfactants were spread on films up to 100 μ m in thickness: AOT was used in order to examine the role of sparingly soluble anionic surfactants on the spreading, and SDS was chosen to examine the role of highly soluble anionic surfactants. This work quantifies the combined effect of solubility and the presence of high surfactant concentrations, showing them to be destabilizing. It also highlights the effect of the film thickness on the dynamics of such systems. The researchers show that below the cmc, the fingering instability is more likely to occur on thinner films, while it was pointed out that at significantly higher concentrations the reverse trend occurs. The spreading front was found to advance in time as $t^{1/4}$. It was also shown that the average finger wavelength is proportional

to $H_b^{2/3}$, where H_b denotes the undisturbed film thickness. This scaling reveals a Marangoni-driven fingering instability, contrary to a van der Waals-driven fingering instability that would have given rise to an H_b^2 scaling instead. In general, Marangoni forces were found to be dominant over surface diffusive effects and gravitational forces.

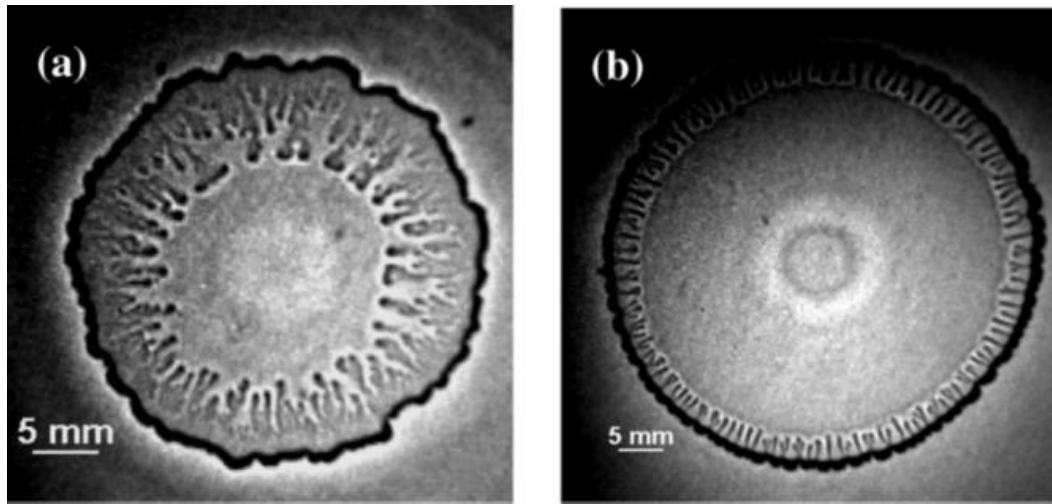


Figure 3.6: Fingering instabilities observed during the spreading of a 9 ml drop of 1.2 cmc SDS solution on (a) a 25 mm water film and (b) a 100 mm water film (From Afsar-Siddiqui et al. 2003).

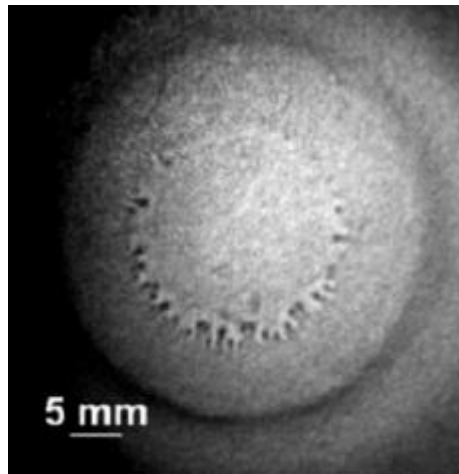


Figure 3.7: Fingering instability observed during the spreading of a 9 μ l drop of 2.8 cmc SDS solution on a 50 μ m thick water film (From Afsar-Siddiqui et al. 2003).

In a more recent study, Cazabat and co-workers (2004) focused on the role of surfactant concentration, while the thickness of the solvent film is preset. $C_{12}E_4$ and $C_{12}E_{10}$ (a liquid) were again used on silicon wafers, and some very important features of the flow were observed, which were not captured by previous models on surfactant spreading: the surfactant-driven thickened rim was found to advance in time like $t^{1/2}$ (consistent with reservoir feeding of surfactant), instead of $t^{1/4}$. This can be justified by the existence of a newly-found mechanism that generates a behaviour that mimics the one that is linked with the spreading of a front being supplied from an infinite reservoir of surfactant. The minimum in the film thickness appears in concentrations above the cmc or for spreading over solid substrates on pre-coated with thick films. On the other hand, in cases of very thin films or very solid substrates, the minimum is absent, contrary to what previous studies had shown. The significant observation is that even though there was no minimum in film thickness, there were still fingering patterns which appear to grow directly out from the side of the drop. It was found in fact that the length and width of the fingers decrease with increasing surfactant concentration.

The degree of the branching of the fingering pattern was also found to decrease when the concentration increased above 0.5cmc, in the case of $C_{12}E_{10}$. However, branching was less obvious for thicker solvent films and in the case of $C_{12}E_4$ there was no branching at all on wafers having a solvent film, where the main drop does not spread.

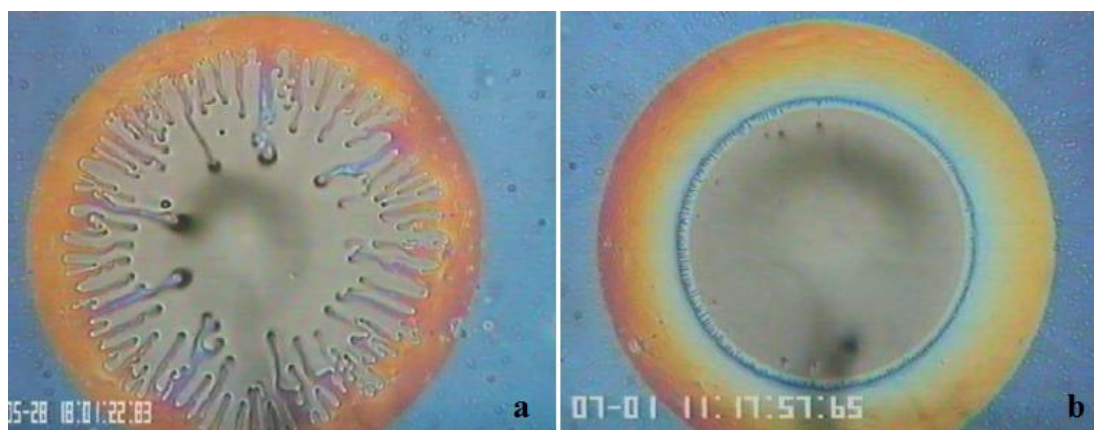


Figure 3.8: Drops of $C_{12}E_{10}$ solution with concentrations 0.5cmc (a) and 1.5cmc (b), spreading on a 120nm thick film (From Hamraoui *et al.* 2004).

This indicates that large surface tension gradients and a reduced interfacial mobility of the surfactant are favourable to branching. The surfactant mobility can be reduced because the molecule is large or because the film is thin. The wetting behaviour of $C_{12}E_4$ was not really understood, and it was suggested that it is a good example of high surface mobility, while $C_{12}E_{10}$ is an example of fast exchange with the bulk.

Fingering instability behaviour has also been reported in the presence of superspreading surfactants. Stoebe *et al.* (1996) have reported the formation of fingers during the spreading of trisiloxane surfactants on organosulfur monolayers. However, the length of the fingers was found to be less than 10% of the dynamic droplet radius, thus the fingering was ignored in the analysis of their experiment. The spreading of Silwet L-77 on a Parafilm surface is accompanied by the formation of short, straight and round-tipped fingers, ahead of which a thin precursor film is observed (Zhu *et al.* 1994). Fingers have also been reported to form during the spreading of the same surfactant on a polystyrene dish (Nikolov *et al.* 2002) and on a very thin decalin film (Chengara *et al.* 2002).

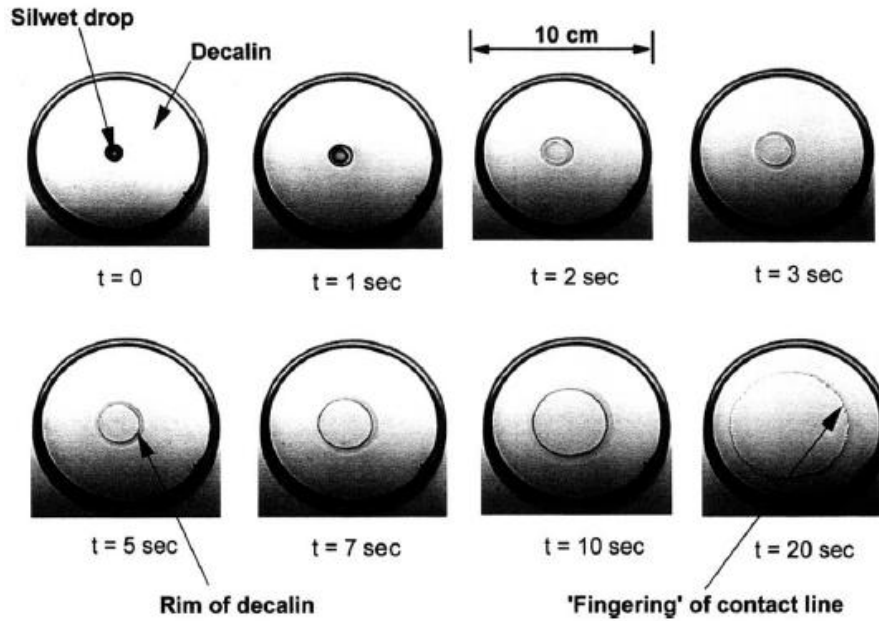


Figure 3.9: Spreading of a 30 μl droplet of 0.1% wt Silwet L-77 solution on a 30 μm thick decalin film. Fingering near the edge of the contact line is observed after 20 sec from the time of droplet deposition (from Chengara *et al.* 2002).

3.1.2 Theoretical Studies

Apart from the various experimental studies, there have also been numerous efforts to model the fingering instability, motivated by the need to isolate the physical mechanism responsible for it. The first effort to investigate the fingering instability mechanism was provided by Troian *et al.* (1989b and 1990). In this work, the existence of a large surface tension gradient which is induced across a thin region ahead of the position of drop deposition is reported. At the leading edge, which represents a boundary between the contaminated and uncontaminated areas of the film, there is a thickening of the film. The advancing front and the droplet edge both spread in time as $t^{1/2}$, confirming the findings of Gaver and Grotberg (1990). The authors likened the mechanism behind a surfactant-induced fingering instability behaviour with a similar mechanism that drives the so-called Saffman-Taylor instability (Saffman and Taylor

1958) between two fluids in a Hele-Shaw cell (Daccord *et al.* 1986). The velocity of the Hele-Shaw flow, U_{HS} , in the direction of the fingers is given by equation 3.1:

$$U_{HS} = -\frac{b_{ch}^2}{12\mu} \left(\frac{\partial P}{\partial x} + \rho g \right) \quad (3.1)$$

where dP/dx denotes the pressure gradient, b_{ch} denotes the width of the channel, and $b^2/12\mu$ is the mobility factor. In the case of Marangoni spreading, the average fluid velocity, U , is given by equation 3.2:

$$U = \frac{h}{\mu} \left(\frac{d\sigma}{dx} \right) \quad (3.2)$$

where h/μ denotes the mobility factor. The pressure gradient in equation (3.1) is equivalent to the surface tension gradient in equation (3.2). The Saffman-Taylor instability is caused by adverse mobility gradient that is established between the less viscous fluid and the more viscous fluid, since the former is more mobile than the latter. According to Troian *et al.* (1989b) a similar adverse mobility gradient is responsible for the fingering instability that occurs in the presence of surfactants. In this case, there is a larger surface tension gradient in the thinner region of the film, therefore a tip of a finger that is situated there will move faster than other protrusions in nearby spots. It is by this mechanism of Laplacian growth that the fingers are believed to grow and develop (Troian *et al.* 1989b).

Matar and Troian (1996 and 1997) conducted a more rigorous stability analysis, which allowed disturbances in both the thickness of the underlying film and the concentration of the surfactant, revealed that the flow was stable to disturbances. The result was still the same even

when weaker capillary and diffusion forces were included (Matar and Troian 2008). The same group of researchers (Matar and Troian 1997, 1998, 1999a and 1999b) studied the spreading of a surfactant monolayer on a liquid film of dimensionless thickness. The researchers worked on regimes where Marangoni stresses, surface diffusion, capillarity and van der Waals forces were present. Linear stability, transient growth analysis and numerical simulations showed that only with significant van der Waals forces being present, there can be a continuing growth of the fingers. Warner *et al.* (2002a and 2002b) showed that even with the absence of van der Waals forces, significant transient perturbation growth can occur, not being localized in the thinning region, and being followed by decay. Fischer and Troian (2003) showed again that perturbation growth can occur in the absence of van der Waals forces, provided there is continuous feeding of surfactant at the flow origin.

The same group of researchers (Warner *et al.* 2004a and 2004b) studied the linear and non-linear stability of thick insoluble and soluble surfactant phases spreading on much thinner liquid films. They introduced the concept of the thickness disparity, an ingredient missing from previous studies; the large thickness disparity between the surfactant droplet and the thin underlying film give rise to adverse mobility gradients that, in turn, promote the formation of fingering patterns.

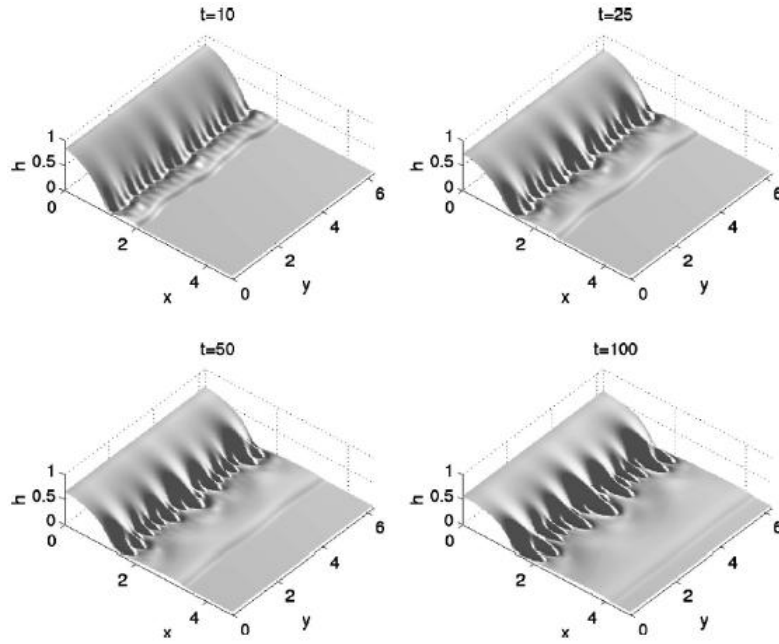


Figure 3.10: Evolution of the film thickness (h) showing the development of fingers in the thinning region (from Warner *et al.* 2004a).

The results of this work suggest that although van der Waals forces may be important in the case of very thin fluid layers, their presence is not necessary for the fingering instability to occur, and thus, they need to be neglected from future studies. It was also shown that the finger growth is stronger in cases where droplets are spreading on thinner underlying films, while for very thick films the growth is decaying, or non-existent. Furthermore, the surfactant solubility was found to have a de-stabilizing effect on the spreading process, with the exception being the case of very highly soluble surfactants where the reverse trend occurs.

These studies were extended by the work of Edmonstone *et al.* (2006) which covered cases in which droplets of surfactant solutions spread on very thin liquid layers, and at high concentrations. The spreading behaviour of surfactants beyond their cmc was examined. This work considered the significant experimental observations made by Hamraoui *et al.* 2004 and is important since it is one of the few studies on the effects that micellar aggregates have on the dynamic evolution of a free surface, because of their formation and breakup. Furthermore, it presented a useful framework for modelling the large scale-evolution of films, threads and

jets laden with surfactant beyond the cmc. It was suggested that the most significant parameters on the flow profile are M , the dimensionless mass of the surfactant that is deposited, and R , a parameter that shows the preference of the surfactant to form micelles. The development of a protuberance that appears at the edge of the drop is caused by the increase of M . Further increase of M separates this protuberance from the drop and a secondary front that lies behind a leading front is formed. In the case that R is increasing, there is a monotonic destabilisation of the spreading process. The fingers are formed, because these features are vulnerable to oblique perturbations.

3.2 Cracking

Daniels *et al.* (2005, 2007) studied the spreading dynamics of non-ionic Triton X-305 (octylphenoxy polyethoxy ethanol) and PDMS (polydimethylsiloxane) droplets on agar gels. By varying the concentration of agar, the spreading behaviour could be made to resemble that of liquid-on-liquid spreading at one extreme and liquid-on-solid spreading at the other. These investigators demonstrated the possibility that the gel undergoes failure as a result of the stresses generated at the droplet-gel interface due to the gradients in interfacial surfactant concentration. They distinguish between two different types of behaviour for weak and strong agar gels depending on the value of the shear modulus, G . For $G \leq 30$ Pa, there is evidence of gel failure and the drop is observed to spread into cracking “arms”, which resemble a “starburst” (Figures 3.11 and 3.12). These cracks have been described as having steep sides extending into the gel surface and being filled with surfactant material.

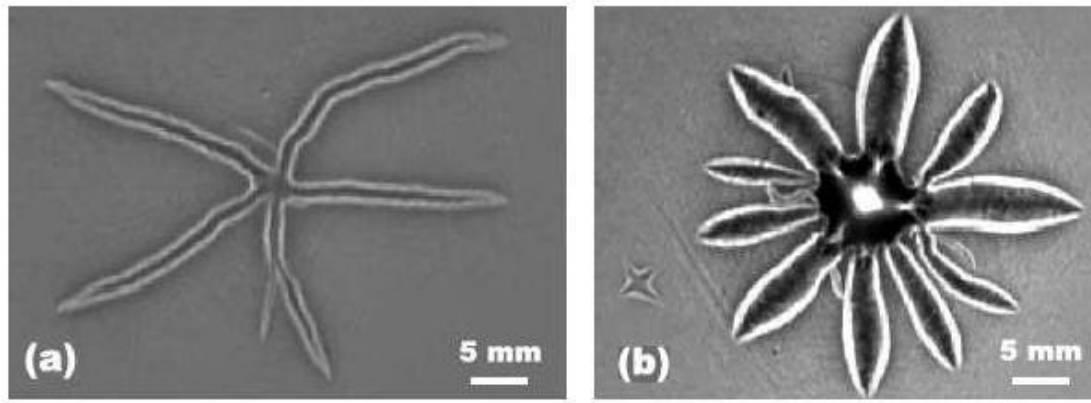


Figure 3.11: Shadowgraph images of starburst formed on the surface of agar gel substrates after the spreading of (a) Triton X-305 and (b) PDMS (from Daniels et al. 2007).

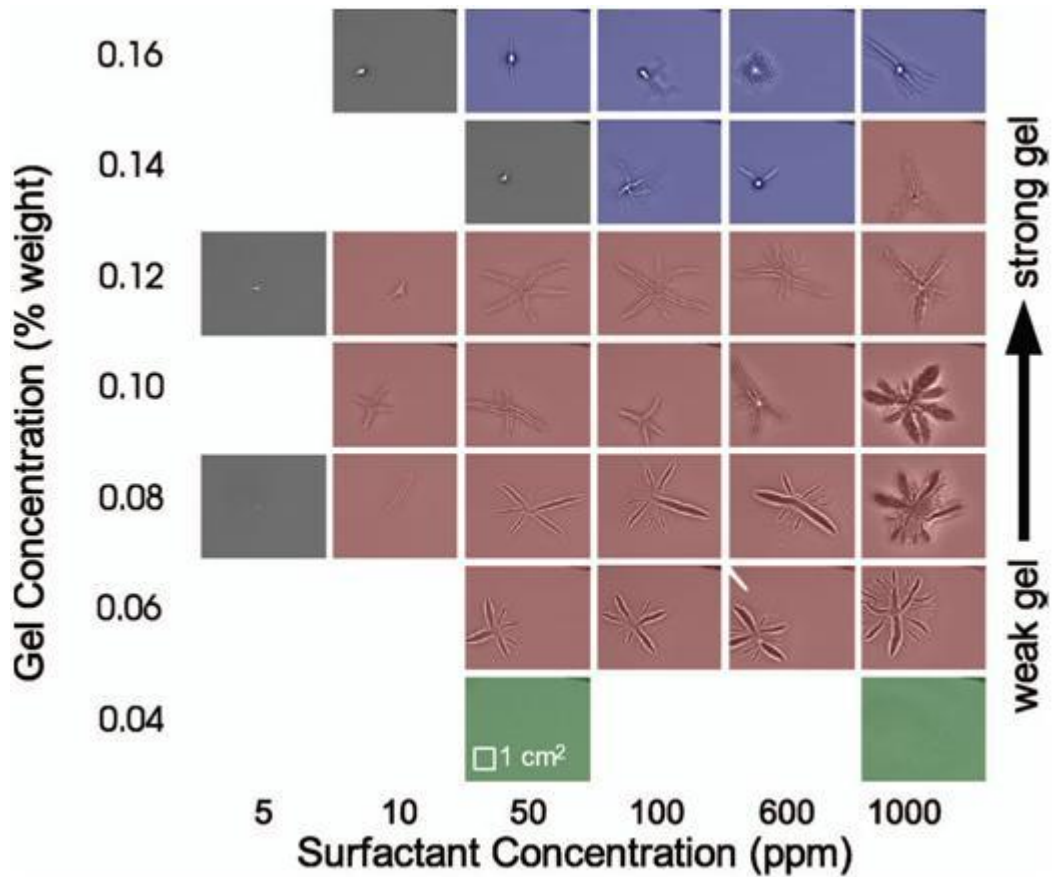


Figure 3.12: Shadowgraph images of patterns produced from the spreading of Triton X-305 solutions on agar gels (from Daniels et al. 2005).

As shown in the red images of Figure 3.12, for weak gels, the droplet spreads in a starburst formation, with 3–10 distinct “arms”. For intermediate gels, the central drop remains, but is

decorated with thin, branching wisps, as shown in the blue images. For sufficiently weak gels, the droplet spreads out as upon a liquid, and no central droplet remains (green images). On the strongest gels, the surfactant drops remain circular. Above $G \geq 30$ Pa, the gel does not exhibit failure and, at early times, the dynamics resembles that which accompanies the spreading of liquid drops on pre-wetted solid substrates. The length of the “arms” is found to advance with time as $t^{3/4}$, indicating similarities with Marangoni-driven spreading on thick films (Fay 1969, Hoult 1972, Jensen 1995). Thus, it is suggested by the authors that the “starburst” patterns are a result of a competition between Marangoni stresses and the gel strength. The presence of these “starburst” can be interpreted as being the gel surface equivalent of the fingering instabilities that can occur in the surface of liquid or solid surfaces, and their observation was significantly influential for the work of the present thesis.

These “starburst” formations have also been likened to cracking patterns observed in Vella *et al* (2006). In this study, “crackings” of similar morphologies (Figure 3.13) have been reported on the surface of a close-packed monolayer of particles (a particle raft) after the spreading of surfactant droplets. The particle raft was situated in the interface between air and a water glycerol mixture, and the surfactant used was polyoxyethylene sorbitan monooleate. The length of these cracks was also found to advance in time as $t^{3/4}$.

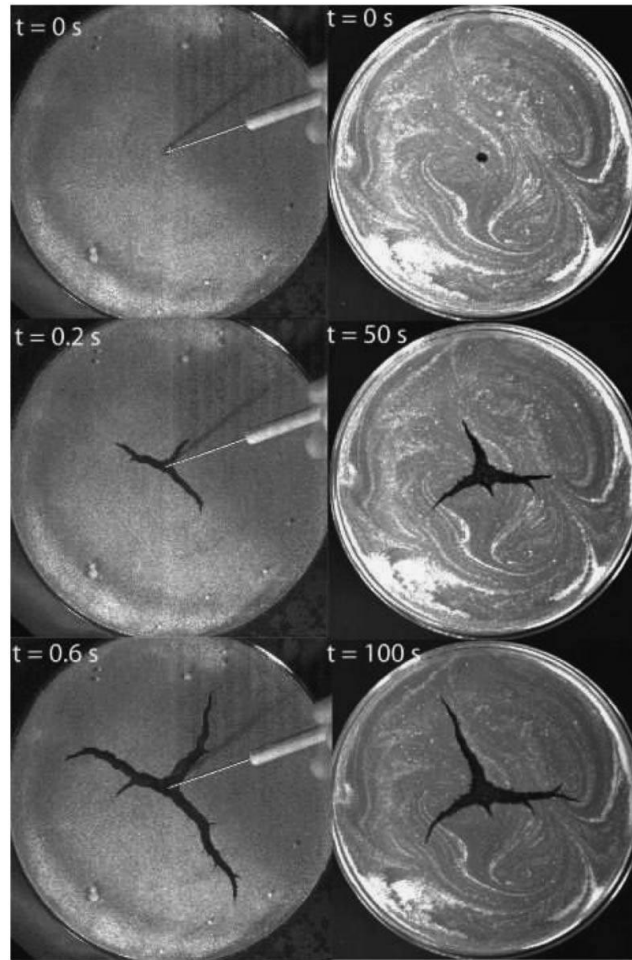


Figure 3.13: Branching fracture of an interfacial particle consisting of $100\mu\text{m}$ Pliolite particles. In the left hand side of the image the particles float at an air-water interface, and in the right hand side they float in an air-glycerol interface. The diameter of the circular disk in both cases is 15 cm (From Vella et al. 2006).

3.3 Dewetting

Fingering (or cracking) behaviour has been reported to occur in the presence of anionic and non-ionic surfactants. However, the use of cationic surfactants has been linked with a behaviour of different nature, where either the surfactant does not spread, or fluid is removed from the region of the original surfactant droplet deposition, creating a hole. This behaviour, which is described by the term “dewetting”, is associated with the strong attraction between the cationic surfactant head of the surfactant and the substrate.

Marmur and Lelah (1981) reported such behaviours for the first time. In this work, it was demonstrated that even though surfactants of all types were spreading on horizontal uncoated glass substrates below the cmc, the cationic surfactants CTAB, dodecylamine HCl, and Hercofloc 812C were not spreading at concentrations below the cmc. In the same conditions, anionic and non-ionic surfactants were spreading while forming fingering patterns. This could be explained by considering the following: for a cationic surfactant, the positive head group is attracted by the negatively charged glass substrate, thus below the cmc it rapidly adsorbs onto the substrate, resulting in higher spreading rates. Above the cmc, it is assumed that the orientation of the molecules of the cationic surfactant is vertical and this prevents the spreading, since a hydrophobic barrier is now placed in front of the drop.

Frank and Garoff (1995a, 1995b and 1996) compared the spreading of aqueous CTAB and SDS on silicon oxide and demonstrated that the behaviour of the two surfactants was different. More specifically, drops of the former were found to exhibit autophobing behaviour at concentrations smaller than 0.45 cmc. Above the cmc, the drops were not spreading. By placing a drop of pure water near an autophobed CTAB drop and allowing the water to spread, the researchers showed that the former drop stops at a very small distance before contacting the latter drop. This indicates the existence of a hydrophobic barrier in front of the point of droplet deposition, as suggested also by Princen *et al.* (1988). By trying the same experiment with SDS instead of CTAB droplets, the water was shown to spread ahead of the spreading surfactant without any interruption.

Birch *et al.* (1994) showed that a drop of cationic surfactant (CTAB) deposited on a negatively charged surface (silicon oxide) will not exhibit fingering behaviour even if a surface tension gradient is present. This is due to the strong attraction between the polar head of the surfactant and the substrate that hinders the water mobility that is required for fingers to form. However, such systems can exhibit dewetting behaviour. The latter can occur when the

surface tension is decreased locally and Marangoni stresses move fluid away from the deposited region, and thus creating a hole (Khesghi and Scriven 1991). Woodward and Schwartz (1997) highlighted the role of the surfactant concentration and the hydrophobicity of the substrate on whether a surfactant can exhibit dewetting or not. In this work, the spreading behaviour of OPA (octadecylphosphonic acid) on a cleaved mica surface was found to switch from wetting to dewetting and autophobing, with increasing surfactant concentration and surface hydrophobicity. Warner *et al.* (2002b) suggests that dewetting is more probable to happen in the local thinned region that is caused by Marangoni-driven spreading. Surfactant adsorbs more rapidly onto the solid substrate from such regions, thus creating a hydrophobic surface that gives rise to dewetting.

Afsar-Siddiqui *et al.* (2004) studied the spreading of the cationic DTAB (dodecyltrimethyl ammonium bromide) on thin liquid films and found three distinctive types of dewetting behaviour, depending on the surfactant concentration and the thickness of the underlying film. At low surfactant concentrations, dewetting is evident via the formation of a hole in the thinned region of the film (Figure 3.14a). At higher surfactant concentrations, the thinned region of the film ruptures leaving a dewetted ring. The surfactant then retracts to a cap at the point of deposition (Figure 3.14b). At even higher concentrations, the deposited surfactant forms a cap at the point of deposition that neither spreads nor retracts. The authors explain this variation of dewetting behaviours by considering the relative Marangoni and bulk diffusion time scales as well as the mode of assembly of the surfactant adsorbed on the solid surface.

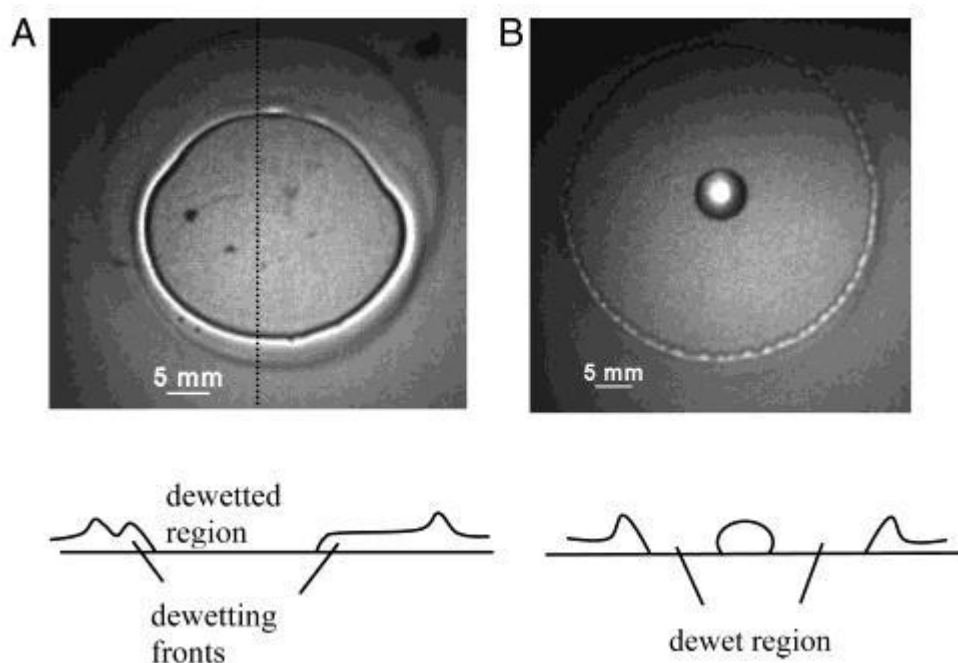


Figure 3.14: (A): A $9\ \mu\text{L}$ droplet of 0.04cmc DTAB spreading on a $50\ \mu\text{m}$ thick water film, where liquid is moving away from this region and a dewetting hole is formed, (B): A $9\ \mu\text{L}$ drop of 0.04cmc DTAB solution spreading on a $100\ \mu\text{m}$ thick water film, where the surfactant has retracted to a rounded cap in the center (From Afsar-Siddiqui et al. 2004).

3.4 Intermediate Behaviour

Fingering and dewetting/autophobic behaviours represent two extremes that are caused by strong repulsion or attraction between the polar head of the surfactant and the underlying substrate, respectively. However, an intermediate behaviour has also been reported in cases where the strength of the surfactant adsorption can be adjusted.

Frank and Garoff (1995a and 1996) demonstrated such intermediate behaviour of a surfactant by using poly(ethylene glycol) monododecyl ether surfactants, C_{12}E_x , since varying x between 5-12 can alter their degree of hydrophilicity. The spreading of C_{12}E_1 on silicon oxide substrates was found to exhibit fingering instabilities similar to those shown in the spreading of SDS on the same substrate. However, the fingers associated with C_{12}E_1 are broader with less interconnected branches. The spreading of C_{12}E_6 is similar to this of C_{12}E_1 , although

isolated drops are observed and the possibility for observing autophobic behaviour is higher. It is, therefore, suggested that with increasing x , $C_{12}E_x$ starts to resemble a cationic surfactant.

Summary

When the interaction between the polar head of the surfactant and the underlying substrate is strongly repulsive, a fingering instability that originates in the Marangoni thinned region of the surface can occur. Such instability is observed over a wide range of experimental conditions, substrate orientations and geometries, and with a variety of anionic and non-ionic surfactants. These fingers can have many forms, including long crack-like spreading “arms”. On the contrary, when the interaction between the polar head of the surfactant and the underlying substrate is strongly attractive, then surfactant adsorption from the thinned region onto the surface creates a hydrophobic region that generates dewetting. A range of intermediate behaviour between these two extremes is also reported when such interactions vary from strongly repulsive to strongly attractive.

Chapter 4

Materials and Methods

Synopsis

This Chapter provides details on the different types of surfactants and gels that are used in the experimental work of this study. Complete details of the preparation of solutions, the experimental set-up and the visualisation technique that is followed in order to capture images of the pattern formation are given. A setup similar to the one used in Daniels *et al.* (2007) is used, since it enjoys a number of advantages, namely, the use of 'tunable' gels (that can exhibit the full spectrum of liquid-like to solid-like behaviour), and geometrical simplicity, which allows emphasis to be given on the understanding of the interactions between the spreading liquid and the gel.

A description of the methods employed to characterize the solutions follows. The surface tension of the surfactants and the gels was measured using the Wilhelmy plate method; the same method was used for determining the cmc of Silwet L-77. Information on the mechanical properties of the gel layers, and more specifically their storage (G') and loss moduli (G'') were provided from oscillation tests run in an AR-G2 rheometer. An attempt to determine approximate yield stress values for different concentrations of the substrates through steady state flow tests was also included.

4.1 Materials

The surfactants used in this study are the anionic SDS and the non-ionic Silwet L-77, and they are spread on agar and gelatine gel layers. Their major properties and hazards are summarized in Table 4.1. They were all used as supplied, with no further purification.

Table 4.1: *Main properties and hazards of the surfactants and the gels used in the current study.*

Name	Source	Type	State	cmc (mg/L)	Solubility in water	Hazard	Precautions
SDS (sodium dodecyl sulphate)	Sigma-Aldrich (UK)	Anionic surfactant	Solid	2307	Highly soluble	Harmful by inhalation; irritating to eyes/skin	Goggles and safety hand gloves; kept away from mouth
Silwet L-77 (polyalkyleneoxide modified heptamethyltrisiloxane)	De Sangosse (UK)	Non-ionic surfactant	Liquid	160	Soluble	Harmful by inhalation; moderately toxic; irritating to eyes/skin	Goggles and safety hand gloves; kept away from mouth
Agar	Sigma-Aldrich (UK)	Polysaccharide- based Gel	Solid	—	—	Overheating/ overflow of solution while in oven	Goggles, hand gloves and lab coats; loosely closing bottle cap.
Gelatine	BDH Chemicals (UK)	Protein-based Gel	Solid	—	—	Overheating/ Overflow of solution while in the oven	Goggles, hand gloves and lab coats; loosely closing bottle cap.

4.1.1 SDS

The choice of SDS (sodium dodecyl sulphate) is dictated by the fact that it has well-characterised properties (Mukerjee and Mysels 1970, Chang and Franses 1992), and it is one of the most common materials used in studies on surfactants (see Frank and Garoff 1995a, and 1996, Birch *et al.* 1995, Shen *et al.* 2002, Berg *et al.* 2005, Lee and Starov 2009, for instance). SDS has been of central importance in studies on Marangoni spreading, like in the work of Berg *et al.* (2009) on the spreading of surfactants on the interface between thick layers of water and decane, and in the work of Afsar-Siddiqui *et al.* (2003) on the spreading of surfactants on thin liquid films. The latter work showed fingering instabilities during the spreading of SDS solutions below and above the cmc. The molecular structure of SDS is given in Figure 4.1. It is a single chained surfactant, with 12 carbon atoms in the hydrophobic chain.

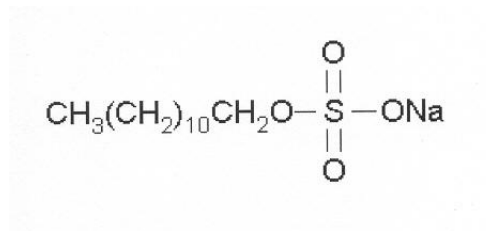


Figure 4.1: Molecular structure of SDS (from the Sigma-Aldrich website).

SDS has many applications in biochemistry, where its aqueous solutions can be used as gelation media for the preparation of PES (polyethersulfone) membranes (Alsari *et al.* 2001). The SDS-PAGE electrophoresis technique, where polyacrylamide gels electrophoresis in the presence of SDS separates proteins according to their molecular weights, is also highly popular (Weber *et al.* 1972, Hartinger *et al.* 1996, Hatch *et al.* 2006). Industrially, SDS is widely used in cleaning and hygiene products, such as shampoos and toothpastes. The cmc of SDS is 2307 mg/L at 25° C (Mukerjee and Mysels 1970).

4.1.2 Silwet L-77

The non-ionic Silwet L-77, first discovered in the late eighties (Zhu *et al.* 1994), is a well known superspreader based on a trisiloxane ethoxylate. Superspreaders are surfactants that are able to drastically reduce the surface tension of water and promote rapid spreading on very hydrophobic substrates even in very small quantities. Silwet L-77 is a straw coloured liquid composed of 85 wt% polyalkylene oxide modified heptamethyltrisiloxane and 15 wt% allyloxypolyethylene glycol methyl ether (De Sangosse UK). When added to water, trisiloxanes (Halverson *et al.* 2009) of this type are capable of lowering the surface tension from 70 mN/m to 20 mN/m.

Wagner *et al.* (1999) studied the spreading of Silwet L-77 on silicon wafers and found it to be much faster than other surfactants tested. Nikolov and co-workers (2002 and 2007) conducted important studies on the spreading of aqueous Silwet L-77 solutions on hydrophobic solids. They identified surface tension gradients in the air-liquid interface as being the driving force behind its spontaneous spreading, thus highlighting the dominant presence of Marangoni stresses. At the advanced edge of the spreading Silwet L-77 drops, the formation of a rim and of fingering instabilities was reported in their experiments. The presence of this rim was also found in theoretical studies. (Beacham *et al.* 2009 and Karapetsas *et al.* 2011a). The authors conclude that trisiloxane ethoxylate solutions can exhibit superspreading behaviour because they are able to maintain high surface tension gradients during the spreading process, since they develop a higher dynamic surface tension compared to organic surfactants. In addition, the hydrophobic segments of trisiloxanes can differentiate them from non-superspreading surfactants. Radulovic *et al.* (2010) also linked the superspreading properties of Silwet L-77 with its molecular structure, and more specifically with the intriguing “T” –shaped formation and the large cross-sectional area of the hydrophobic trisiloxane chain (Figure 4.2). A shorthand notation has been adopted for trisiloxane surfactants – M(D’En)M. M is

$(\text{CH}_3)_3\text{SiO-}$, D' is $(\text{CH}_3)\text{Si}(\text{CH}_2)_3$ and En is $-(\text{OCH}_2\text{CH}_2)_n\text{OP}$ with P typically being $-\text{H}$, $-\text{CH}_3$, or $-\text{CHCO}_2\text{H}$ (Halverson *et al.* 2009)

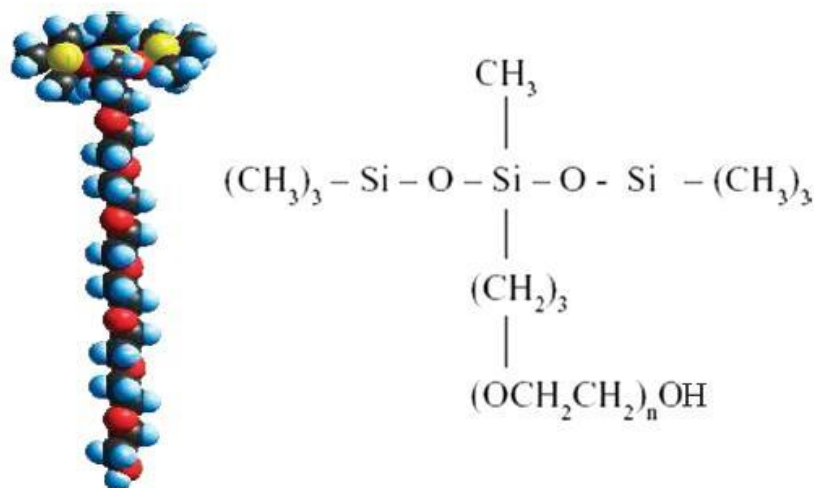


Figure 4.2: “T” shape and molecular structure of the trisiloxane molecule. Blue atoms are hydrogen, red atoms are oxygen, black atoms are carbon, yellow atoms are silicone (from Radulovic *et al.* 2010).

Silwet L-77 is widely used in the agricultural industry as pesticide adjuvant to improve the spreading and wetting properties of pesticide sprays. The effectiveness of Silwet L-77 spray is evident on the wetting of plant surfaces. Tang *et al.* (2008) compared the spreading behaviour of Silwet L-77 on wet and dry lotus leaves. It was found that the drop spreading on the wet surface was easier than on the dry surface, thought to be due to the water in the grooves of the wet surface. The spreading of Silwet L-77 aqueous drops on the wet surface was found to be mainly controlled by Marangoni stresses, due to the surface tension gradient along the air–liquid interface. Figure 4.3 shows a schematic representation of a surfactant spreading on a wet surface.

According to Tang *et al.* (2008), the grooves of the wet surface are filled with water and the grooves of the dry surface are filled with air. Due to the peculiar topography of the lotus leaf, the surfactant drop was seen to have difficulty in penetrating into the grooves. As for the wet

surface, a wetted interface formed instantly after the drop contacts with the wet surface. The authors also discovered that the existence of water in the grooves made the surfactant concentration at the contact line lower than that at the drop tip, creating the surface tension gradient along the air–liquid interface. This surface tension gradient leads to the generation of Marangoni stresses which enhance the spreading of the drop; as a result the high spreading velocity is explained by the strong surface tension gradient.

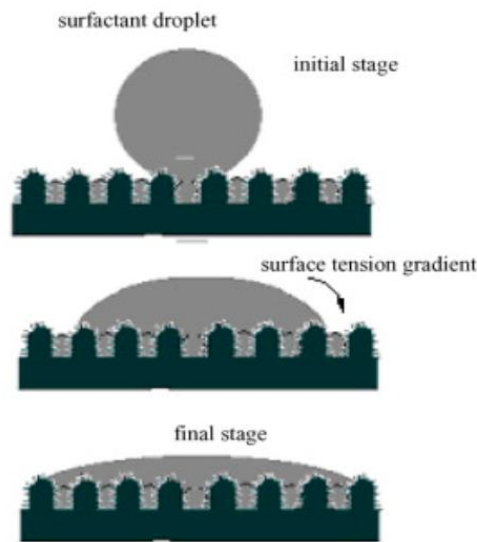


Figure 4.3: Schematic representation of surfactant spreading on a wet lotus leaf (from Tang *et al.* 2008).

In our study, the spreading dynamics can be examined as a function of the critical micelle concentration of the surfactants, thus its importance in the understanding of the pattern formation is significant. Thus, the critical micelle concentration of Silwet L-77 was measured using the Willhelmy plate method (described in Section 4.6.1), and was found to be $\approx 150 \pm 16$ mg/L at 20°C (Figure 4.4). This value is within the range of the different values found in the literature, namely between 80 mg/L (Tang *et al.* 2008) and 600 mg/L (Whitacre 2008).

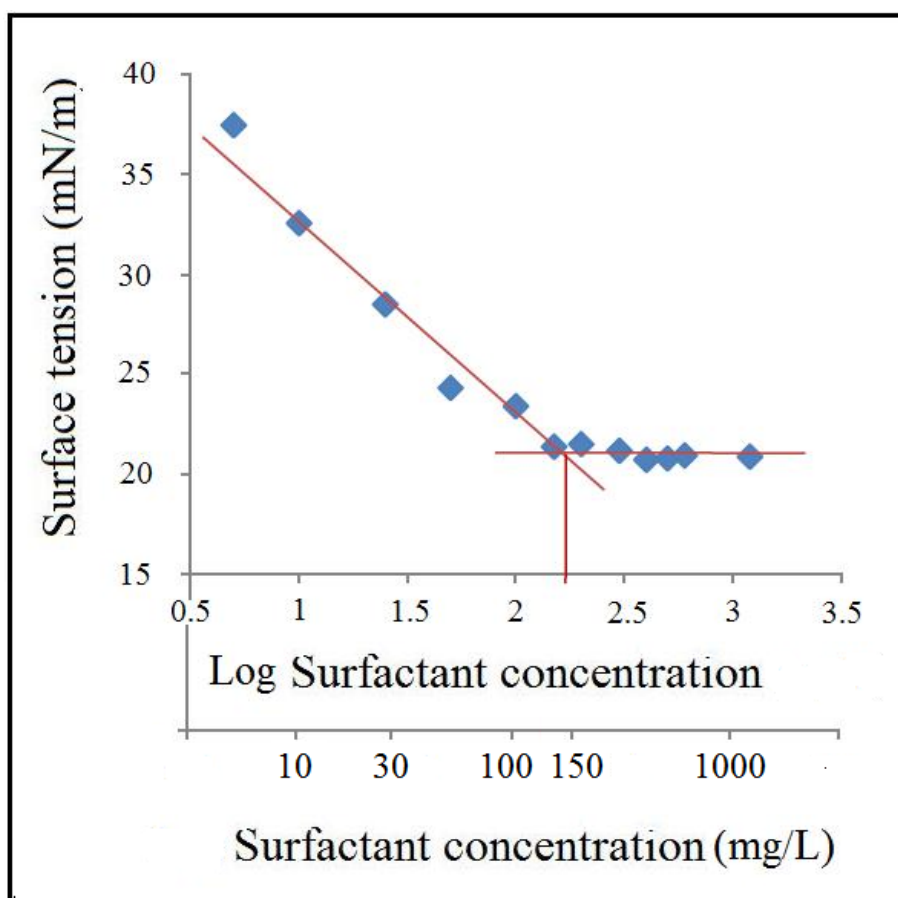


Figure 4.4: Logarithmic plot of surface tension of Silwet L-77 against surfactant concentration. Critical micelle concentration (cmc) is 150 mg/L.

4.1.3 Agar

Agar is a polymer made from subunits of galactose, and it is one of the most extensively studied and used polysaccharides. It is mainly used as a medium for bacteria and fungi growth in microbiology (Kiyohara *et al.* 1982, Wolfe and Berg 1989). Its purified form, agarose is widely used in analytical gel electrophoresis (Johansson 1972, Jeppsson *et al.* 1979). However, agar without any purification can also be a good alternative for this technique (Viljoen *et al.* 1993).

Agar gels are weak gelling systems, since gelation is caused by weak interaction between the polymer chains. They are ‘tunable’ gels, since they can behave either as viscoelastic solids or

as liquids, depending on the concentration of their solutions. Optical studies have demonstrated that the gelation of agar is accompanied by a conformational transition of the polysaccharide chain from a random coil structure to a system of double helices, followed by aggregation of the double helices (Tokita and Hikichi 1987). The viscoelastic properties of the gel can be controlled by altering the concentration of agar. Hirata (1998) studied the fracturing of agar due to the fluid intrusion by changing the viscoelastic properties of the solution. With increasing concentration, the agar solution changes from a viscous fluid to an elastic body. The author observed viscous fingering in the low concentration agar gel and single plane cracking with a high concentration agar gel. Middle range concentrations exhibited a new kind of pattern growth which is termed ‘viscoelastic fracturing’. This pattern is thought to be formed due to two competing mechanisms, viscous flow and fracture.

4. 1. 4 Gelatine

Gelatine is a protein-based gelling agent derived from the collagen present inside the skin and bones of animals. A gel is formed via the building of a triple-helix structure during the sol-gel transition phenomenon (Michon *et al.* 1993). Gelatine is readily soluble in water at temperatures above 40°C. It forms a high viscosity solution with water and has interesting thermally reversible so-gel transitions features. Aggregation of gelatin molecules takes place on cooling and the system changes from viscous solution to elastic solid during gelation (Ohkubo *et al.* 1999). The mechanical properties of gelatine are extremely sensitive to temperature variations and time. The rigidity decreases gradually with increasing temperature from 0°C to melting point for all concentrations of gelatine. Studies and measurements show that the rigidity of gelatine is approximately proportional to the square of its concentration (Ferry 1948). The effect of concentration on rheological behaviour is complicated. However, an increase in gelatine solution concentration results in a change from viscous fluids to gel-

like solids (Ohkubo *et al.* 1999). The viscoelastic properties can be controlled by changing the concentration of gelatine in the solution.

4.2 Preparation of Gel Solutions

Agar powder (Sigma Aldrich UK) was weighed on a Pioneer OHAUS scale. The concentrations (X_{agar}) used ranged from 0.04 wt% to 0.14 wt% and this was determined by $X_{agar} = M_{powder} / (M_{powder} + M_{water})$, where M is the mass of each component. Subsequently, the agar powder was mixed with 100 ml (100 g) of deionised water in a 500 ml glass bottle. The bottle was then tightly closed and shaken. After this, it was put in a microwave oven and heated for approximately 2 minutes. This method of heating was chosen as it resulted in good dissolution of the agar particles and subsequent homogenizing of the resultant gel solution. After heating, the glass bottle was placed in a beaker of cold water and left undisturbed for about 5 minutes in order to let the agar solution cool down to room temperature. After this, the mixture, still in its liquid form, was poured into a 14cm diameter Petri dish and allowed to set. Due to the wettability of the gel, it was found that the minimum thickness of a gel layer that can be formed inside a Petri dish of the specific size was 4mm. This thickness was used as the standard gel layer thickness during the majority of the experimental runs of this work. Approximately 50 mL of liquid agar solution was required to fill the 14cm diameter Petri dish until the 4mm mark. In case the layer thickness exceeded 4 mm while pouring the mixture from the glass bottle to the dish, the appropriate quantity was removed using a plastic pipette, until the 4 mm thickness was restored. The same method was employed in order to achieve gel layer thicknesses of 2 mm (see section 5.4). Even after removing adequate quantities of the mixture with the pipette, no smaller thickness than 2 mm could be achieved without observing dewetting of the layer.

The gels had to become stiff enough for cracks to form upon drop deposition on the surface, therefore they were allowed to settle from 24 to 72 hours, with the variations of time being necessary, since the time required for the gels to set depended on their concentrations, with high-concentrated gels requiring less time to settle than low-concentrated gels. It was found that, the gels allowed to set in covered Petri dishes, needed very long times to become stiff or in many cases remained in a liquid form since no water was allowed to evaporate. On the other hand, if there was too much evaporation, a dewetting phenomenon would occur during the first 24 hours, preventing the formation of a gel of uniform thickness. To avoid these two extremes, the Petri dishes were left uncovered, but were placed inside a closed cupboard. In this way, it was found that only a small quantity that represents approximately 3% of the original weight of mixture was lost every 48 hours due to evaporation.

Gelatine gels were prepared by mixing gelatine powder (BDH Chemicals UK) with deionized water and following the same procedure as described above. The concentrations ($X_{gelatine}$) used ranged from 0.7 wt% to 1.7 wt%. In contrast to the agar gels, the gelatine gels inside the Petri dishes were allowed to set in a refrigerator at 4°C. Again, the highly concentrated gelatine gels needed less time to set than the low concentration ones, with the overall maximum time needed being 72 hours.

It is important to note that both types of gels (especially the lowest-concentration ones from each type) were very sensitive to any kind of vibrations and their rheological properties could easily be altered by moving them before they have set. This is due to the fact that their structures can easily be destroyed under shear movements and normal forces. Therefore, to minimise any effects this could have on the experimental results, the gels were moved as little as possible.

4.3 Preparation of Surfactant Solutions

SDS powder (Sigma Aldrich UK) was weighed on a Pioneer OHAUS scale and mixed with deionised water in 50 mL plastic beakers. The aqueous SDS solutions that resulted were of concentrations 0.4, 0.8, 1.2, 2, 2.8 and 4 cmc. SDS dissolves very easily, so minimal shaking was enough for it to dissolve.

Pure Silwet L-77 (De Sangosse UK) is liquid, therefore in order to determine the appropriate volumetric quantity needed to prepare aqueous solutions of required concentrations, the fundamental relationship of density to mass and volume was used, with the density of Silwet L-77 being 1.007g/mL (from the De Sangosse webpage). The required volume of Silwet L-77 was measured using a micropipette fitted with pipette tips to accommodate droplet sizes ranging from 1 μ L to 1000 μ L (FinnPipette, Thermo Labsystems UK). Small volumes of Silwet L-77 were then delivered to 50mL plastic beakers containing deionised water. The resulting solutions were then shaken for 10-20 minutes using a mechanical shaker. The solutions prepared were of concentrations 0.3, 0.6, 1, 2, 4, 6, 8, 10, 50 and 100 cmc.

Both surfactant solutions produced some foam after shaking, so they were allowed to stand for at least one hour before being used, so that the foam would break and the homogeneity of the solution would be ensured. The solutions were all used within 24 hours to avoid a decrease in surface activity (Burcik and Vaughn 1951). Hence, the entire procedure of SDS and Silwet L-77 solution preparation was repeated for spreading experiments on every new batch of gels tested.

4.4 Experimental Procedure and Visualisation Technique

The spreading is visualized using shadowgraphy (Settles 2001) in a set up that has similarities with the one used by Daniels *et al.* (2007) and enjoys the benefit of geometrical simplicity. The circular Petri dish containing gel layers of different types and concentrations was

positioned on a flat surface above a paper screen. A Dino X-Lite digital microcamera with a 1.3 Megapixel resolution and a magnification capability of up to 500X (model AM-413M, Dino-Lite Europe) was used to record the spreading at a rate of 30 frames per second. To make the spreading patterns visible, since both the gels and the surfactant droplets were transparent, the Petri dish was illuminated using extra light from a white light fibre-optic lamp at maximum intensity (model KL 1500 LCD, SCHOTT UK). The latter was held at a slight angle above the Petri dish and moved around until optimal shadows of the spreading patterns were projected on the paper screen. A schematic sketch of the experimental setup is shown in Figure 4.5.

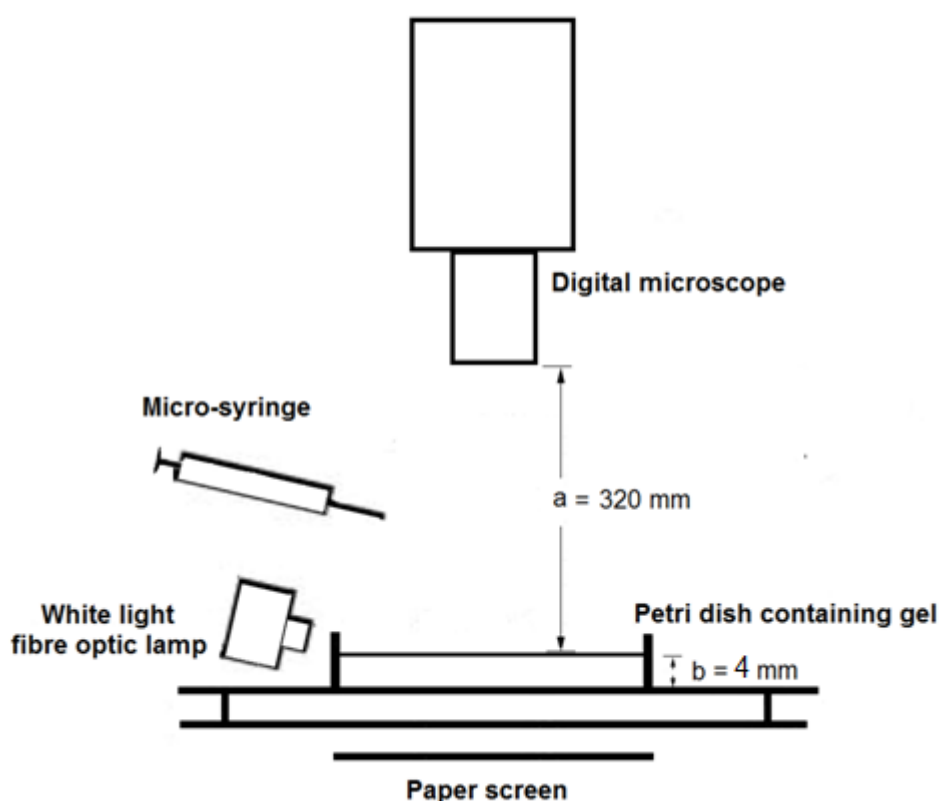


Figure 4.5: Schematic sketch of the experimental setup.

A 5 μl drop of surfactant of known concentration was delivered to the surface of the gel using a 20 μl precision micro-syringe (Hamilton UK). The drop was first released and allowed to

hang from the tip of the needle, and to then contact the surface of the gel layer in order to spread. This was done so as to minimise any effects that the dropping velocity would have on the gel fracture process. The spreading was followed for some seconds after deposition and recorded by the digital microscope. Each spreading run was repeated 3 times to ensure good reproducibility, and all the experiments were conducted at ambient temperature and humidity. The quantitative characteristics of the “arms” are measured using the software of the Dino X-Lite microcamera.

4.5 Cleaning Procedure

The water used to clean the glassware and prepare solutions was deionised and passed through a water purification unit comprising three cartridges: reverse osmosis, ion exchanger and activated carbon (Barnstead Nanopure Systems, UK). The purified water had a resistivity of 18 M Ω cm and a surface tension of 72.2 ± 0.5 mN/m at 23°C.

The Petri dishes were first rinsed in deionised water and then subsequently immersed in a bath of pure Xylene and allowed to soak for 12 hours. Xylene was chosen as the most appropriate glass-cleaning detergent, since it is a very potent solvent. After this, the dishes were flushed repeatedly with 99.97 wt% ethanol to remove the Xylene. Finally, the dishes were placed for up to 1 hour in deionised water in the ultrasonic bath. This ensured that all traces of detergent and all impurities such as oil, dust or surfactant residue were completely removed. The dishes were moved around in the bath, so that complete and uniform cleaning would be ensured (Birch 2000). All the glass vessels used to prepare the surfactant and the gel solutions, and the syringes used for the surfactant droplets deposition were cleaned in a similar manner. Upon pouring deionised water into the glass beakers cleaned according to the same procedure, it was observed that no water droplets clung to the walls of the beaker. This

verified the absence of impurities which interfere with the cohesive forces binding the water molecules to each other.

Several drying techniques were used. Immediately after taken out of the bath, the Petri dishes were blow dried using dry compressed air (RS Ltd., UK). The dishes were held using plastic holders in an almost vertical position. A jet of air was directed from top to bottom, chasing the water film down and preventing the formation of streaks. The reverse of the dishes was dried first, and the drying of the inside face followed (Birch 2000). The reverse of the dishes was dried very effectively, however it was made possible for water chased down the inside face to become trapped between the base and the rim of the dish, therefore complete drying was not achieved. Hence, the dishes were left to dry upside down in a drying oven for up to 30 minutes.

The Wilhelmy plate (Section 4.6.1) was cleaned by rinsing in deionised water and then in acetone. A second rinse in deionised water followed, and subsequently the plate was heated until red hot so as any residual impurities and traces of acetone would be removed.

4.6 Methods of Characterisation

4.6.1 Surface Tension Measurements

The surface tension of the surfactant and the solutions was measured by using roughened platinum Wilhelmy plate suspended from a Krüss microbalance (Model K10 automatic tensiometer, KRÜSS USA, NC). The plate was suspended from the microbalance and dipped partially in a glass beaker containing surfactant solution. The force was zeroed and the plate was automatically raised and detached from the liquid surface and a constant value for surface tension was displayed. Equation 4.1 below shows the relationship between the surface tension of a liquid and the force on the plate:

$$W_t - W_p = P_p \sigma \quad (4.1)$$

where W_t is the force needed to detach the plate from the liquid surface, W_p is the weight of the plate in air, P_p is the perimeter of the plate and σ is the liquid surface tension. The left hand side of the equation 4.1 is equal to the right hand side, when the contact angle of the liquid with the plate is zero (Aveyard and Haydon, 1973). A contact angle equal to zero can be achieved by complete cleaning of the platinum plate according to the procedure described in section 4.5.

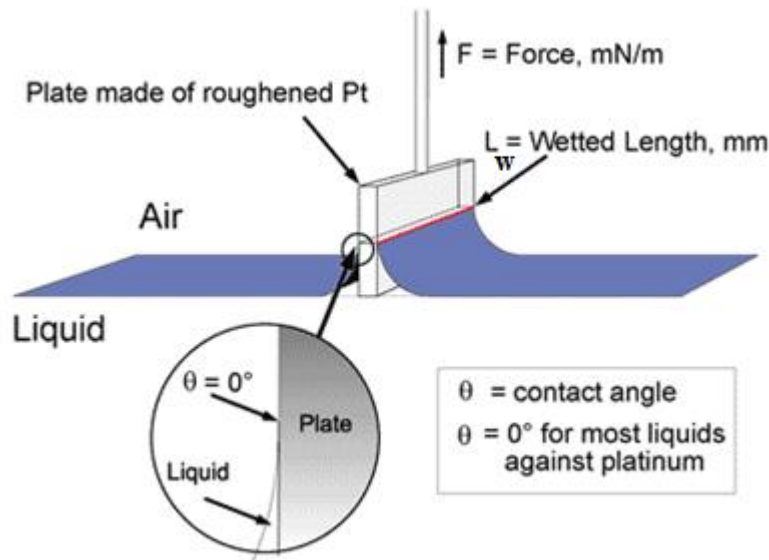


Figure 4.6: Schematic diagram of the Wilhelmy plate method. F is force acting on the balance, L_w is the wetted length and, θ is the contact angle, (From the KRÜ SS website).

It was found that for SDS solutions of concentrations between 0.4 cmc and 4 cmc, the corresponding surface tension is between 60 mN/m and 33 mN/m; for Silwet L-77 solutions of concentrations between 2 cmc and 8 cmc, the corresponding surface tension is between 23 mN/m and 20 mN/m. The surface tension of the gel solutions was measured following the same technique; it was found that for $0.08 \text{ wt}\% \leq X_{agar} \leq 0.14 \text{ wt}\%$, the corresponding surface tension is $68 \text{ mN/m} \leq \sigma_{agar} \leq 60 \text{ mN/m}$, and that for $0.7 \text{ wt}\% \leq X_{gelatine} \leq 1.7 \text{ wt}\%$, the corresponding surface tension is $65 \text{ mN/m} \leq \sigma_{agar} \leq 55 \text{ mN/m}$. These values were used to

determine the spreading pressure, S , employed in Chapter 6. The uncertainty for the surface tension measurements was ± 0.5 mN/m.

4.6.2 Rheological characterisation of agar and gelatine solutions

Gel strength is usually considered as the most important quality of the substrates. This can be determined by the values of their mechanical properties such as the storage modulus, G' , and the loss modulus G'' . The higher the values of these moduli, the stronger the gel. The tangent of the phase angle, $\tan\delta = G''/G'$, is another useful parameter for quantifying the presence and extent of elasticity in a gel. In addition, yield stress (the stress at which a material starts to deform plastically) is considered by many to be an important engineering parameter and a typical feature of the rheological properties of filled polymers (Malkin 1990, Oliveira *et al.* 2010). The rheology of agar and gelatine gels has been studied in the past. However, existing studies in the literature are mostly referring to gel concentrations much higher than those that are significant for this work (Tokita and Hikichi 1986, Ohkubo *et al.* 1999, Boran *et al.* 2010). Hence, the rheological properties of the agar and gelatine solutions used in this study were measured by running the appropriate tests on an AR-G2 rheometer (from TA Instruments, USA). This specific rheometer was chosen since it can easily characterise sensitive samples, since it has a magnetic thrust bearing which applies ultralow torques to the samples. A complete description of the steps followed during these measurements and of the results obtained is given herein.

A Peltier system on the lower place of the rheometer where the gel samples were placed allowed to temperature to be controlled with accuracy of ± 0.1 °C. Parallel disks geometry was used, having a titanium rotating disk of 40 mm diameter while the gap was up to 1150 μm , depending on the quantities and the response waveform of the gel sample. For the oscillatory measurements the default value limits of the rheometer were 10-5 rad for the displacement and 5 micro N.m for the torque, while the tolerance within measurement was 5 %

for the displacement and 1% for the torque. The software of the apparatus could depict the applied and measured waveforms for each final point of every oscillatory measurement, so that they could be seen easily whether the results were in-phase or out-of-phase. It was also able to provide additional information by showing the 64 points consisting of each of the final waveforms.

The agar and gelatine samples were prepared following the same procedure described in Section 4.2. Any measurement for gelatine gels reported here was after the time period of 24 hours that the solution was left inside the refrigerator. Special care was taken on the loading of the samples in order to prevent destruction of the structure of the gels due to shear movements and normal forces. For the agar gels, the first sample for each concentration was effectively created on the lower plate of the rheometer (the Peltier base), by pouring the prepared solution into a polypropylene ring having the same diameter with the rotating disk. A closed plastic cylindrical cover was used to avoid evaporation and remained there for over 5 hours. Then the ring slowly removed and gradually the titanium upper disk squished the sample with steps of about 10 microns to a gap of 1000 μm , where good waveforms were observed during preliminary tests. After the procedure of setting the gap, the sample at the fixed gap left at rest for at least 3 hours, covered again with the cylindrical cover. When rheological measurements on a sample from a previous batch were needed, (after 48 or 72 hours, for instance) then the sample preparation was as follows: the glass pot containing the gel was slowly tilted to get almost tangentially the sample from the gel batch, rather than vertically, so a slice of gel was obtained without any cracks in the structure and placed at the plate of the rheometer. The disk over the sample gone slowly down, the adequate gap was fixed as previously described, and any overfilled removed gradually with a spatula. The same procedure as in the case of the first sample was repeated afterwards.

After the preparation process described above, rheological measurements were conducted with oscillatory and steady state flow conditions. Oscillatory measurements were performed at 20°C to record the evolution of the mechanical properties in time, namely G' , G'' and η' against time, after gelation of agar solutions. At the selected time intervals, typical frequency and temperature sweeps were also performed. Preliminary oscillatory time sweep measurements on agar samples of concentrations of 0.08 wt% and 0.12 wt% during a period of 72 hours showed that after 10-12 hours from preparation, a stable response was achieved, since practically constant values of G' and G'' with an increase of 10% were obtained. By applying strain values up to 0.4%, it was observed that the storage modulus G' was about an order of magnitude higher than the loss modulus G'' for applied frequencies of 0.2 rad/s to 3.14 rad/s, retaining notably both its values in time, even after 96 hours in certain cases. However, for agar gels of concentration of 0.14 wt%, a slower built-up process of the structure was recorded, leading to a terminate value of storage modulus after 24 hours from preparation, as Figure 4.7 shows.

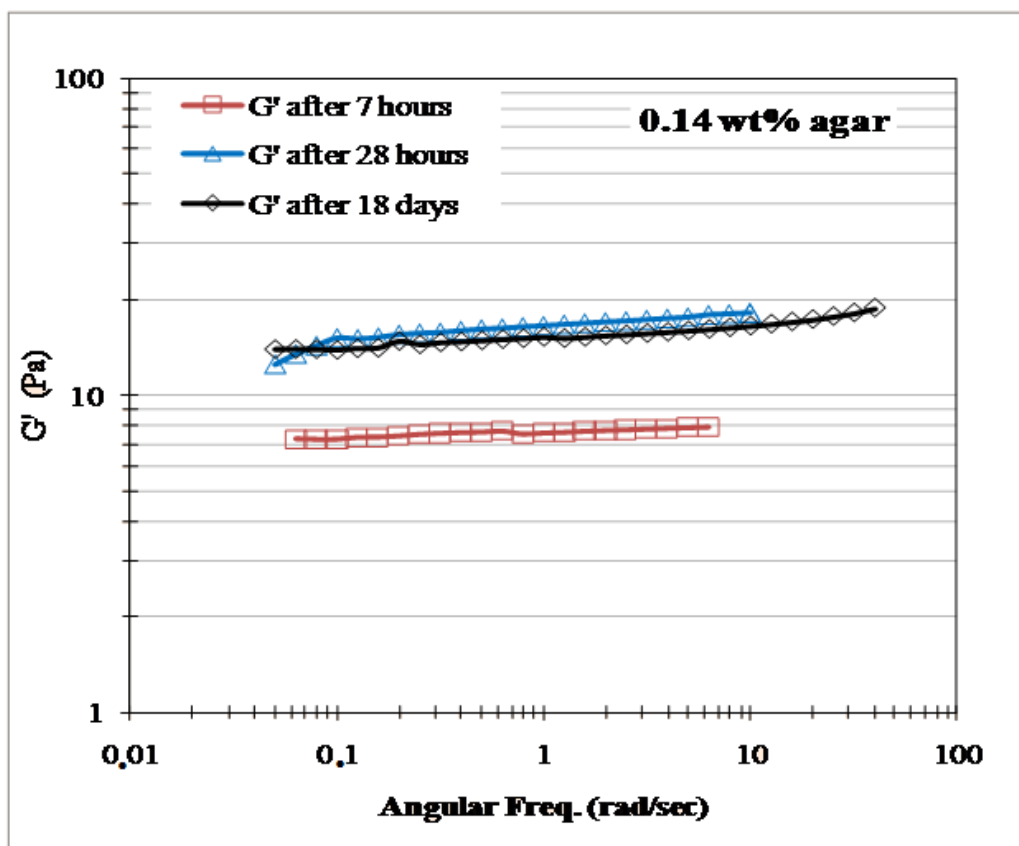
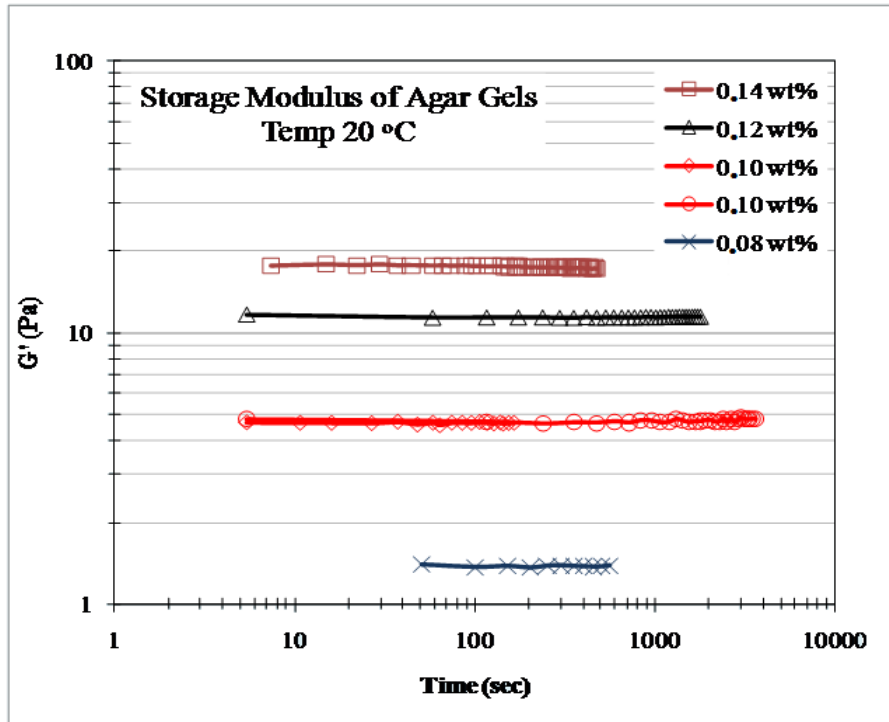


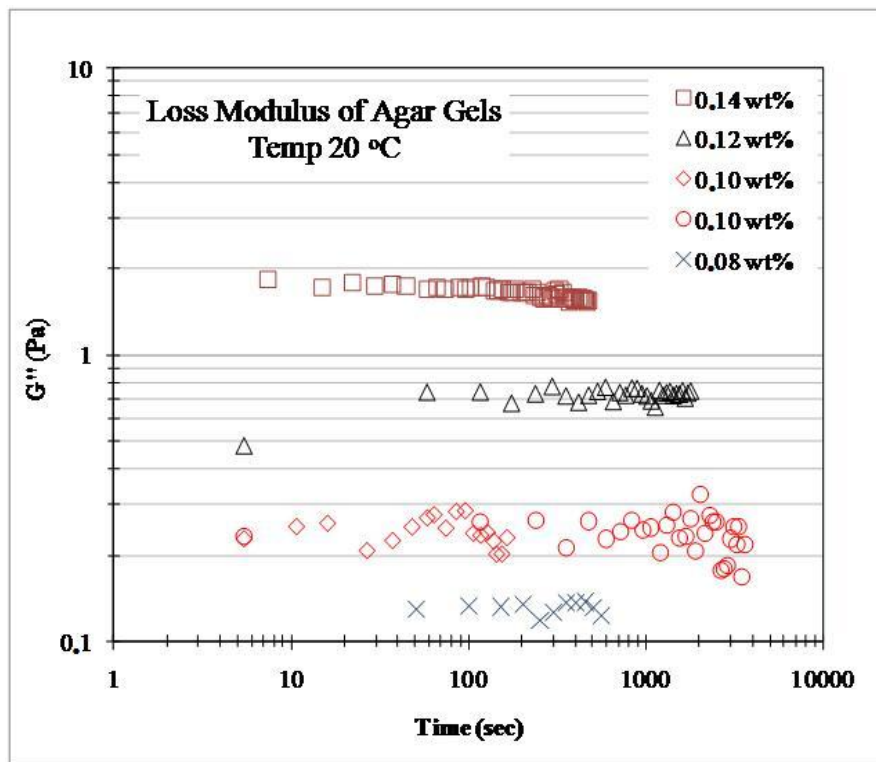
Figure 4.7: The effect of gelation time on storage modulus for 0.14 wt% agar for measurements after 7 hours, 28 hours and 18 days (Temp. 20 °C). The lines connecting the data points are for guidance of the eye.

The results show that there are no practical differences in the G' values after 28 hours from the time of preparation in a frequency sweep. Hence, the values obtained after 28 hours were used in the following results as representative of the mechanical properties of 0.14 wt% agar gels.

For agar gels of concentrations from 0.08 wt% to 0.14 wt% , representative results for the storage modulus G' and loss modulus G'' over time sweeps are shown in Figures 4.8 (a) and (b), respectively. It should be noted that in all cases the raw phase difference between the applied and the response of the gels was between 3.5 to 5.5 degrees, indicating almost elastic behaviour even in the lower wt% agar concentration.



(a)



(b)

Figure 4.8: Time sweeps for agar gels of concentrations from 0.08 wt% to 0.14 wt% for (a) storage modulus, and (b) loss modulus. The frequency was 3.14 rad/s, except of concentration 0.08 wt% where it was 0.25 rad/s. The lines connecting the data points are for guidance of the eye.

For lower agar concentrations of 0.08 wt% G' was about 1.38 Pa while for the higher concentrations of 0.14 wt% it was approximately 17.5 Pa. The experiments were performed at the same frequency of 0.5 Hz (3.14 rad/sec) except of the 0.08 wt% agar, where this frequency was close to the non-linear region. This concentration seems to have a narrow linear viscoelastic region and low frequencies are needed to give relatively smooth waveforms, i.e. after the 0.5 Hz distort waveform was recorded so the frequency 0.04 Hz was chosen for the time sweeps. As it is shown in Figure 4.8 the storage modulus is constant over wide period of measuring time (over an hour), while the loss modulus appears more sensitive in time, showing some fluctuation, mainly for lower agar concentrations. From these data the following plot of the concentration effect on the storage modulus G' and loss modulus G'' is formed.

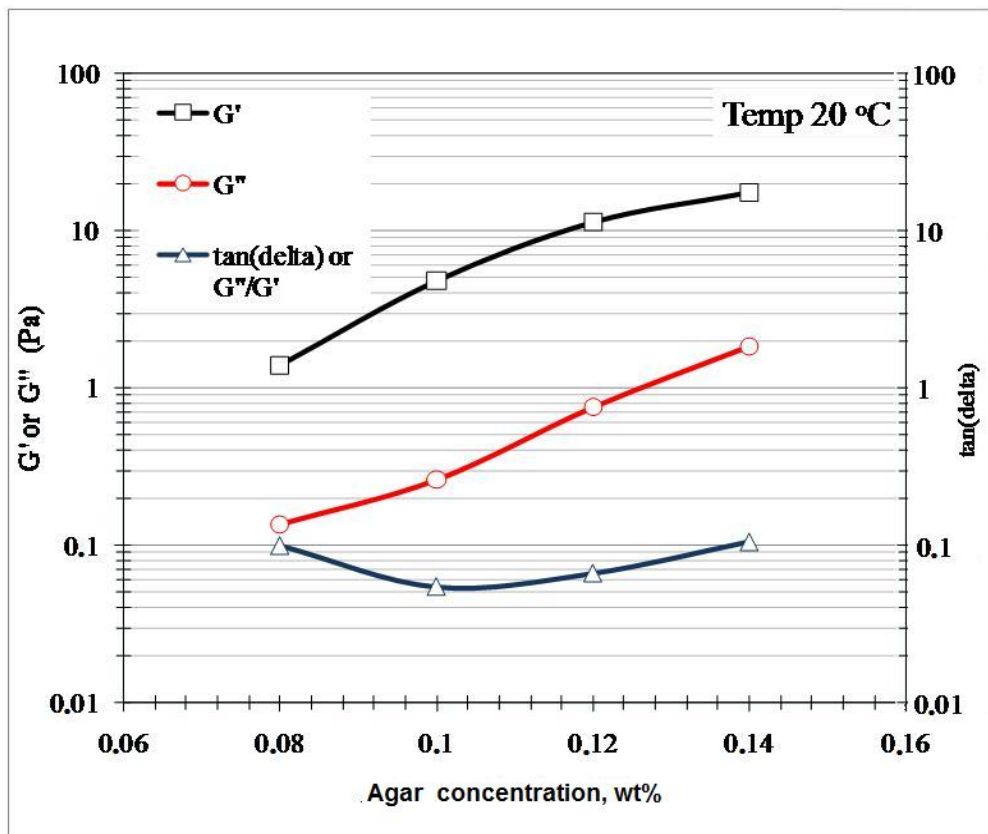


Figure 4.9: The effect of wt% agar concentration on G' and G'' .

Data in Figure 4.9 indicate that there is a semi-logarithmic correlation of the mechanical properties with the wt% agar concentration, while the elastic character of the material is dominant, i.e. $\tan\delta \ll 1$, throughout the investigated wt% range. A steady state flow test followed, showing that possible yield stress values of about 1 Pa must be expected only for the high concentration of 0.14 wt%, as it is shown in Figure 4.10.

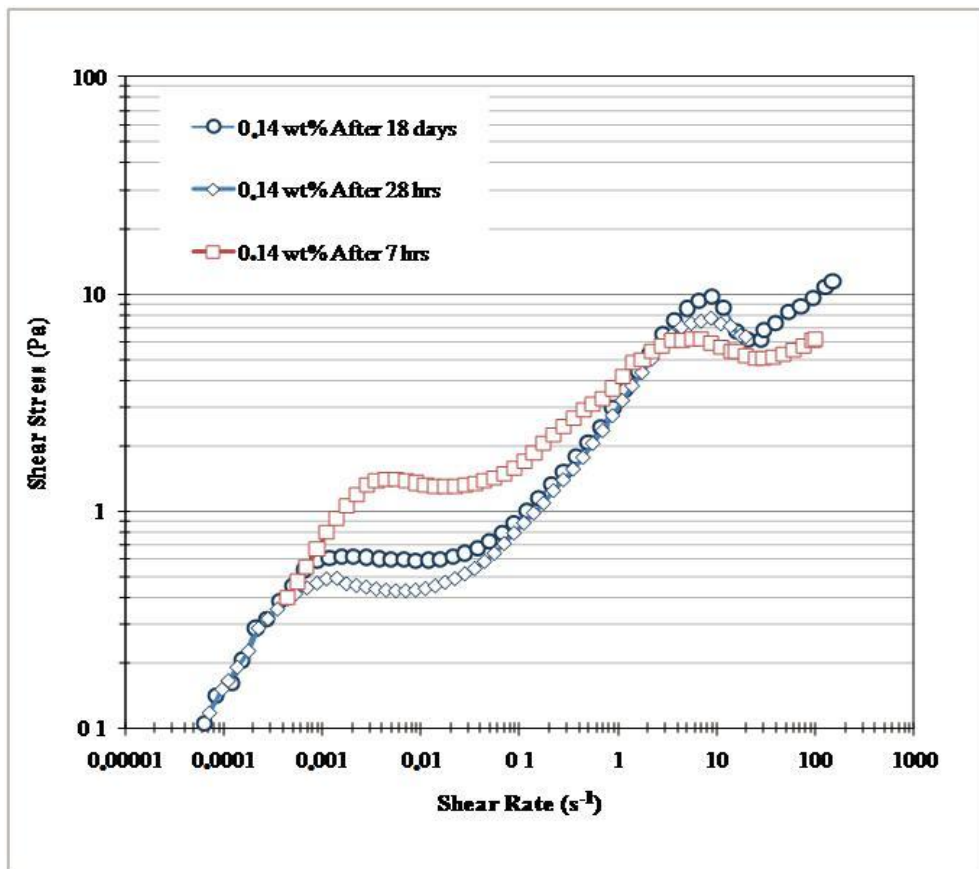


Figure 4.10: Ascending flow curves for the 0.14 wt% agar concentration (Temp. 20°C).

Initially, at low shear rates ($\dot{\gamma} < 3 \times 10^{-3} \text{ s}^{-1}$) all data points collapse on a line indicating an initial state of deformation, necessary to reform the gel structure, while in the range of 10^{-3} s^{-1} to 10^{-1} s^{-1} an extensive shear stress plateau is observed, indicating a yield stress behaviour. Following the gels with the terminated structure, i.e. after one day from preparation, fall on the same line and for $\dot{\gamma} > 10 \text{ s}^{-1}$ all samples exhibit non-monotonic flow curve, since a part of

the curve has negative slope. In Figure 4.10, one can see that the yield stress value, particularly for the case of 7 hours after the preparation, is much closer to the loss modulus (G'') value than to the storage modulus (G'). Under steady shear, because of the large deformation involved, the weak gel structure of agar is broken. However, under small amplitude oscillatory condition (in linear viscoelastic region, as the present dynamic data), the deformation is so small that the gel structure is rather intact. Only when the fluid obeys the Cox-Merz rule direct comparison between the shear viscosity data and complex viscosity data can be made; here clearly this is not the case. From Figure 4.10, it is noticeable that there is a characteristic relaxation time for the structure of 0.14 wt% agar gel of the order of magnitude of 10^3 sec, i.e. the reciprocal of the $\dot{\gamma}$ values signifying the passing from deformation to yielding state.

Concerning the measurements on gels prepared by gelatine it must be pointed out that the viscoelastic response of gelatine gels strongly depends on the thermal history of the sample and on the actual temperature of the measurement; for instance, the storage modulus of 1.1 wt% gelatine from 4°C to 20°C decreases from 19 Pa to 3 Pa. Accordingly, for 1.7 wt% gelatine from 4°C to 20°C decreases from 100 Pa to 20 Pa. Another difference from the agar gels was the fact that the adequate gap for non distorted waveforms was smaller, i.e. 650 microns for the 0.7 wt% gelatine, 850 microns for the 1.1 wt% gelatine and finally 1000 microns for the higher concentration of 1.7 wt%. The observed drift to higher values of G' and G'' in 0.14 wt% agar was also observed in gelatine gels; indeed more pronounced. Results for 1.1 wt% over approximately 4 days are shown in Figure 4.11 below.

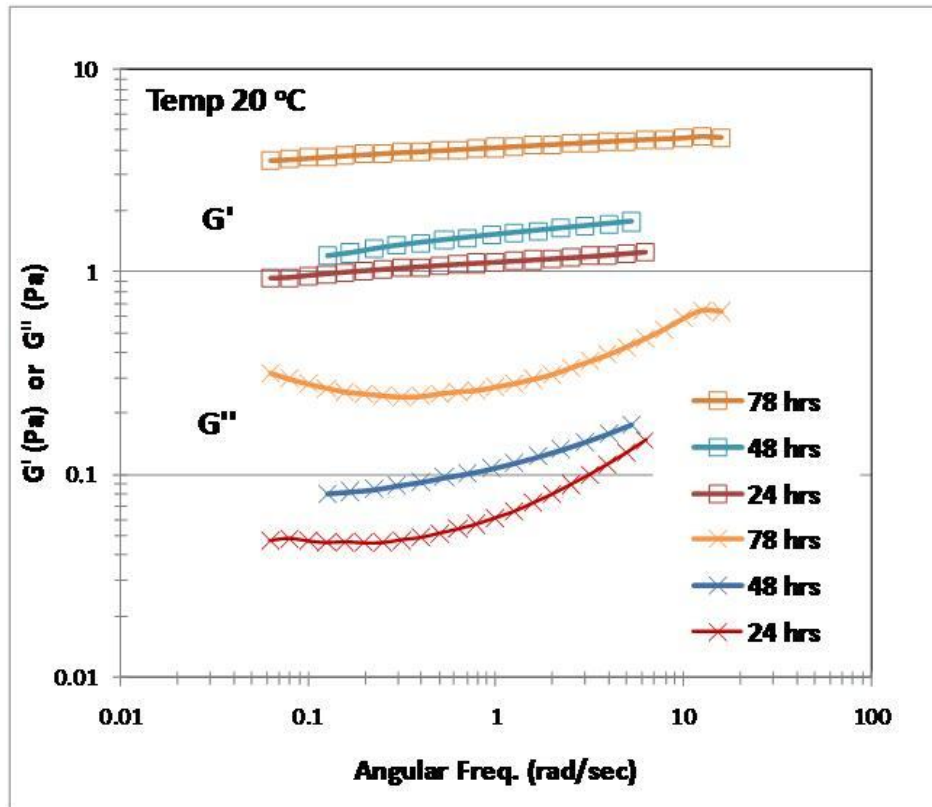


Figure 4.11: Effect of time over the values of G' and G'' for gels of 1.1 wt% gelatine. The lines connecting the data points are for guidance of the eye.

It must be pointed out that in this fluid, again, the storage modulus G' was about an order of magnitude higher than the loss modulus G'' for applied frequencies of 0.08 to 10 rad/s. For the higher concentration of 1.7 wt% gelatine, however, a greater divergence between G' and G'' was observed, while for the lower concentration (0.7 wt% gelatine) the G' was higher than the G'' only by a factor of 2.5. These results are presented in Figure 4.12. For the concentrations of 1.1 wt% and 1.7 wt% gelatine, the raw phase difference between the applied and the response of the gels was between 1.5 to 3.5 degrees, indicating fairly elastic behaviour; yet, in the lower gelatine concentration of 0.7 wt% the raw phase difference was approximately 20 degrees. This observation is in line with the increased applied strain of 15% for the lower gelatin concentration; the higher the strain for clear and non-distorted waveforms, the reduced the gel-like behaviour of the fluid. As Figures 4.11 and 4.12 show, for the concentrations of

1.1 wt% and 1.7 wt% the storage modulus is constant over wide ranges of frequencies, while the loss modulus appears more affected by the measurement parameters.

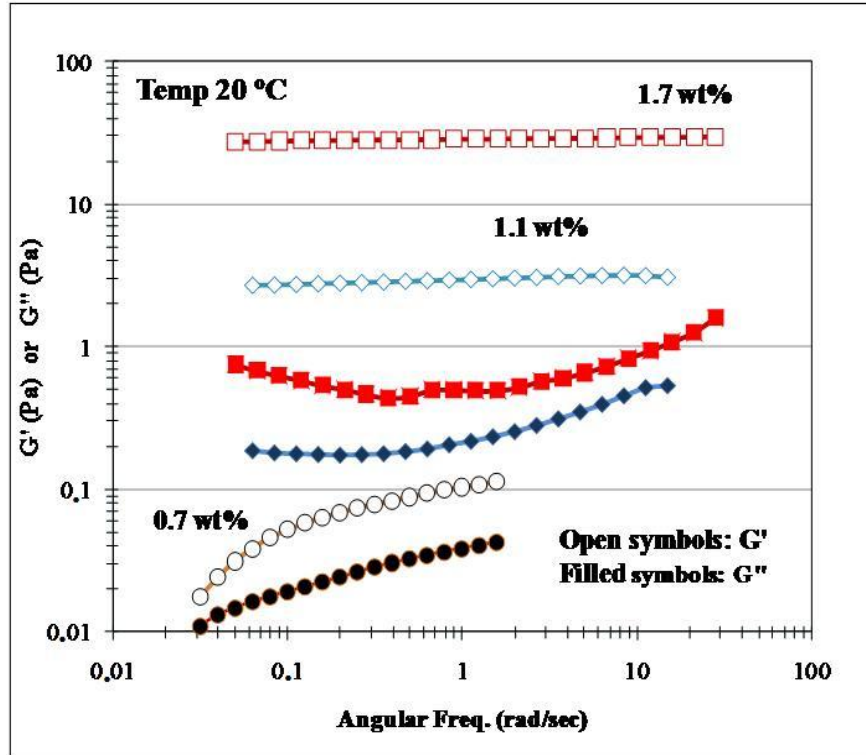


Figure 4.12: Frequency sweeps for gelatine of 0.7, 1.1, and 1.7 wt% gelatine.

Most of the reported results for gelatine correspond to concentrations over 1% and to lower temperatures, e.g. 16°C. Direct comparison to these results is difficult to make since the thermal history of the gels plays a crucial role in rheological behavior of gelatine gels. To this end, by using the terminated values for the mechanical properties of the gelatine gels (data in Figure 4.12), the following figure (Figure 4.13) is presented, where the effect of gelatine concentration wt% on the G' and G'' is shown.

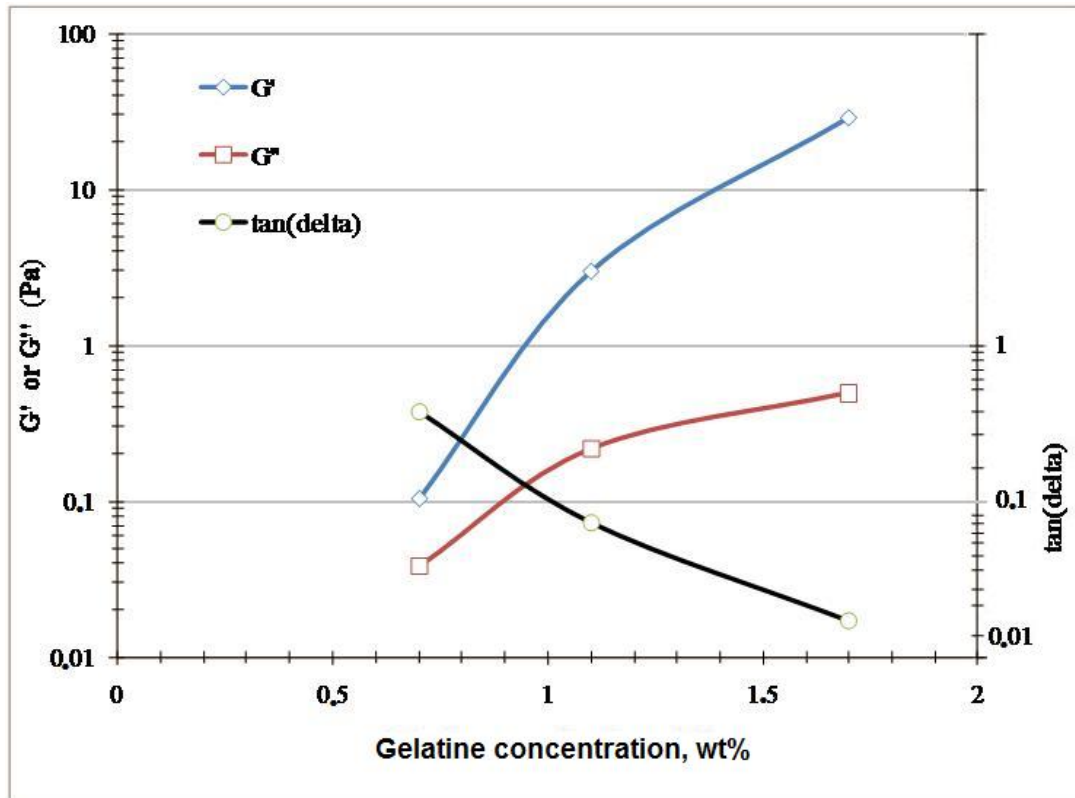


Figure 4.13: The effect of wt% gelatine concentration on G' and G'' .

By comparing the results in Figure 4.9 and 4.13 for 20°C, and taking the storage modulus as a measure of elastic behaviour is easy to say that the same elastic behaviour will be expected with an order of magnitude less in substance in case of agar. In addition, the more sensitive parameter of $\tan\delta$ shows that there is more balanced correlation of G' to G'' for the agar gels. It is postulated from the data trend in Figure 4.13, that also the gelatine data will reveal this balanced correlation of G' to G'' (or $\tan\delta$ almost constant) after 2% to 3% in gelatine concentration.

Finally, the steady state flow curves of the gelatine concentrations investigated are presented in Figure 4.14 below. These down curves (descending $\dot{\gamma}$ -values) reveal extensive plateau values over three orders of magnitude of $\dot{\gamma}$, i.e. $10^{-4} \text{ s}^{-1} < \dot{\gamma} < 10^{-1} \text{ s}^{-1}$. Although the shape of the curves related to higher concentrations is not smooth, yield stress values of 1 Pa and 10 Pa could correspond to 1.1 wt% and 1.7 wt%, respectively, while a good approximation for the

yield stress for the 0.7 wt% gelatine would be a value of 0.08 Pa. The ascending curves (not shown here) were similar to the ones of agar, having negative slope around $10^{-1} \text{ s}^{-1} < \dot{\gamma} < 1 \text{ s}^{-1}$, indicating that these highly structured fluids begin to flow by forming bands and after an increased $\dot{\gamma}$ -value the sample behaves as a homogenous material.

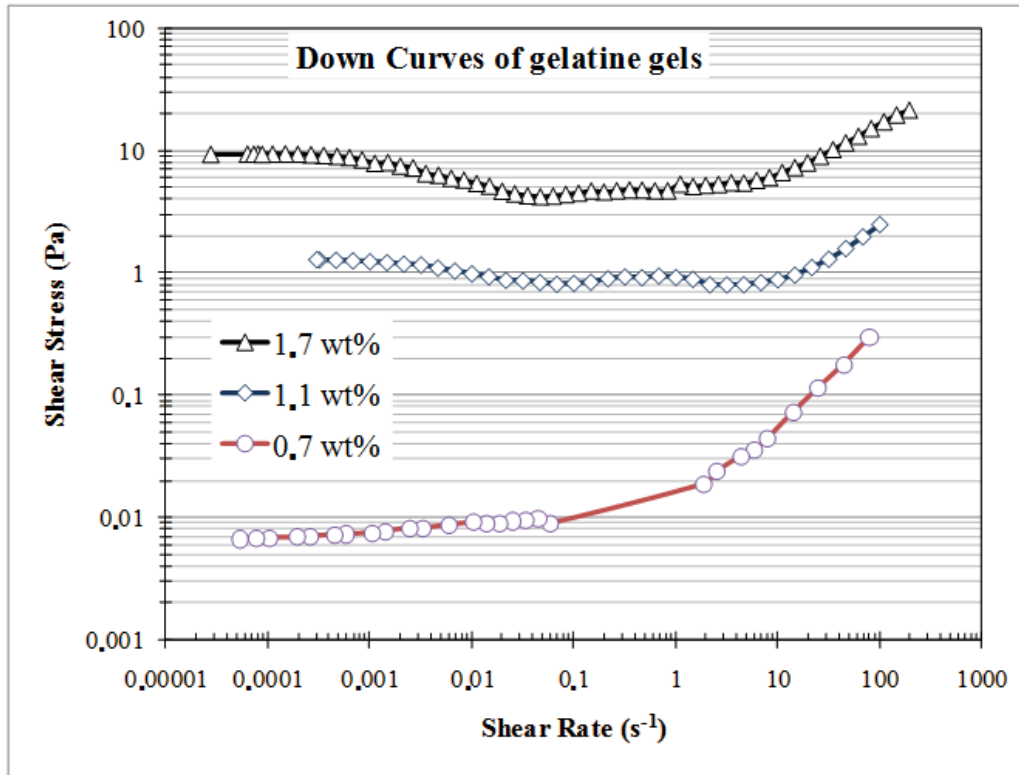


Figure 4.14: The steady state flow curves of gelatine samples of different concentrations.

Chapter 5

Cracking and Pattern Formation

Synopsis

In this chapter, the results of a set of experiments that investigate the spreading of surfactant solutions of different types on non-Newtonian substrates of different types are presented. The primary aim is to demonstrate that the formation of the crack-like “starburst” patterns can be observed on the surface of different types of compliant substrates following the spreading of surfactant solutions. Then, the different ways that the surfactant and substrate chemistry and concentrations can affect the qualitative and quantitative characteristics of the cracking patterns are investigated. The spreading behaviour of a highly soluble anionic surfactant, SDS, over a range of surfactant concentrations and agar gel concentrations is first presented. This is compared with a similar study using the non-ionic Silwet L-77 in order to examine the effect of superspreading on gels, which has been neglected in the literature so far. The spreading of Silwet L-77 on gelatine gel substrates is examined next, in order to make comparisons between the spreading behaviour on polysaccharide-based gels and on protein-based gels. Preliminary observations on surfactant spreading on gel layers of slightly smaller thickness are also included.

5. 1 Spreading of SDS on Agar Gels

5.1.1 Qualitative Behaviour

The spreading of droplets of aqueous SDS solution, over a range of surfactant concentrations on gel layers of varying concentrations and strengths, yields three types of qualitatively different regimes: the droplet remains approximately circular at the point of deposition; cracking patterns develop ahead of the deposition point; or the droplet spreads out, as it would on a liquid substrate, with no pattern formation. It is clear that the “starburst” patterns formation can occur only in “intermediate” conditions, when the specific concentration of the gel prevents it from having either a dominant solid-like or liquid-like behaviour, on the contrary it allows it to have elements from both behaviours. Figure 5.1 shows a pattern map depicting a summary of the observed behaviour corresponding to the experimental conditions investigated in this study.

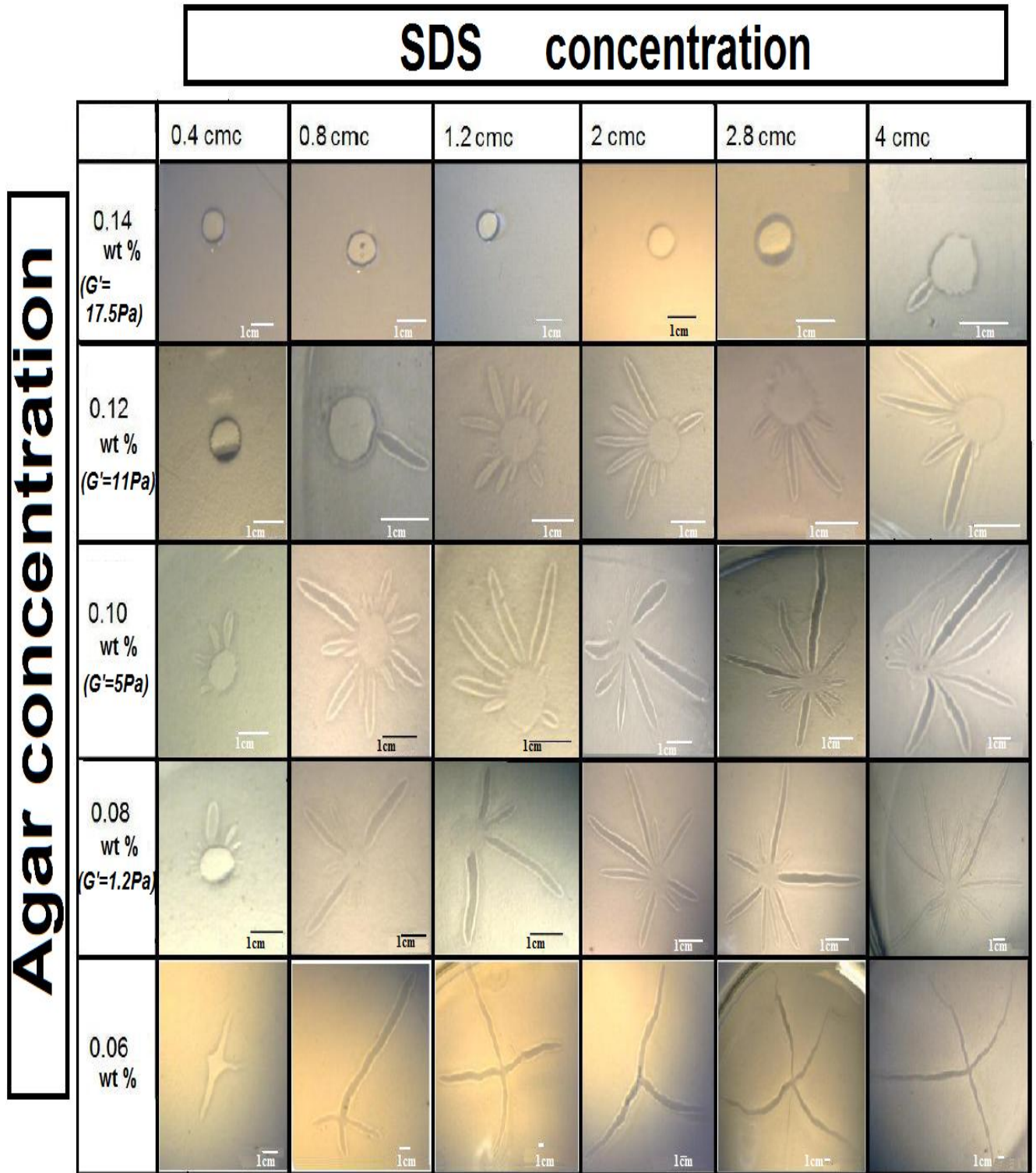


Figure 5.1: Pattern map showing fully-developed patterns from SDS droplets of different concentrations which have spread on approximately 4 mm-thick agar gel layers of varying concentrations.

Below the cmc of SDS, there is only little evidence of flow instabilities, with very small “arms” protruding from the area of drop deposition, and only for gel concentrations below 0.10 wt%. An increase in the surfactant concentration up to and around the SDS cmc results mainly in the development of a flow instability which is much more evident than in the case of lower SDS concentrations. Above the cmc, there is clear formation of patterns with visible and well-defined “arms” for all cases investigated between gel concentrations of 0.06 wt% and 0.12 wt%. Almost immediately after deposition, these “arms” are observed to grow from the point of the drop deposition region and to extend further into the surfactant-free regions of the gel surface. The “arms” are mostly straight, with some exceptions observed in the patterns formed from 0.8 cmc to 1.2 cmc and from 4 cmc drops (see Figures 5.2 B and 5.2 F), and also in the patterns seen in the weakest gel of 0.06 wt% concentration (see for instance Figure 5.2 E). On weaker gels (concentrations from 0.06 wt% to 0.08 wt%), the arms are noticeably longer and wider. On intermediate gels (from 0.08 wt% to 0.12 wt%), the patterns are generally smaller in size. When highly-concentrated surfactant droplets are used, both long and numerous “arms” can be seen (see Figure 5.2 F). No clearly visible “arms” can be observed in gel concentrations of 0.14 wt% and above, the single exception being the “arm” that is observed for a highly-concentrated drop of 4 cmc. Thus, this is the upper limit of the flow instability for SDS. On much weaker gels and concentrations near 0.04 wt% and below, the drops spread out as they would on a liquid substrate, and there is no formation of patterns or any other visible sign of them; these results are not shown in Figure 5.1 for the sake of brevity.

Figure 5.3 shows a typical example of the spatio-temporal evolution of the patterns. As it can be seen, the “arms” start to grow from the region of drop deposition that seems to be like a “circular disk”, and they propagate along the surface of the gel. The crack propagation seems

to be very fast initially, and to slow down later. Most patterns observed here have been developed fully after a time of approximately 30 seconds.

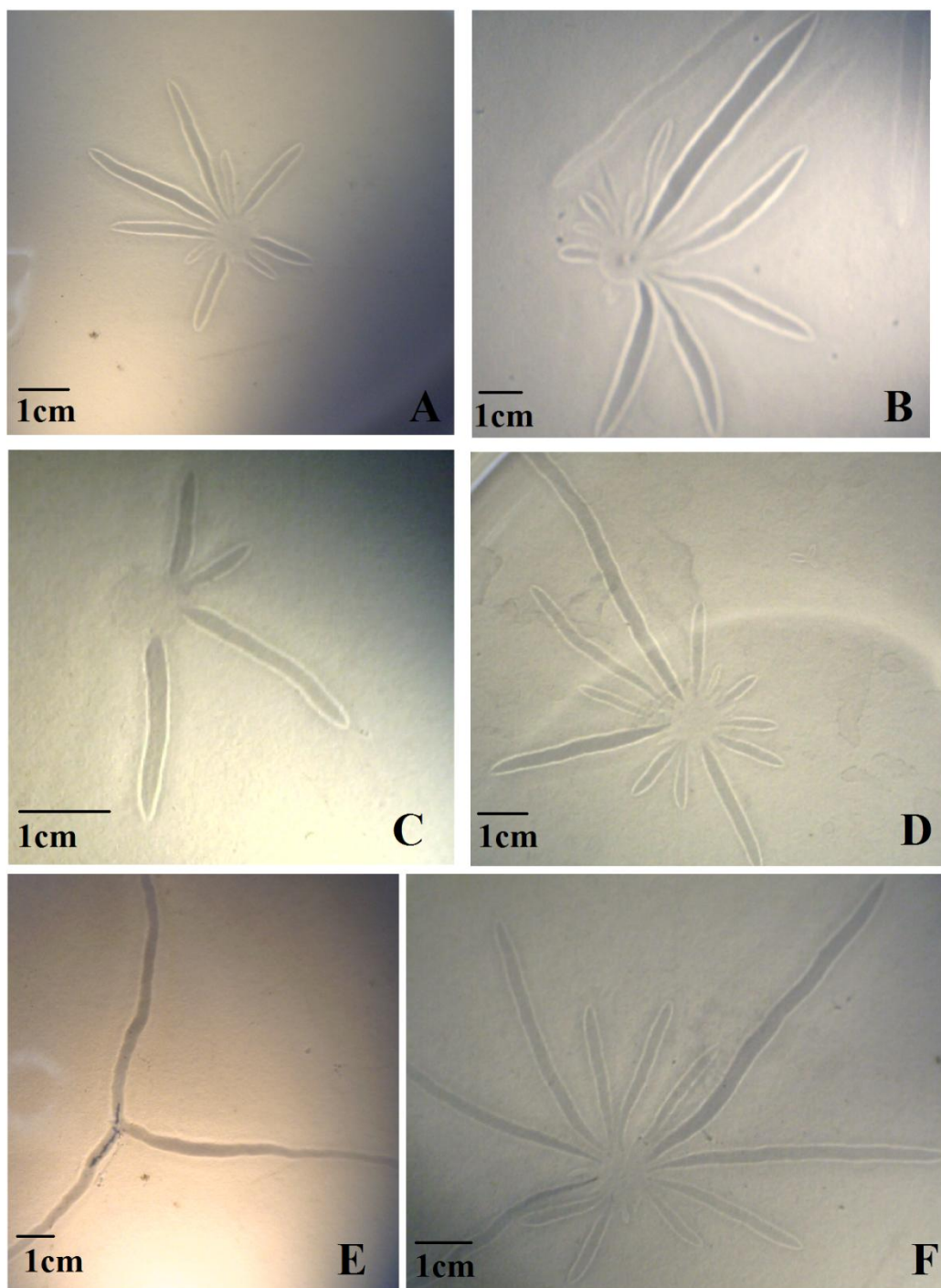


Figure 5.2: Close-up view of shadowgraph images of fully-developed patterns after the spreading of: A) SDS 2cmc on 0.08 wt% agar, B) SDS 4 cmc on 0.10 wt% agar, C) SDS 1.2 cmc on 0.08 wt% agar, D) SDS 2.8 cmc on 0.10 wt% agar, E) SDS 2 cmc on 0.06 wt% agar and F) SDS 4 cmc on 0.08 wt% agar.

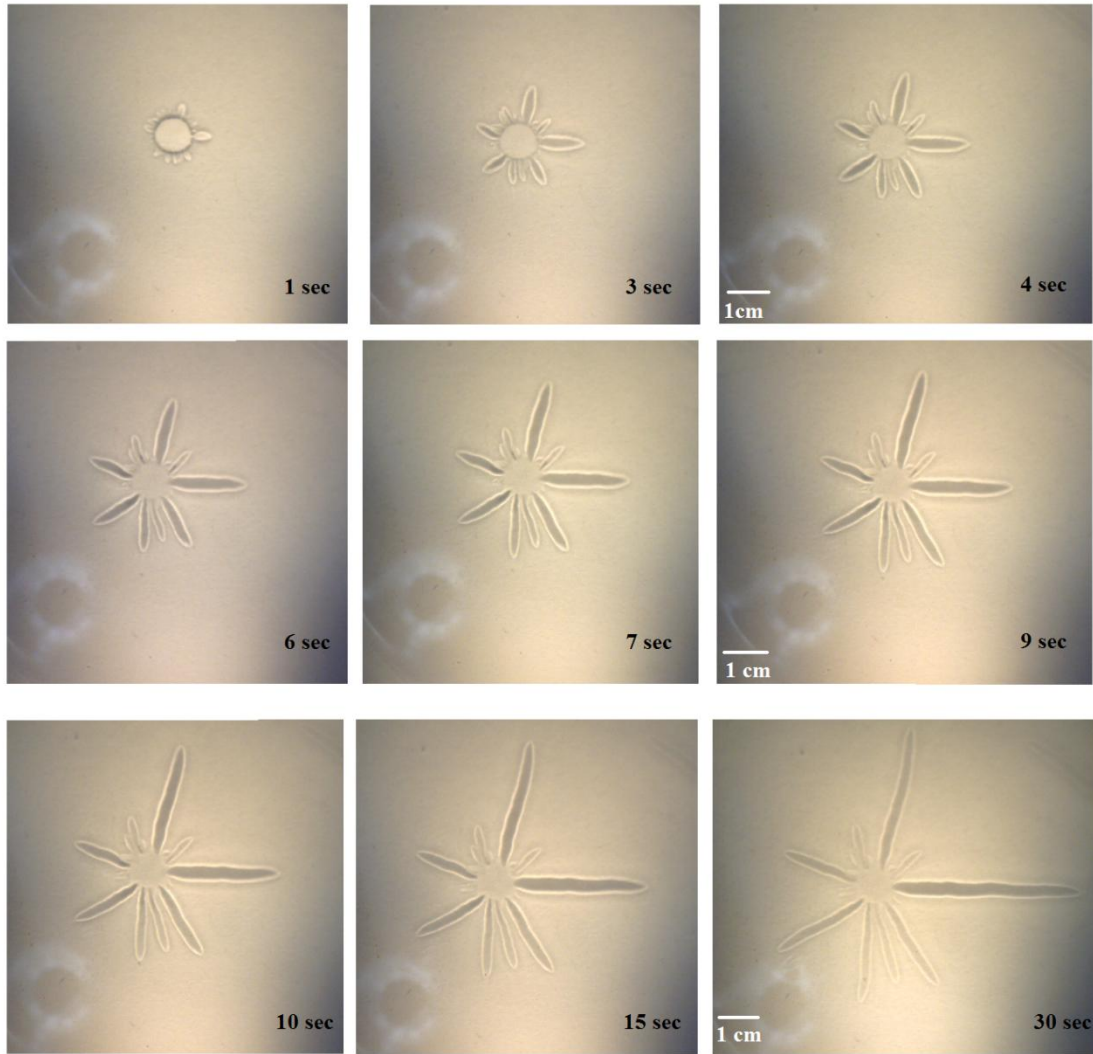


Figure 5.3: Spreading pattern evolution with time after the deposition of SDS 2.8 cmc droplet on a 0.08 wt% agar gel. After $t = 30$ s the evolution was completed.

5.1.2 Quantitative Behaviour

During typical spreading processes either of liquids on other liquids or on solids, the spreading ‘front’ advances with time following a power-law of the following form:

$$L(t) \sim kt^n \quad (5.1)$$

where $L(t)$ denotes the radial extent of spreading, k is the spreading coefficient, t is the spreading time, and n is the spreading exponent; the latter provides an indication of the balance between the dominant forces involved in the spreading phenomena (De Gennes 1985). In this study, the spreading fronts are clearly non-axisymmetric with spreading “arms” being formed instead. Therefore, we cannot describe a uniformed spreading front and a radial extent of spreading; what is important instead is the length of the spreading “arms”, and how this changes with time. Hence, in the power law described by (5.1), L will denote the length of a spreading “arm” for the remainder of this work. Values for the spreading exponent of each one of the “arms” of a single pattern were obtained from logarithmic plots of the evolution of its length, for approximately the same time duration in each case. From such plots and by considering that:

$$\log L = \log k + n \log t \quad (5.2)$$

both n and k can be determined. Each “arm” of the same pattern was found to have a somewhat different spreading exponent value; these were then ensemble-averaged for the experimental runs associated with a surfactant and a gel concentration pairing in order to find a single spreading exponent value for the each pattern. The results are shown in Figure 5.4.

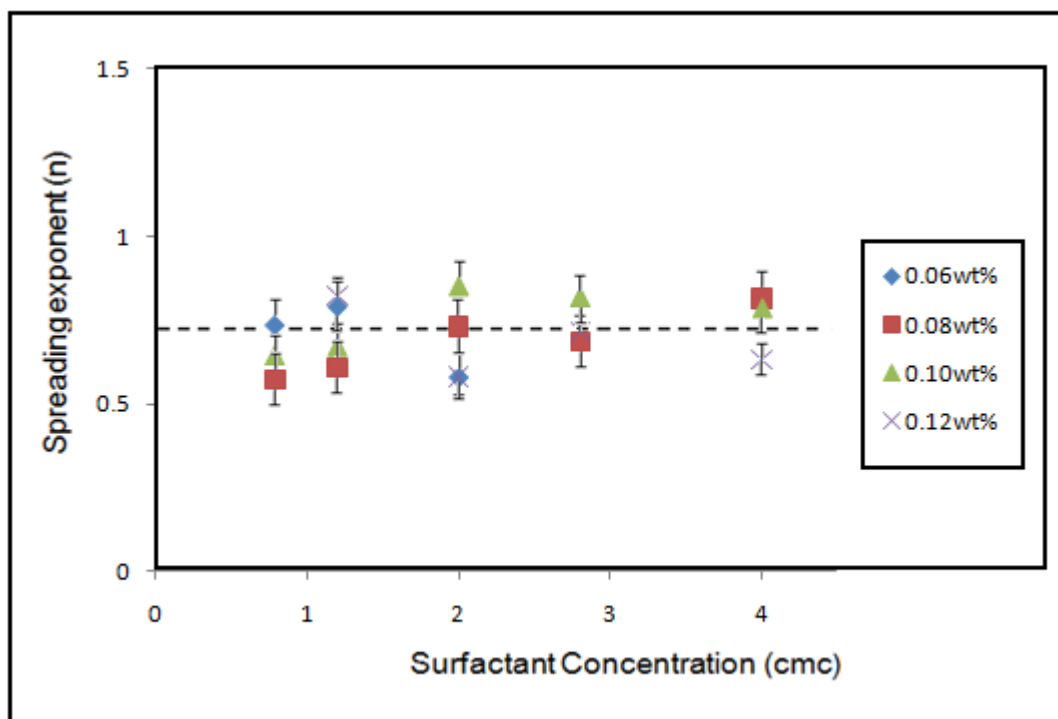


Figure 5.4: Variation of the spreading exponent with SDS concentration, for spreading on agar gel layers of different agar concentrations. These points represent the average of multiple runs. The dashed line is the theoretical value of $3/4$ which is characteristic of Marangoni-driven spreading on thick layers (Fay 1969, Hoult 1972, Jensen 1995).

The smallest value of the spreading exponent found here was approximately $1/2$ and the largest value was 0.85 . The majority of the values were found to be very close $3/4$, independently of surfactant concentration and gel concentration. Therefore, there seems to be a broad agreement with the $t^{3/4}$ scaling prediction, which is characteristic of Marangoni-driven spreading of a finite mass of surfactants on thick films, suggesting that Marangoni stresses are dominant (Fay 1969, Hoult 1972, Jensen 1995). The $t^{1/2}$ scale is characteristic of diffusive spreading of surfactants or the spreading of surfactant from an infinite reservoir (Ahmad and Hansen 1972). These findings are further discussed in section 5.1.3 below as well as in Chapter 6.

In order to determine the spreading rate, or in other words the velocity of the evolution of the spreading “arms”, we consider the following: Differentiating (5.1) gives:

$$\frac{dL}{dt} = nkt^{n-1} \quad (5.3)$$

where dL/dt denotes the growth velocity of an “arm”. Fitting $n=3/4$ in (5.3), gives:

$$\frac{dL}{dt} = \frac{3}{4}kt^{-1/4} \quad (5.4)$$

dL/dt is proportional to the spreading coefficient k , therefore k can be used to describe the spreading velocity; the higher the value of k , the higher the velocity. Figure 5.5 summarises the different values of k found for different agar gel and SDS concentrations.

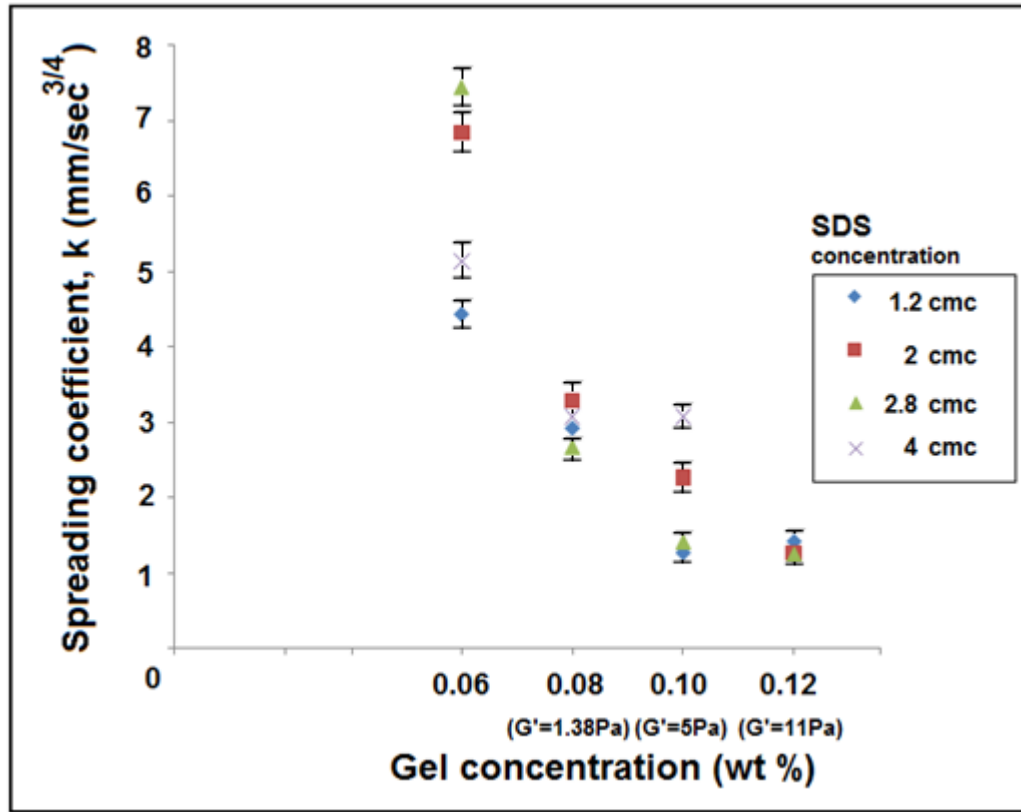


Figure 5.5: The dependence of the spreading coefficient on agar gel concentration for spreading of SDS droplets.

The minimum value of k is observed for a 1.2 cmc SDS drop spreading on a 0.12 wt% gel, and the maximum value of k is reported for a 2.8 cmc SDS drop spreading on a 0.06 wt% gel. The general trend discerned from Fig. 5.5 is that k has higher values for weaker gels, and lower values for stronger gels, thus it is suggested that faster evolution of cracks occurs on the surface of weaker gels, while slower evolution occurs on stronger gels. It seems that the driving force of the spreading is more favourable to overcome the retarding effects of the gel rheology in cases where the gel is weak. An increase in the concentration (strength) of the gel, increases the resistance of its rigidity against the force that promotes the propagation of the crack, resulting in smaller spreading rates. For a fixed gel concentration, the values of k seem to be independent of SDS concentration; there only seems to be a small tendency for

increasing SDS concentration to increase k , but this is mostly the case for surfactant concentrations up to 2 cmc.

The observation that higher spreading rates occur on the surface of weaker gels and slower spreading rates occur on the surface of stronger gels is demonstrated in the example shown in Figure 5.6 where dL/dt , as described in (5.4), is plotted against time for different agar gel concentrations. It is observed that dL/dt is decreasing while the gel concentration increases. In addition, for each gel concentration, dL/dt is observed to have its highest value for very early times, and to decrease afterwards.

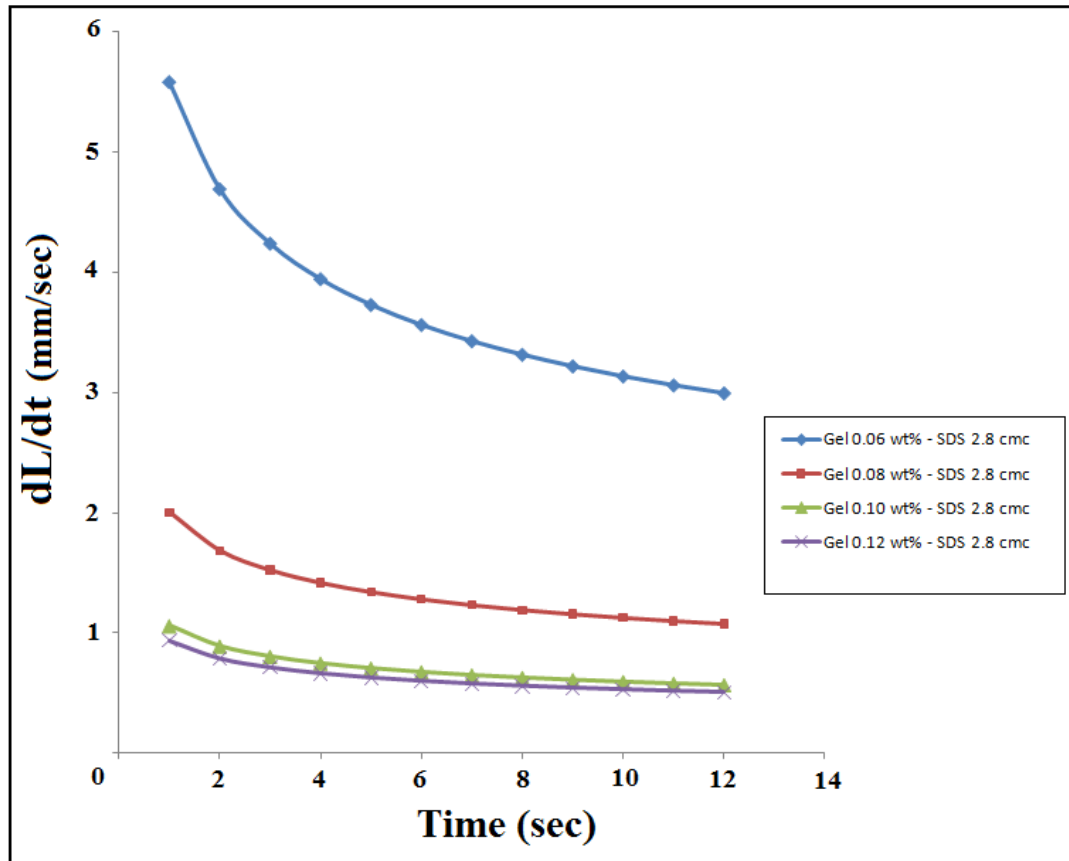


Figure 5.6: Plot of dL/dt against time for spreading of an SDS 2.8 cmc droplet on agar gels of varying concentrations.

Table 5.1 below summarizes the number of major spreading “arms” formed across a range of agar gel and SDS concentrations tested. The cases where there is no pattern formation are not shown here, and the maximum number of “arms” reported was 11, for highly-concentrated drops on moderately strong gels.

Table 5.1: *Number of major “arms” formed in patterns across the range of agar gel and SDS concentrations tested. These values represent the average of multiple runs. Typical standard error values vary from ± 0.5 to ± 1 .*

Agar gel conc. (wt%)	SDS concentration				
	0.8 cmc	1.2 cmc	2 cmc	2.8 cmc	4 cmc
0.06	4	4	3	4	4
0.08	3	4	6	7	11
0.10	5	5	6	11	7
0.12	1	7	7	5	5

Daniels *et al.* (2007) associated the flow instability with the number of “arms” that can form, and reported that an increase of surfactant concentration can lead to an increase in the number of “arms” in every case studied. In the present work, it is clear from Table 5.1 that there seems to be no distinct trend to be noted and the number of arms is scattered fairly evenly across the gel and surfactant concentration ranges studied. However, it can be seen that with highly concentrated surfactant solution, there is a higher propensity for larger number of arms to be formed. This is more evident in the case of 0.08 wt% gels. In the rest of the cases, there is mostly a trend for increased number of arms while the surfactant concentration reaches 2cmc to 3 cmc, but there is a decrease afterwards. For the smallest gel concentration

examined, 0.06 wt%, the number of arms seems to be always the same, with the single exception being a decrease in spreading of the 2 cmc drop. The same gel concentration region is also where the longest “arms” are reported, as the findings of Table 5.2 indicate.

Table 5.2: Minimum and maximum “arm” lengths (in cm) across the agar gel and SDS concentrations tested. These are measured using the software of the microcamera with an error of ± 0.01 cm.

Agar gel conc. (wt%)	SDS concentration									
	0.8 cmc		1.2 cmc		2 cmc		2.8 cmc		4 cmc	
0.06	Min	0.89	Min	1.91	Min	3.79	Min	3.09	Min	2.64
	Max	8.58	Max	7.10	Max	7.52	Max	6.20	Max	6.22
0.08	Min	0.46	Min	0.88	Min	0.73	Min	0.74	Min	1.12
	Max	1.92	Max	4.22	Max	3.03	Max	4.03	Max	5.50
0.10	Min	0.31	Min	0.41	Min	0.91	Min	0.41	Min	0.39
	Max	1.67	Max	3.71	Max	5.01	Max	3.47	Max	6.27
0.12	Min	-	Min	0.18	Min	0.73	Min	0.56	Min	0.87
	Max	-	Max	2.12	Max	3.03	Max	2.95	Max	2.17

The smallest “arms” reported are 0.18 cm long in the case of 1.2 cmc drop spreading on a 0.10 wt% gel, while the longest “arms” have a length over 8 cm for 0.8 cmc drops spreading on a 0.06 wt% gel. Only in this gel concentration region are the “arms” exceptionally long and limited by the diameter of the Petri dish. Between 0.08 wt% and 0.12 wt% the patterns are smaller and broadly of similar size, with the length of their “arms” being between 2mm and 5mm. In a manner similar to the trends presented in Table 5.1, the changes in surfactant

concentration do not seem to change the length of the arms monotonically. However, there is a much clearer trend regarding the effect of changing the gel concentration on the width of the “arms”, with the latter being thinner, as the gel becomes stronger. This behaviour is illustrated in Figure 5.7, where storage modulus is a measure of gel concentration (strength). Thus the data presented in Figure 5.7 and Tables 5.1 and 5.2 indicate that increasing the gel strength results in shorter and thinner arms whose number depends to a certain extent on the SDS concentration.

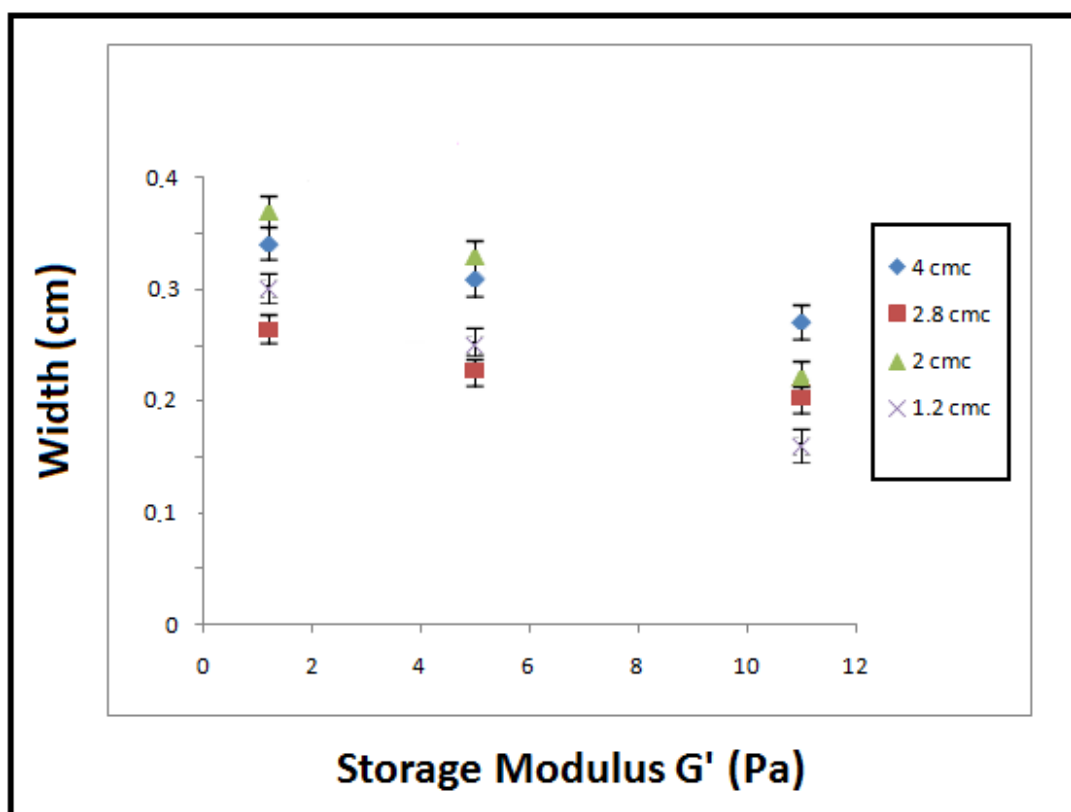


Figure 5.7: Dependence of the width of the pattern “arms” on the storage modulus of the agar gel. Each point represents the average of multiple runs. $G' = 1.38$ Pa corresponds to 0.08 wt% agar, $G' = 5$ Pa corresponds to 0.10 wt% agar, and $G' = 11$ Pa corresponds to 0.12 wt% agar.

5.1.3 Relative Strength of Forces

The rich dynamics of the systems of spreading liquids and underlying substrates owes its existence to the interplay between different mechanisms and effects that play a role in the spreading process. These include Marangoni stresses, viscous retardation, gravitational forces, surface and bulk diffusion and sorption kinetics. The values for the spreading exponents shown in Figure 6.4 are in broad agreement with the prediction that for Marangoni-driven spreading on a thick fluid layer, the spreading front advances in time as $t^{3/4}$ (Fay 1969, Hoult 1972, Jensen 1995). This strongly suggests that Marangoni stresses provide the main driving force for the spreading of SDS droplets on agar gels. This is supported by the surface deformations that appear as cracking “arms” and resemble the fingering instabilities behaviour that is characteristic of Marangoni flow (Afsar-Siddiqui *et al.* 2003). The time scale over which Marangoni forces act, t_m , is given by:

$$t_m = \frac{\mu L^2}{SH_o} \quad (5.5)$$

where S is the spreading coefficient, or in other words, the surface tension between the surfactant and the gel, H_o and μ are the thickness and the viscosity of the underlying fluid, respectively (as mentioned in section 2.2) and L is the length of the spreading “arms”. For the cases investigated here, it is $\mu \approx 1$ mPas, $0.002 \text{ m} \leq L \leq 0.085 \text{ m}$ (Table 5.2), $22 \text{ mN/m} \leq S \leq 35 \text{ mN/m}$, $H_o = 4 \times 10^{-3} \text{ m}$. This gives t_m values of the order 10^{-4} s to 10^{-1} s . Other forces might also be participating in the spreading process; therefore it is worth examining relative significance of Marangoni stresses to other effects, like diffusion and gravity. As mentioned in section 2.3, the relative strength of Marangoni stresses to surface diffusion transport is given by the surface Peclet number, Pe_s :

$$Pe_s = \frac{SH_o}{\mu D_s} \quad (5.6)$$

where D_s is the surface diffusivity and H_o is the film thickness. For SDS, $D_s \approx 10^{-10} \text{m}^2/\text{s}$ (Chang and Franses 1992). This gives Pe_s values of the order of 10^8 . Since $Pe_s \gg 1$, it is suggested that Marangoni stresses dominate over surface diffusive effects. The surface diffusive time scale, t_{Ds} , is given by:

$$t_{Ds} = \frac{L^2}{D_s} \quad (5.7)$$

Values for L range from 0.002 m to 0.085 m (Table 5.2) therefore t_{Ds} is of the order of 10^4s to 10^6s , indicating that surface diffusion is not significant until very late times.

The relative strength of Marangoni stresses to bulk diffusion transport is given by the bulk Peclet number, Pe_b :

$$Pe_b = \frac{UH_o}{D_b} = \varepsilon \left(\frac{SH_o}{\mu D_b} \right) \quad (5.8)$$

where $\varepsilon = H_o/L_o$ is the aspect ratio of the developed crack and has to be much less than 1 for the lubrication approximation to hold in the theoretical studies on drop spreading. Here L_o is the length of the developed crack, which can be in the order of 10^{-3}m when the cracks start to develop and then increase to the order of 10^{-2}m at later times. Therefore ε is initially in the order of 1, and decreasing thereafter; Pe_b is initially the order of 10^8 and can decrease to the order of 10^6 when the developed cracks become longer, suggesting that Marangoni stresses once again dominate, and that bulk diffusive transport can be more significant than surface diffusion. Surface and bulk diffusion coefficients were assumed to be of the same order of magnitude (Shen *et al.* 2002). It should also be noted that SDS is highly soluble, thus surface and bulk concentrations can come to equilibrium very quickly. The bulk diffusive time scale, t_{Db} , is given by:

$$t_{Db} = \frac{H_o^2}{D_b} \quad (5.9)$$

and is in the order of 10^4 s, indicating once again that bulk diffusion is not significant until very late times.

For thick underlying films, Marangoni stresses and hydrostatic pressure are expected to act in opposition during the spreading process (Gaver and Grotberg 1990, 1992). First introduced in section 2.3, the Bond number, Bo , expresses the relationship between the two physical mechanisms and is defined as (Gaver and Grotberg, 1990):

$$Bo \equiv \frac{\rho H_o^2 g}{S} \quad (5.10)$$

where ρ is the density of the underlying fluid and g is the gravitational acceleration. Bo is likely to achieve its greatest value for low surfactant concentrations on a thick substrate. For our experimental set-up, typical values for the relevant parameters are $\rho \approx 1000 \text{ Kg/m}^3$, $H_o = 4 \times 10^{-3} \text{ m}$, $g = 9.8 \text{ m/s}^2$, and $22 \text{ mN/m} \leq S \leq 34.5 \text{ mN/m}$. This gives $4.6 \leq Bo \leq 7.2$ suggesting that gravitational forces play a significant role in the spreading on thick films. The significance of gravitational forces might be responsible for hindering further growth of the cracks (see Chapter 6).

In addition to diffusion and gravity, sorption kinetics can also affect the strength of Marangoni stresses. The solubility parameter, β , is a measure of the relative significance of adsorption and desorption at the air-liquid interface (Jensen and Grotberg 1993):

$$\beta = \frac{k_a}{k_d H_o} \quad (5.11)$$

where k_a and k_d are the adsorption and desorption coefficients, respectively. The time scales are defined as:

$$t_a = \frac{H_o}{k_a} \quad (5.12)$$

and

$$t_d = \frac{1}{k_d} \quad (5.13)$$

therefore:

$$\beta = \frac{t_d}{t_a} \quad (5.14)$$

An estimation of the sorption kinetics time scales and the solubility parameter, β , for SDS solutions below the cmc is provided in Table 5.3.

Table 5.3: Sorption kinetics for SDS solutions below the cmc (k_a and k_d values are from Chang and Franses, 1995)

k_a (ms ⁻¹)	t_a (s)	k_d (s ⁻¹)	t_d (s)	β
3	1.3×10^{-3}	2.73×10^6	3.6×10^{-7}	2.7×10^{-4}

For highly soluble SDS, both k_a and k_d , increase at the same rate while surfactant concentration increases towards the cmc (Chang and Franses, 1995). Above the cmc, there is a high bulk micelle concentration that leads to accumulation of surfactant that decreases the surface tension gradients. This process, however, is diffusion controlled (see also Afsar-Siddiqui *et al.* 2003) and insignificant for the thick layers tested here.

5.1.4 Summary of SDS spreading

When spread on the surface of thick agar gel layers, a drop of SDS solution can break into a distinct crack-like formation that resembles a “starburst”. However, this formation can occur only within a “window” of specific agar gel concentrations (strengths) and SDS concentrations. This is for agar gel concentrations between 0.06 wt% and 0.12 wt% ($G' \leq$

11Pa) where the gel does not behave purely as a solid or as a liquid, and for SDS concentrations from near the cmc, and up to several times the cmc. The “arms” of these formations are mainly straight, and their number and length seem to change randomly while the system parameters change. It is evident that their width, however, decreases while the gel concentration (and strength) increases. It is also clear that for stronger (highly-concentrated) gels, the speed of crack evolution is slower than in weaker (lowly concentrated) gels. Marangoni forces seem to drive the process of the development of cracks, and they dominate over surface and bulk diffusion effects; gravitational forces are also significant.

5. 2 Spreading of Silwet L-77 on Agar Gels

5.2.1 Qualitative Behaviour

The spreading of drops of aqueous Silwet L-77 solution over a range of surfactant and gel concentrations gives rise to a range of behaviours broadly similar to those observed in the spreading of SDS. The main difference is the fact that the “starburst” patterns can now be formed over wider ranges of gel and surfactant concentrations. Figure 5.8 below shows a map of the fully-developed patterns observed within the experimental conditions of this study.

The presence of Silwet L-77 can make it possible for these formations to occur on the surface of the strongest agar gels investigated in this work, with concentrations around 0.14 wt%, or even on the surface of weaker gels, with concentrations around 0.04 wt%, something that was not observed in the case of SDS. In addition, droplets of SDS of very low concentrations, (below 0.4 cmc) produce no visible arms, while Silwet L-77 droplets of lower concentrations can still generate cracks, which although shallow and small, are, nevertheless, still visible. For gel concentrations outside the 0.04 wt% - 0.14 wt% range no pattern formation is observed,

with the substrate behaving more like a liquid below 0.04 wt% and more like a solid above 0.14 wt%.

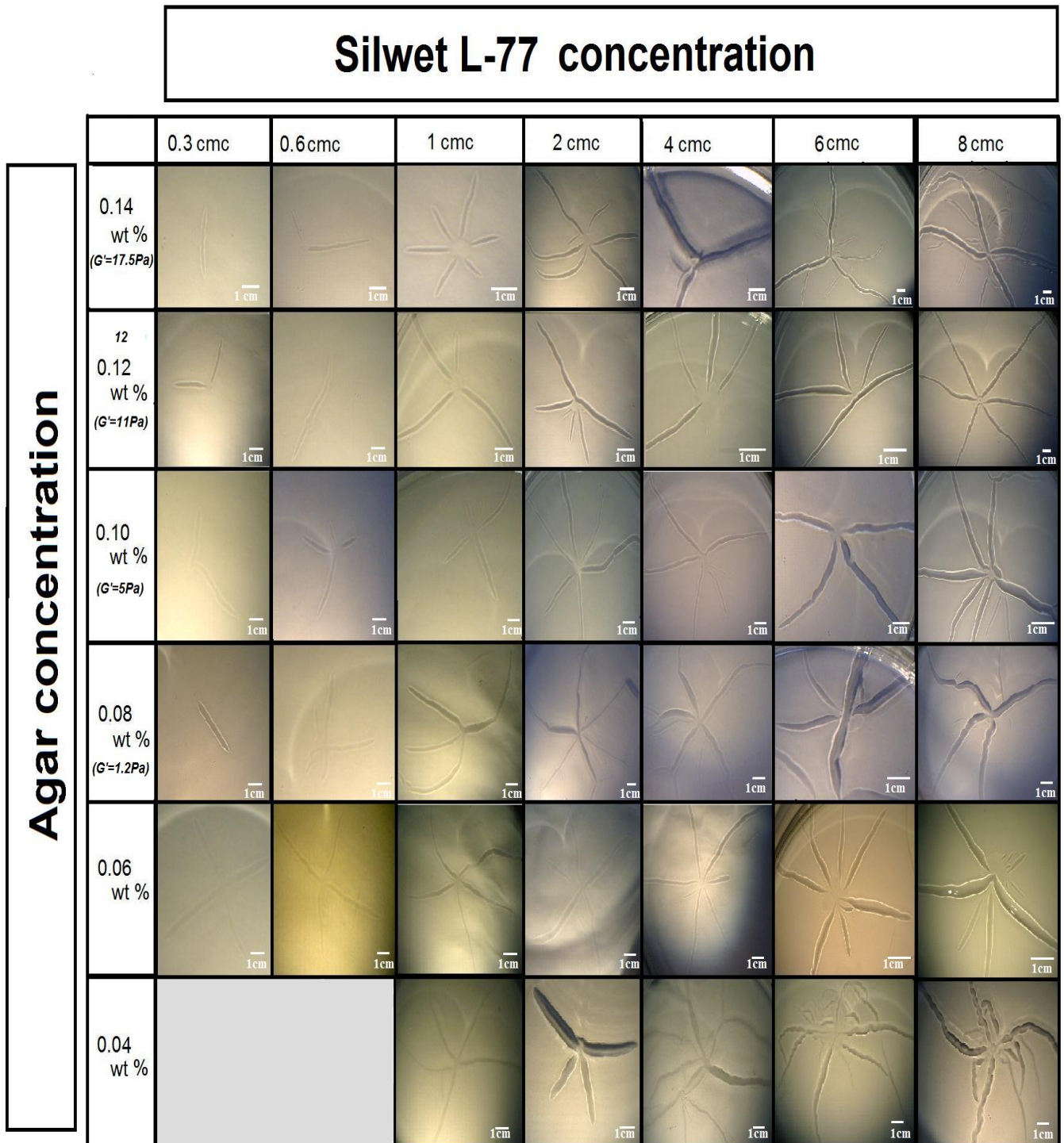


Figure 5.8: Pattern map showing fully-developed patterns from Silwet L-77 droplets of different concentrations which have spread on approximately 4 mm thick agar gel layers of varying concentrations.

Patterns with curved “arms” dominate, while straight “arms” are rare. It is also important to note that in most of the cases, and mostly for agar concentrations lower than 0.10 wt%, the cracks start to form and propagate directly from the spot where the deposited droplet contacts the gel surface. However, in concentrations higher than 0.10 wt%, it can be seen that the deposition and spreading of surfactant droplets were observed to form initially a small circular “disk” from where the arms grow (in the cases of 8 cmc drops spread on 0.12 wt% gels and of 1 cmc drops spread on 0.14 wt% gels, for instance). For lower surfactant concentrations, the pattern morphologies look comparatively less complicated, while increasing the surfactant concentration leads to more complex morphologies. For instance, the patterns that occur when droplets of very high surfactant concentration (between 6cmc and 8cmc) are spread on agar gels of concentrations near 0.04 wt% have “arms” with no well-defined edges, but ridges along the edges can be observed instead (Figures 5.9E, and 5.9F). When the more concentrated droplets spread on much stronger gels (concentrations near 0.14 wt%), thin cracks emerge from the edges of the main cracks (Figures 5.9A and 5.9B). The formation of the latter can be a result of the relief of the surface tension-induced stresses from new “arms” emanating from the existing ones, since the crack formation is limited by the diameter of the Petri dish.

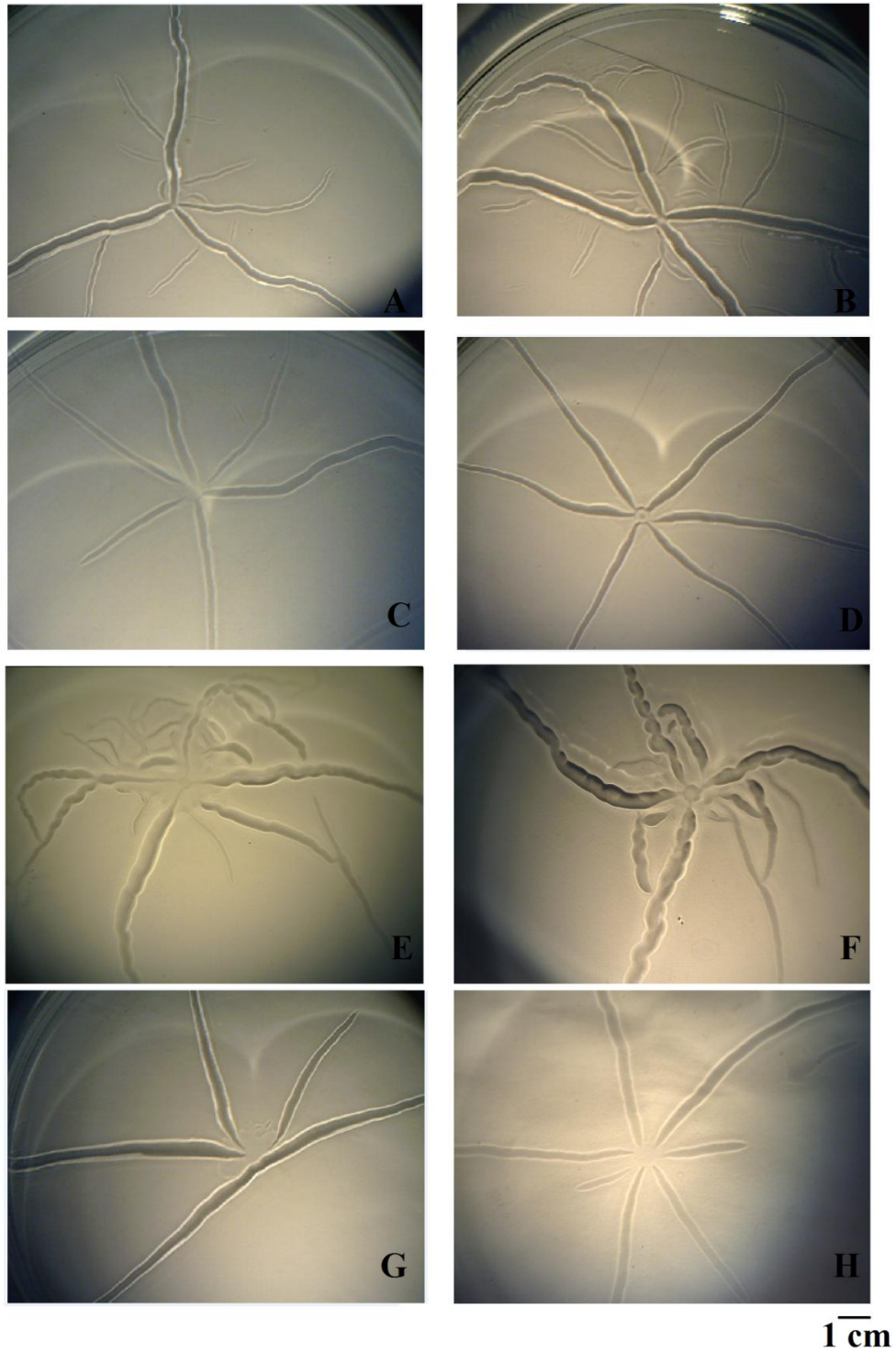


Figure 5.9: Close-up view of shadowgraph images of fully developed patterns after the spreading of: A) Silwet L-77 6 cmc on 0.14 wt% agar, B) SDS Silwet L-77 8 cmc on 0.14 wt% agar, C) Silwet L-77 2 cmc on 0.10 wt% agar, D) Silwet L-77 8 cmc on 0.12 wt% agar, E) Silwet L-77 6 cmc on 0.04 wt% agar, F) Silwet L-77 8 cmc on 0.04 wt% agar, G) Silwet L-77 6 cmc on 0.12 wt% agar and H) Silwet L-77 4 cmc on 0.06 wt% agar.

Figure 5.10 below shows a typical example of the spatio-temporal evolution of the patterns. Most patterns observed took less time to fully develop compared to the case of SDS, and the growth of the cracks has been completed usually after 15-20 seconds. This is somewhat faster compared to SDS spreading, where the crack growth was completed usually after 30 seconds. This difference manifests the superior spreading ability of Silwet L-77, and it should be attributed to the fact that Silwet L-77 is more surface active than SDS.

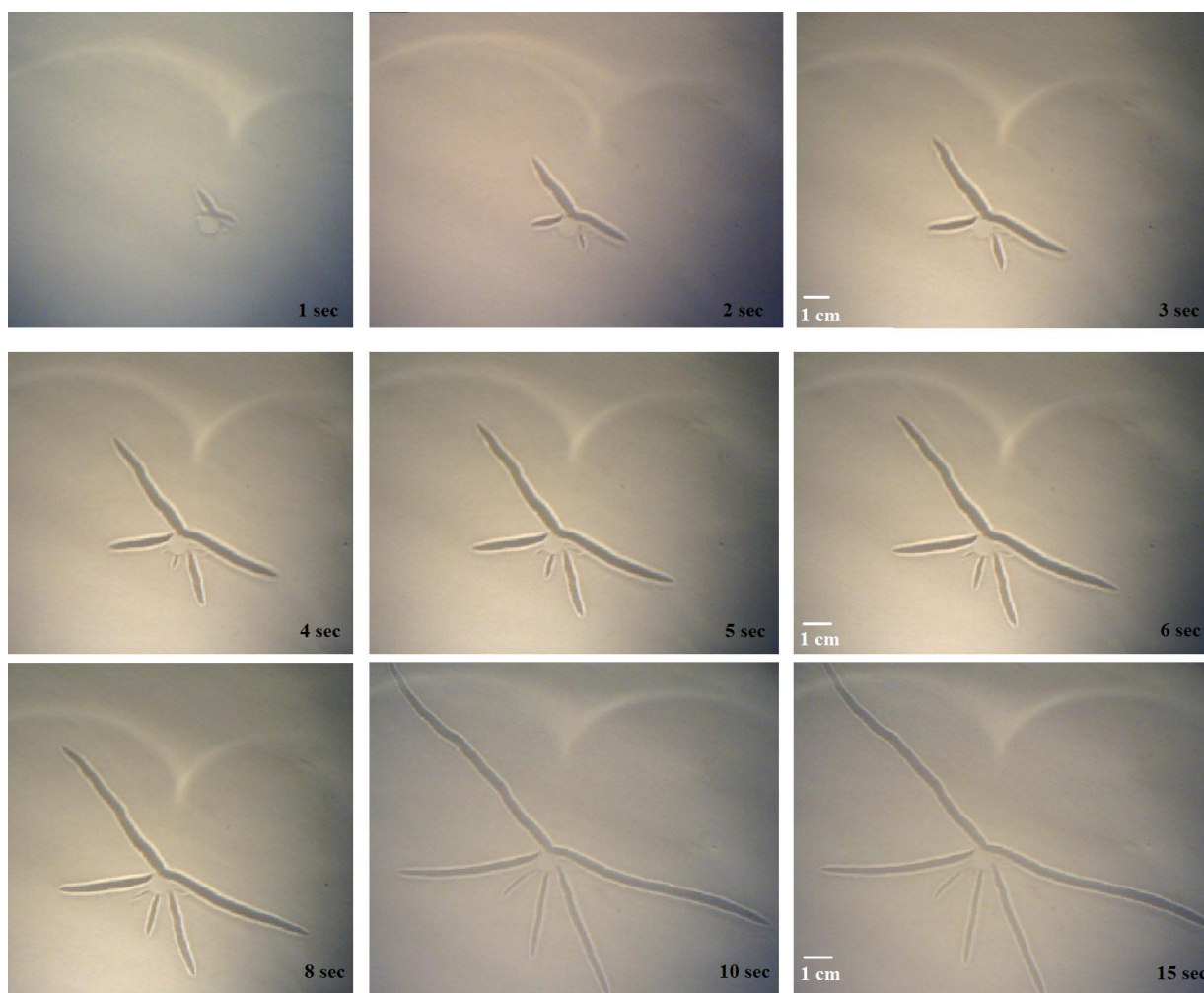


Figure 5.10: Spreading pattern evolution with time after the deposition of Silwet L-77 2 cmc droplet on a 0.12 wt% agar gel. After $t = 15$ sec the evolution was completed.

5.2.2 Quantitative Behaviour

The values for the spreading exponent, n , of the power law $L(t) \sim kt^n$ for each one of the “arms” of a pattern observed were obtained from logarithmic plots of the evolution of the arm’s length against time, in a similar way as with the spreading of SDS. Again, different values of n were reported for different “arms” within the same pattern, and these were averaged in order to determine a single exponent value for each pattern. Figure 5.11 shows that in the majority of the cases observed the value of n is close to $3/4$, with values near $1/2$ also observed. These findings are independent of surfactant and gel concentrations and suggest that the spreading is Marangoni-driven for the same reasons as those discussed in section 5.1.3 above.

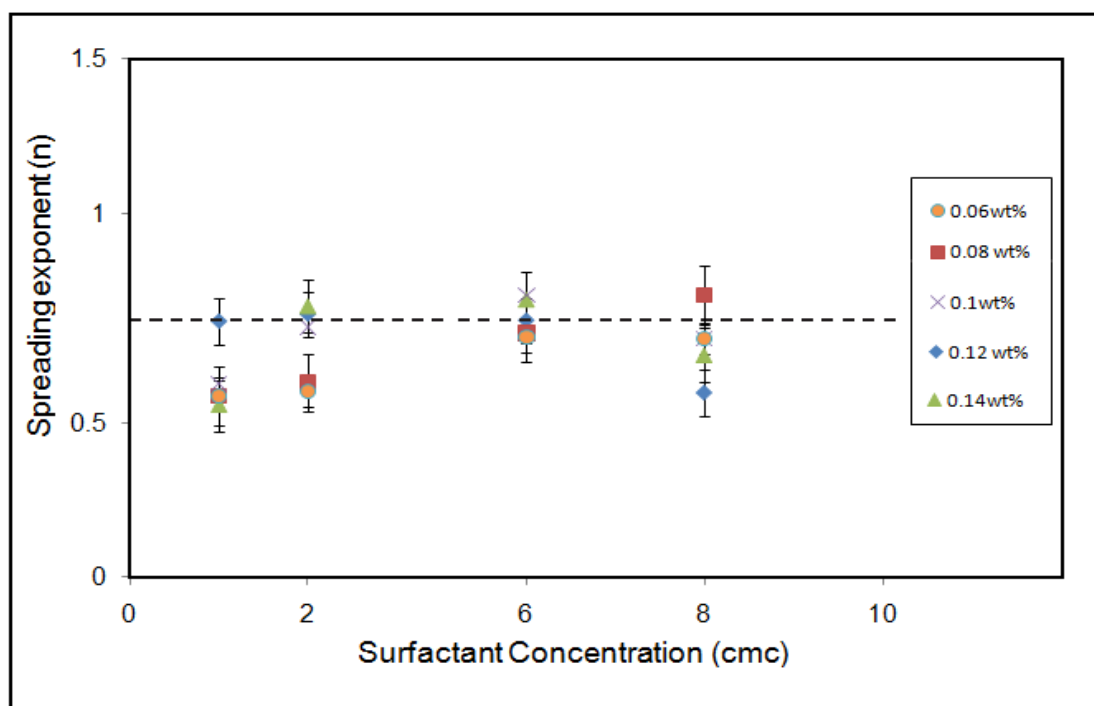


Figure 5.11: Variation of the spreading exponent with Silwet L-77 concentrations, for spreading on agar gel layers of different concentrations. These points represent the average of the multiple runs. The dashed line is the theoretical value of $3/4$ which is characteristic of Marangoni-driven spreading on thick layers.

Figure 5.12 below summarises the different values of k found for different gel and SDS concentrations. The superspreading behaviour of Silwet L-77 is evident when the velocity of the evolution of the cracks is considered; this velocity for the spreading of Silwet L-77 is much higher than the velocity of SDS spreading, and this can be suggested by comparing the values of the spreading exponent k in Figures 5.5 and 5.11. When Silwet L-77 is used on the same substrate, higher values of k can be achieved, namely from $2.5 \text{ mm/sec}^{3/4}$ to $14.3 \text{ mm/sec}^{3/4}$, while for SDS the values of k vary between $1.2 \text{ mm/sec}^{3/4}$ and $7.5 \text{ mm/sec}^{3/4}$.

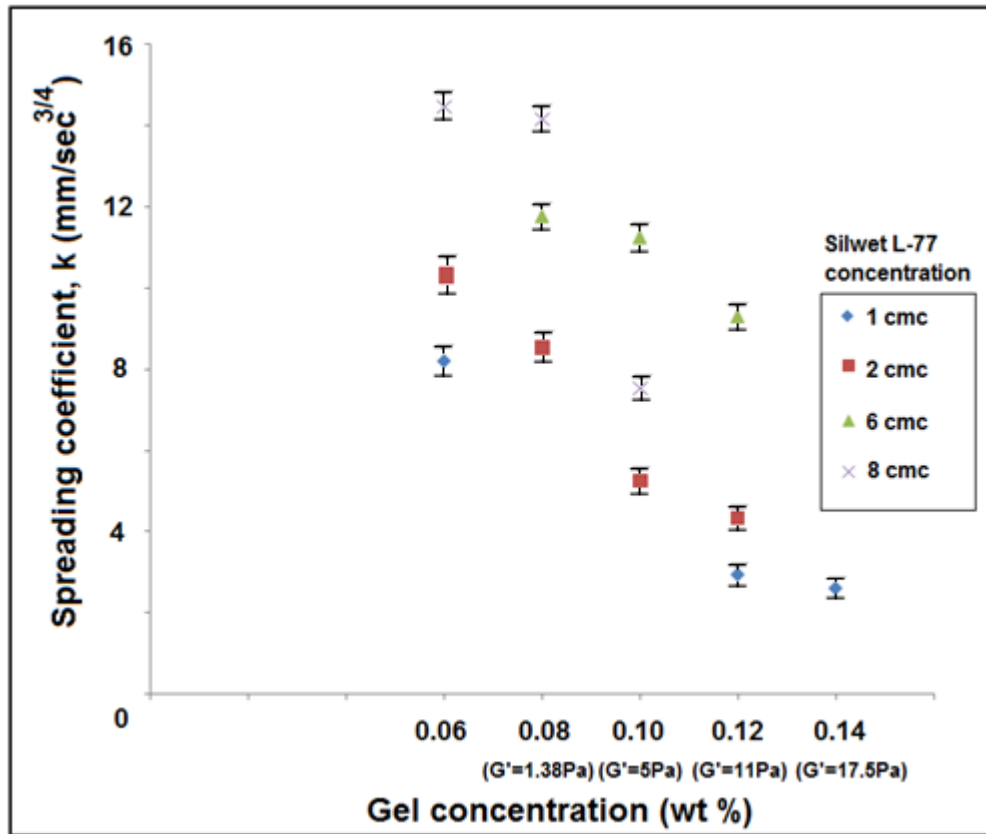


Figure 5.12: The dependence of the spreading coefficient on agar gel concentration for spreading of Silwet L-77 droplets.

The ability of Silwet L-77 to promote more rapid crack propagation speeds than SDS is illustrated in the example in Figure 5.13, where dL/dt is plotted against time for Silwet L-77

and SDS droplets spreading on agar gel substrates of the same concentrations. The spreading rates associated with Silwet L-77 are constantly higher than those of SDS.

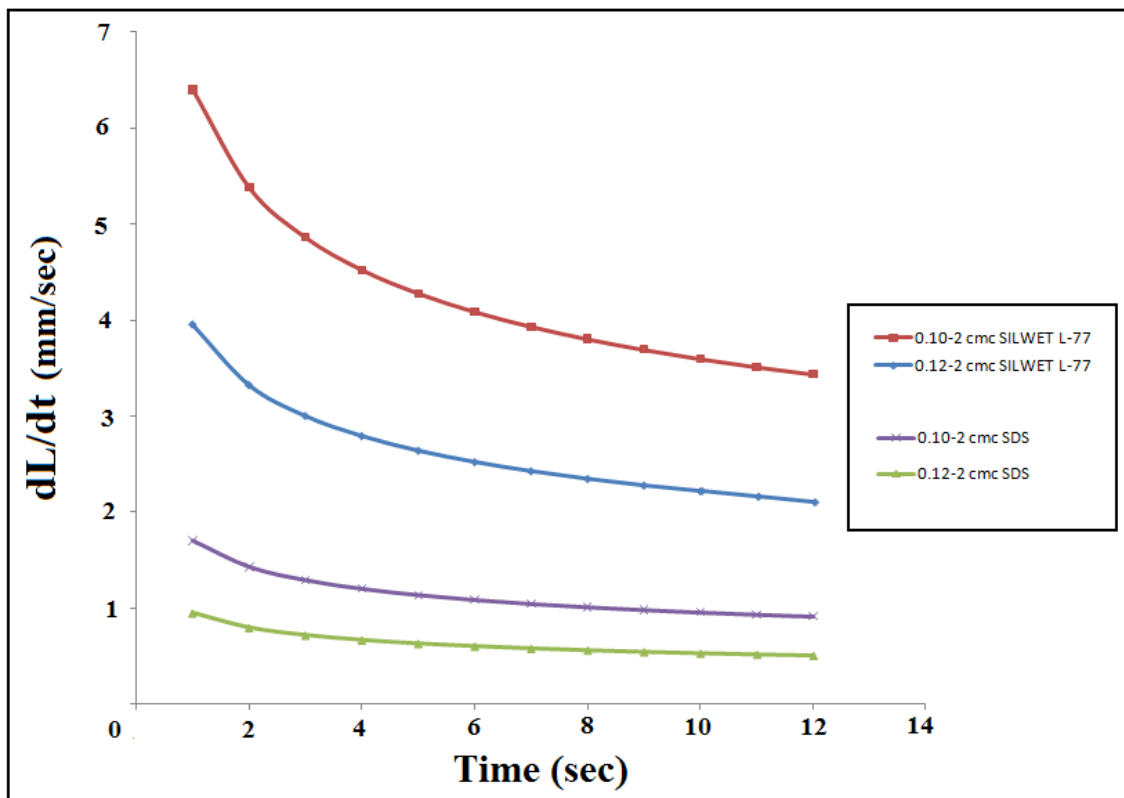


Figure 5.13: Comparison between the spreading rates of 2 cmc Silwet L-77 on 0.10 wt% and 0.12 wt% agar gel, and the spreading rates of 2 cmc SDS on the same substrates.

This finding becomes even more intriguing, given that the concentrations of Silwet L-77 used in the experiment are much smaller than those of SDS since the cmc of Silwet L-77 is much smaller than the cmc of SDS. In other words, Silwet L-77 can promote extremely rapid spreading and cracking, since even at concentrations smaller by an order of magnitude than those of SDS, it can generate higher “arm” formation and crack propagation speeds. This can be explained by the fact that Silwet L-77 is more surface active than SDS and also by the significance of the adsorption of superspreading surfactants at the substrate (discussed further in Chapter 6). Such rapid spreading rates can be a tentative evidence for supposing that there

is no accumulation of the superspreading surfactant at the contact line, and this can be achieved possibly by adsorption of the surfactant at the contact line and its subsequent diffusion away from this region, which reduces the surfactant concentration in relation to that upstream, sustaining the magnitude of the Marangoni stresses. Superspreading trisiloxane surfactants, such as Silwet L-77, that are adsorbed at the air/liquid interface, are more likely to transfer directly onto the substrate, compared to non-superspreading surfactants (Maldarelli 2011). Figure 5.13 demonstrates that the crack propagation is faster on the surface of weaker gels, while it is slower on stronger gels.

Table 5.4 shows the number of major spreading “arms” formed across a range of agar gel and Silwet-L77 concentrations tested. The gel substrates of concentration 0.04 wt% are omitted from Table 5.4, since measuring the number of “arms” was unrealistic in this concentration region due to the very complicated morphologies observed. The thin “arms” that can emerge from the main “arms” are also excluded.

Table 5.4: Number of major “arms” formed in patterns across the range of agar gel and Silwet L-77 concentrations tested. These values represent the average of multiple runs. Typical standard error values vary from ± 0.5 to ± 1 .

Agar gel conc. (wt%)	Silwet L-77 concentration						
	0.3cmc	0.6cmc	1cmc	2cmc	4cmc	6cmc	8cmc
0.06	4	4	3	5	6	7	4
0.08	1	4	4	5	5	5	4
0.10	2	4	4	6	5	5	4
0.12	2	2	4	6	4	5	6
0.14	2	2	6	7	3	4	4

The numbers of “arms” shown here vary from 1 to 6. Similarly to SDS, the number of arms is scattered fairly evenly across the gel and surfactant concentration ranges here, and no clear trend can associate their change in number with changes in surfactant or gel concentrations. However, there seems to be a “peak” surfactant concentration towards where the number of arms tends to increase, and decreases thereafter. This “peak” is observed in concentration near 2 cmc for most cases, with the exception being the “peak” of 6 cmc of gel concentration of 0.06 wt%.

Table 5.5 summarises the minimum and maximum length values for the “arms” formed by the spreading of Silwet-L77. The minimum length observed is 0.83 cm for a 1 cmc drop spreading on a 0.14 wt% gel, and the maximum length is 7.56 cm for a 8 cmc drop spreading on a 0.10 wt% gel. The smallest “arms” reported have a length of 0.83 cm long in the case of 1 cmc drop spreading on a 0.14 wt% gel, while the longest “arms” have a length of 7.46 cm for 8 cmc drops spreading on a 0.12 wt% gel. Changes in surfactant concentration do not seem to change the length in a consistent way.

Table 5.5: Minimum and maximum “arm” lengths (in cm) across the agar gel and Silwet L-77 concentrations tested. These are measured using the software of the microcamera with an error of ± 0.01 .

Agar gel conc. (wt%)	Silwet L-77 concentration									
	1 cmc		2 cmc		4 cmc		6 cmc		8 cmc	
0.06	Min	3.48	Min	2.74	Min	3.23	Min	4.32	Min	4.48
	Max	4.89	Max	4.79	Max	5.33	Max	5.67	Max	4.91
0.08	Min	1.22	Min	2.37	Min	2.90	Min	2.29	Min	4.39
	Max	5.78	Max	6.53	Max	5.96	Max	3.62	Max	6.47
0.10	Min	0.95	Min	2.12	Min	3.54	Min	3.74	Min	3.86
	Max	2.46	Max	4.12	Max	4.95	Max	5.08	Max	7.56
0.12	Min	0.84	Min	2.07	Min	2.20	Min	4.44	Min	3.90
	Max	2.61	Max	5.74	Max	7.36	Max	7.03	Max	7.46
0.14	Min	0.83	Min	3.45	Min	3.65	Min	4.28	Min	3.67
	Max	2.29	Max	4.49	Max	4.23	Max	7.45	Max	7.41

The increase in gel concentration seems to have an effect on the width of the “arms”, with the “arms” becoming thinner with increasing concentration. This behaviour is illustrated in Figure 5.14, where the storage modulus is a measure of the gel concentration (strength).

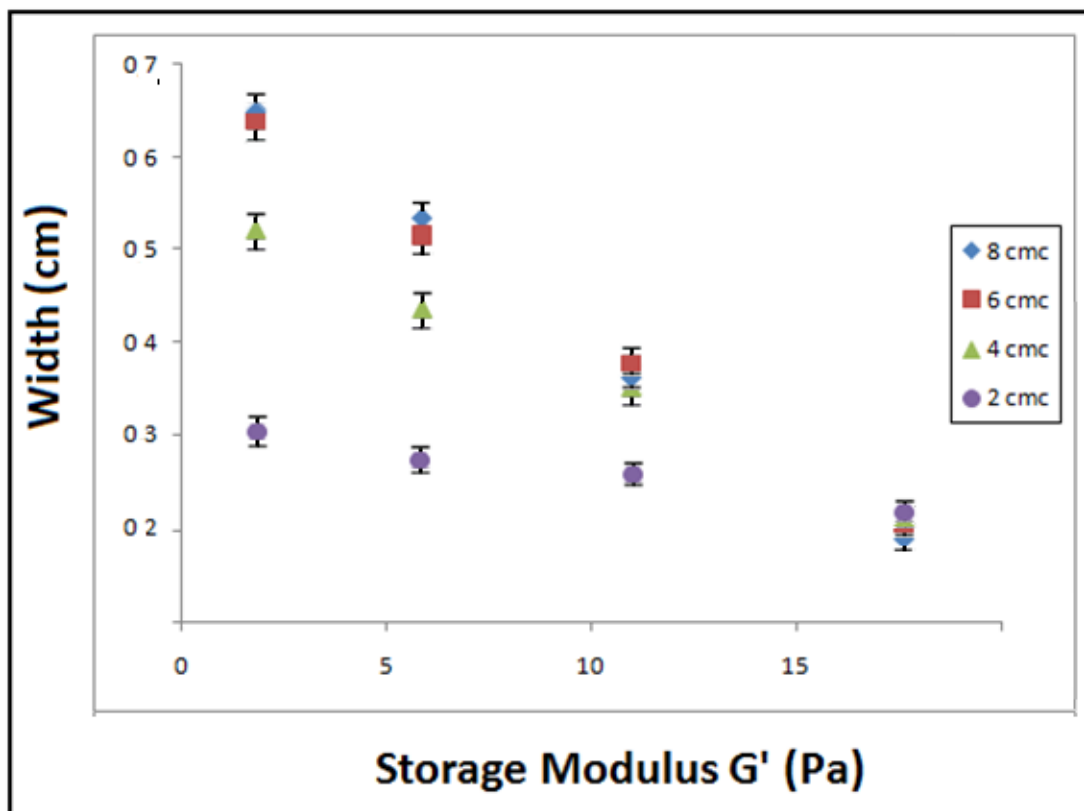


Figure 5.14: The dependence of the width of the pattern “arms” on the storage modulus of the agar gel. Each point represents the average of multiple runs. $G' = 1.38$ Pa corresponds to 0.08 wt% agar, $G' = 5$ Pa corresponds to 0.10 wt% agar, $G' = 11$ Pa corresponds to 0.12 wt% agar and $G' = 17.5$ Pa corresponds to 0.14 wt% agar.

5.2.3 Relative Strength of Forces

The spreading exponents shown in Figure 5.11 indicate that the spreading is Marangoni-driven at all surfactant and gel concentrations. In addition, the formation of spreading “arms” resembles the fingering instabilities that are associated with Marangoni flow. The significance of Marangoni stresses in relation to other participating forces is demonstrated in this section.

For the different gel and Silwet L-77 concentrations tested, S varies from 36 mN/m to 47.5 mN/m, L varies from 0.008 m to 0.075 m (Table 5.5), and time scale over which Marangoni stresses act, t_m , varies from 10^{-4} s to 10^{-3} s. The relative strength of Marangoni forces to diffusive transport can be characterised by considering the Peclet number. The surface Peclet

number, Pe_s achieves values of 10^8 , and the ratio of Marangoni to surface diffusion time scales, t_m/t_{Ds} is of the order of 10^{-6} , suggesting that Marangoni stresses strongly dominate over surface diffusive effects for the time scales associated with spreading. For the same parameters, Equation 5.8 gives values of the bulk Peclet number, Pe_b , from 10^8 to 10^6 and the ratio of Marangoni to bulk diffusive time scales, t_m/t_{Db} , achieves values from 10^{-8} to 10^{-7} , indicating that bulk diffusive effects are more significant.

The Bond number, Bo , determines the relative strength of Marangoni forces to gravitational forces, and it is likely to achieve large values for spreading on thick underlying layers. The parameters for Silwet L-77 spreading on agar gels, via equation 5.10, give Bond number values from 3.3 to 4, indicating that gravitational forces are significant. However, they seem to be less significant than in the case of SDS spreading on the same substrates. An estimation of the sorption kinetics time scales and the solubility parameter, β , for Silwet L-77 solutions is provided in Table 5.6. It was assumed that the k_a and k_d values for Silwet L-77 are of the same order of magnitude with the corresponding values for superspreading trisiloxane surfactants of similar molecular structure (from Kumar *et al.* 2003).

Table 5.6: Sorption kinetics for Silwet L-77 solutions (k_a and k_d values are for superspreading trisiloxane surfactants from Kumar *et al.* 2003).

k_a (ms ⁻¹)	t_a (s)	k_d (s ⁻¹)	t_d (s)	β
1.63×10^{-5}	2.4×10^2	1.95×10^{-5}	5×10^4	2×10^2

5.2.4 Summary of Silwet L-77 spreading and comparison with SDS spreading on Agar Gels.

The spreading of aqueous Silwet L-77 solution droplets on agar gels can lead to the formation of spreading “arms” that propagate on the gel surface. Compared with the spreading behaviour of SDS, this of Silwet L-77 shows many similarities and also many differences. Most notably, the crack formation associated with Silwet L-77 has much more complicated morphologies. The spreading “arms” are either very curved, or they have ridges along their edges. They are generally larger in size compared to the ones formed by SDS droplets, but their length and number changes randomly while the surfactant and gel concentrations change. However, their width clearly decreases with increased gel concentration. Cases where thin and smaller “arms” emerge from the main “arms”, were also reported.

The superspreading behaviour of Silwet L-77 manifests itself by promoting very rapid crack evolution, even for concentrations smaller by an order of magnitude than those of SDS. For weaker gels, the crack evolution is faster than the one for stronger gels, as is the case with SDS spreading. The fact that the “window” of surfactant and gel concentrations where the cracks can be observed is much wider, compared to SDS spreading (agar gel concentrations from 0.04 wt% to 0.14 wt%, and surfactant concentrations from below the cmc, up to 8 cmc) can be also attributed to superspreading. Strong Marangoni stresses promote crack formation. These dominate over surface and bulk diffusion forces. Gravitational forces are also important, but seem to be less significant than those generated during SDS spreading.

5. 3 Spreading of Silwet L-77 on Gelatine Gels

5.3.1 Qualitative Behaviour

Crack-like patterns were also observed on the surface of gelatine gel substrates after the deposition and subsequent spreading of aqueous Silwet L-77 solution droplets. The main difference is that the cracks are now formed for gel concentrations that are much higher than those in the case of agar. More specifically, visible crack patterns can be observed for gel concentrations between 0.7 wt% to 1.7 wt%, one order of magnitude higher than the 0.04 wt % - 0.14 wt % limits reported so far. Cracks are seen for a very wide range of surfactant concentrations, from below the cmc, to well above the cmc. However, the quantitative characteristics of the patterns do not change much after the surfactant concentration exceeds 10 cmc (see also Section 5.3.2). The results obtained from the deposition and spreading of Silwet L-77 droplets on the surface of gelatine gels are summarised in the pattern map presented in Figure 5.15. Changes in the system parameters, which are the surfactant and gel concentrations, promote discernible variations in the morphologies observed. Lower gel concentrations such as 0.7 wt% and 0.9 wt% show wider and more clearly visible major arms. Intermediate gel strengths such as 1.1 wt% and 1.3 wt% give interesting crack patterns with a large number of “arms”. Branching arising from the major spreading “arms” is also observed in these concentration regions.

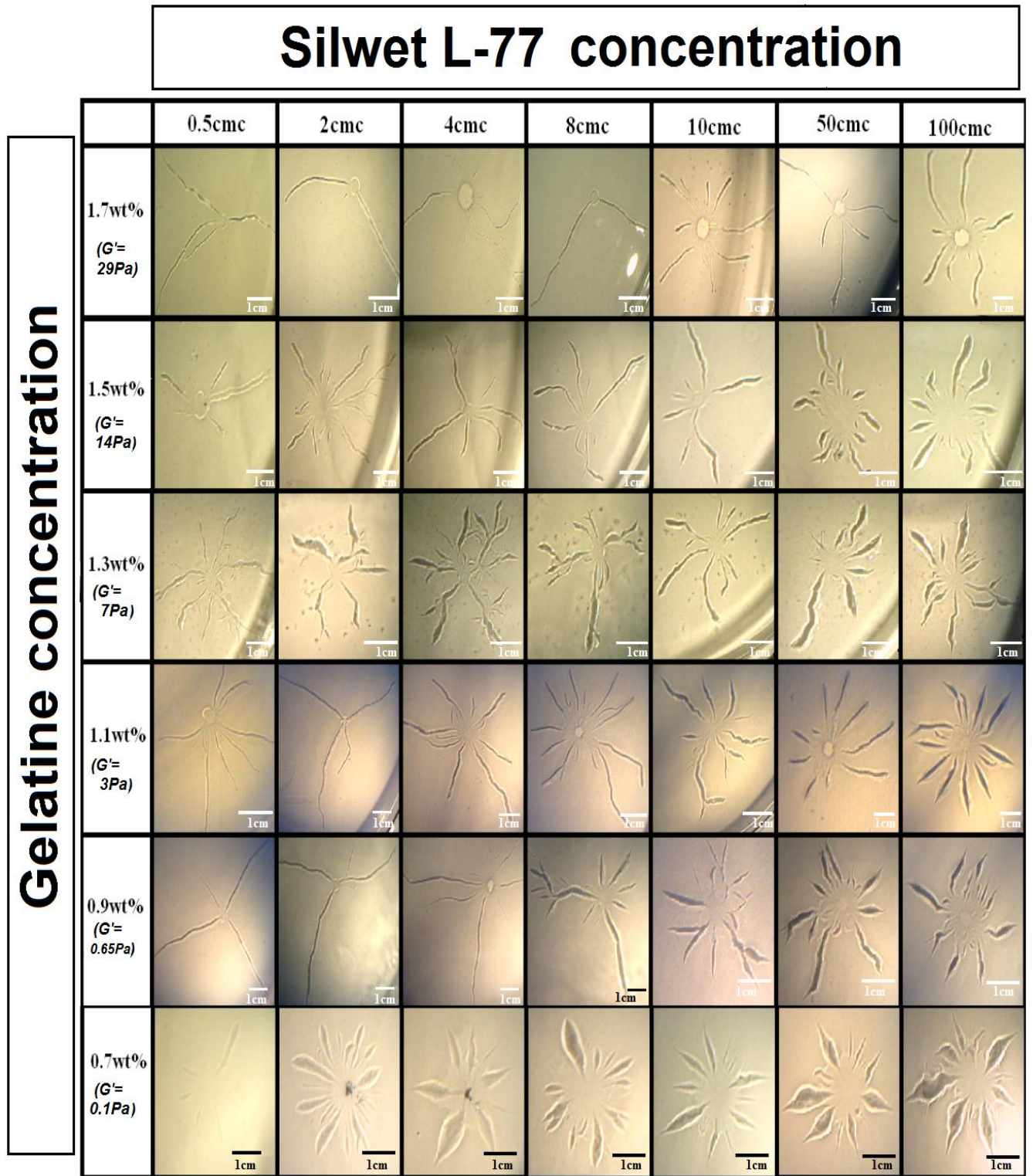


Figure 5.15: Pattern map showing fully-developed patterns from Silwet L-77 droplets of different concentrations which have spread on approximately 4 mm-thick gelatine gel layers of varying concentrations.

For gels concentrations between 1.5 wt% and 1.7 wt% the “arms” are much thinner and fewer in number with minimal branching. For gelatine concentrations outside the range of 0.7wt% to 1.7wt%, no visible crack patterns or other signs of deformation are observed. On extremely weak gel samples below 0.7wt%, surfactant droplets spread as they would on any liquid substrate. Also, on high gel strength samples above 1.7wt%, the droplets remain essentially axisymmetric. Varying the surfactant concentration also gives interesting comparative results. Lower Silwet surfactant concentrations such as 0.5 cmc and 2 cmc give relatively thinner and fewer arms. However, higher concentrations, between 10 cmc and 100 cmc, are characterized by patterns with much wider “arms” and considerable branching. Similarly to agar, the presence of ridges along the “arms” is common among gelatine concentrations below 0.9 wt% (Figure 5.16) and branching wisps are common among gelatine concentrations above 0.9 wt% (Figure 5.17). Elements of both of these morphologies can be seen in gelatine concentrations of 0.9 wt%.

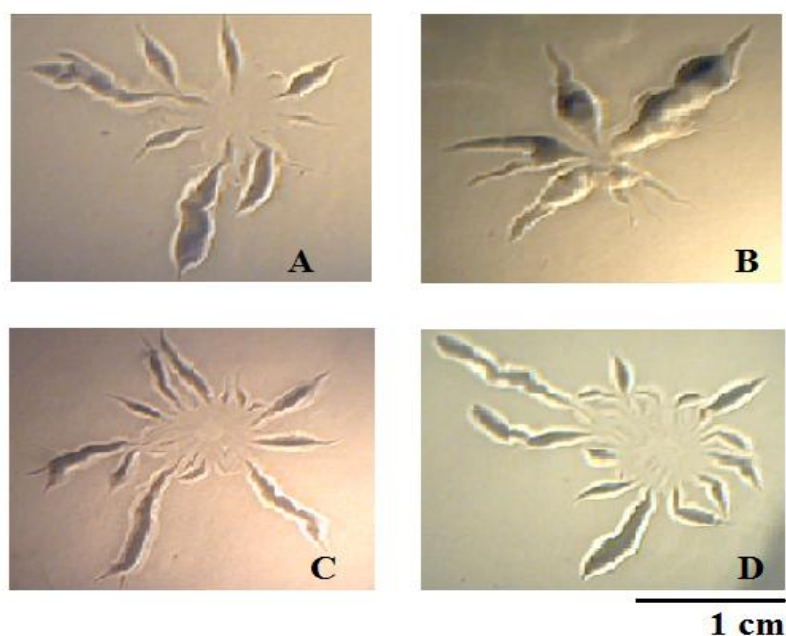


Figure 5.16: *Ridges along the “arms” of fully developed patterns after the spreading of: A) Silwet L-77 10cmc on 0.8 wt% gelatine, B) Silwet L-77 30 cmc on 0.8 wt% gelatine, C) Silwet L-77 50 cmc on 1.5 wt% gelatine. and D) Silwet L-77 100 cmc on 0.9 wt% gelatine.*

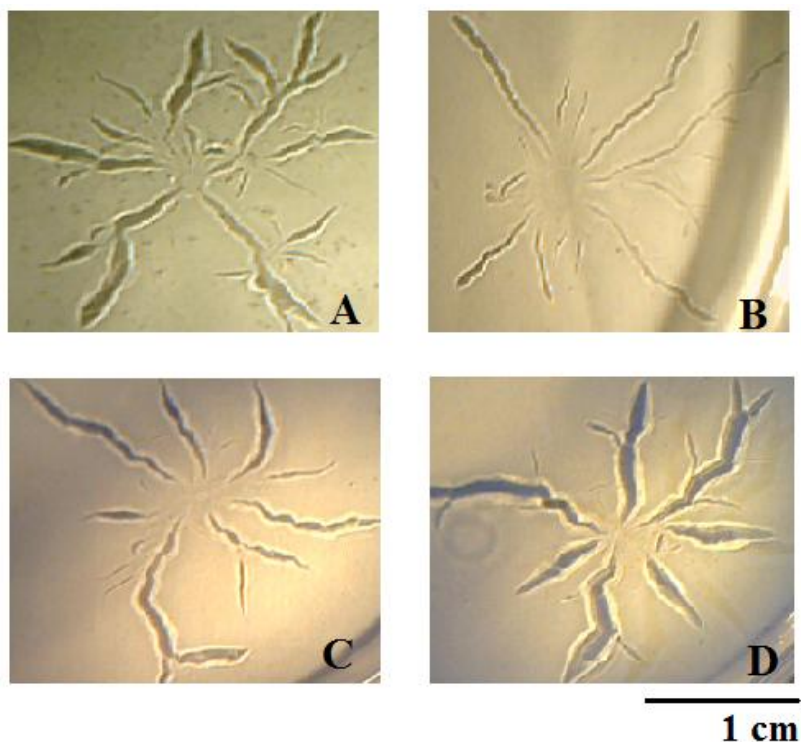


Figure 5.17: Branching wisps observed on fully-developed patterns after the spreading of: A) Silwet L-77 4cmc on 1.3 wt% gelatine, B) Silwet L-77 2 cmc on 1.5 wt% gelatine, C) Silwet L-77 10 cmc on 1.1 wt% gelatine, and D) Silwet L-77 30 cmc on 0.9 wt% gelatine.

An additional and strikingly interesting observation in the case of gelatine only, is what seems to be a rapid “self-healing” behaviour. The cracks formed by the spreading of Silwet L-77 on gelatine layers close in just a short span of time after their formation. In some cases, it is observed that the cracks begin to close while the major arms are still propagating outward from the point of deposition (see Figure 5.18). The gelatine layer heals itself and this phenomenon begins to occur from the drop deposition spot outwards. “Self-healing” is seen in agar as well, however it takes much longer times and it starts only after the “arms” have developed fully. One may expect that the fast “self-healing” behaviour of gelatine is linked to its rheological properties; however the gelatine concentrations tested here represent storage modulus values similar to those associated with the agar concentrations tested in the previous parts of this study. The only exception is the 1.7 wt% concentration region, where $G' = 29$ Pa,

which is somewhat larger than the modulus of the highest agar concentration (15 Pa). Therefore, the roots of this difference should be attributed to the loss modulus (G'') of gelatine which, for the concentrations studied here, varies from 0.04 Pa to 0.5 Pa. These values are smaller compared with the corresponding values for agar, which vary from 0.14 Pa to 2 Pa. Gelatine exhibits a stronger liquid-like behaviour compared to agar and this can lead to faster flow that occurs simultaneously with crack propagation, and therefore result in healing. In agar such healing is less rapid, since the flow is slower.

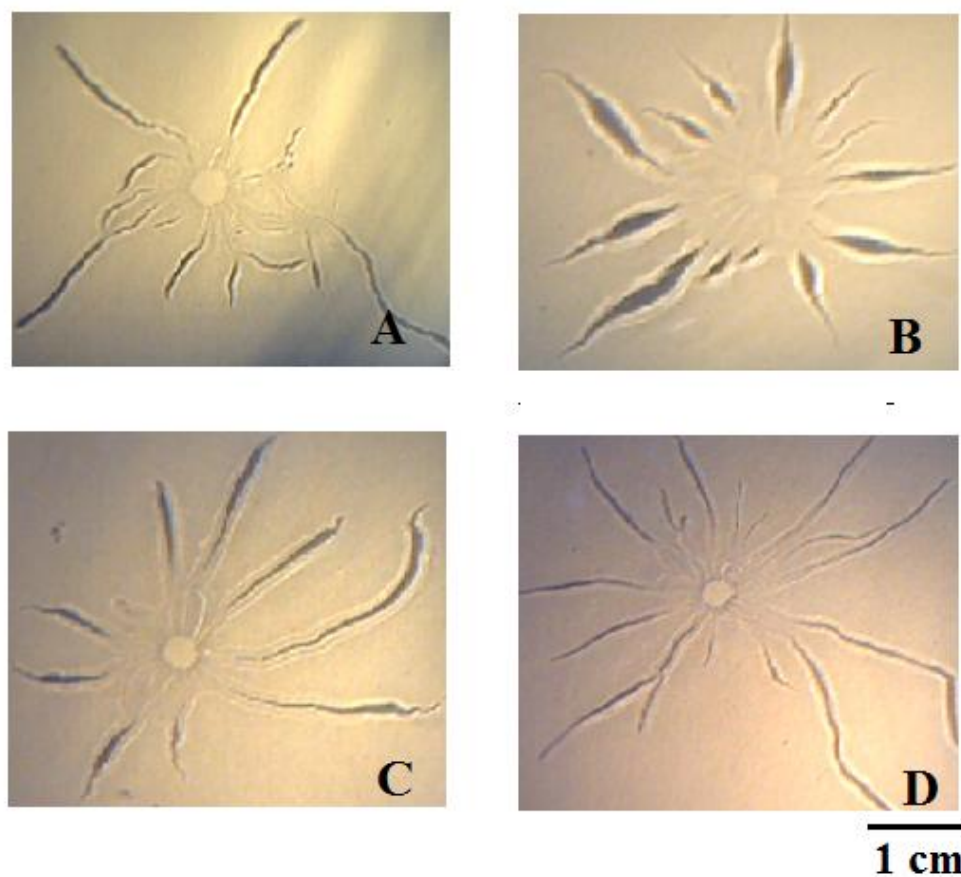


Figure 5.18: “Self-healing” on patterns formed from the spreading of: A) Silwet L-77 20cmc on 1.1 wt% gelatine, B) Silwet L-77 30cmc on 0.9 wt% gelatine, C) Silwet L-77 50cmc on 1.1 wt% gelatine. and D) Silwet L-77 8cmc on 1.1 wt% gelatine.

A typical example of the spatio-temporal evolution of the patterns on gelatine is shown in Figure 5.19. The evolution of the patterns can last for much longer times compared with agar, even up to 100 seconds.

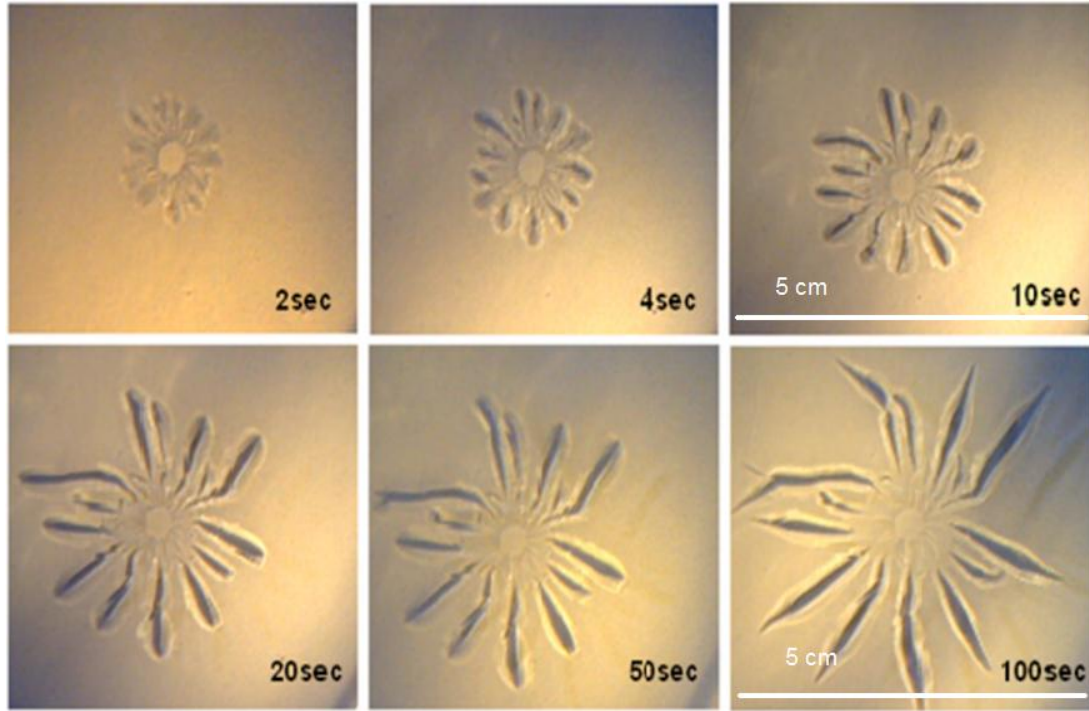


Figure 5.19: Spatio-temporal evolution of a pattern formed on the surface of a 1.1 wt% gelatine gel after the deposition and spreading of a Silwet L-77 100cmc droplet. After $t = 100$ s the evolution was completed.

5.3.2 Quantitative Behaviour

The spreading exponent, n , of the power law $L(t) \sim kt^n$ for each pattern was obtained in the same way as described in sections 5.1.2 and 5.2.2, and the results are shown in Figure 5.20. The smallest value observed here is near 0.60 and the largest value is near 0.80. Resemblance to the $t^{3/4}$ scaling is obvious for all gelatine and surfactant concentrations, since the majority of the values of the spreading exponent is constantly close to $3/4$, suggesting that Marangoni

forces play a significant role in the spreading. The findings on the spreading exponent are discussed separately in Chapter 6.

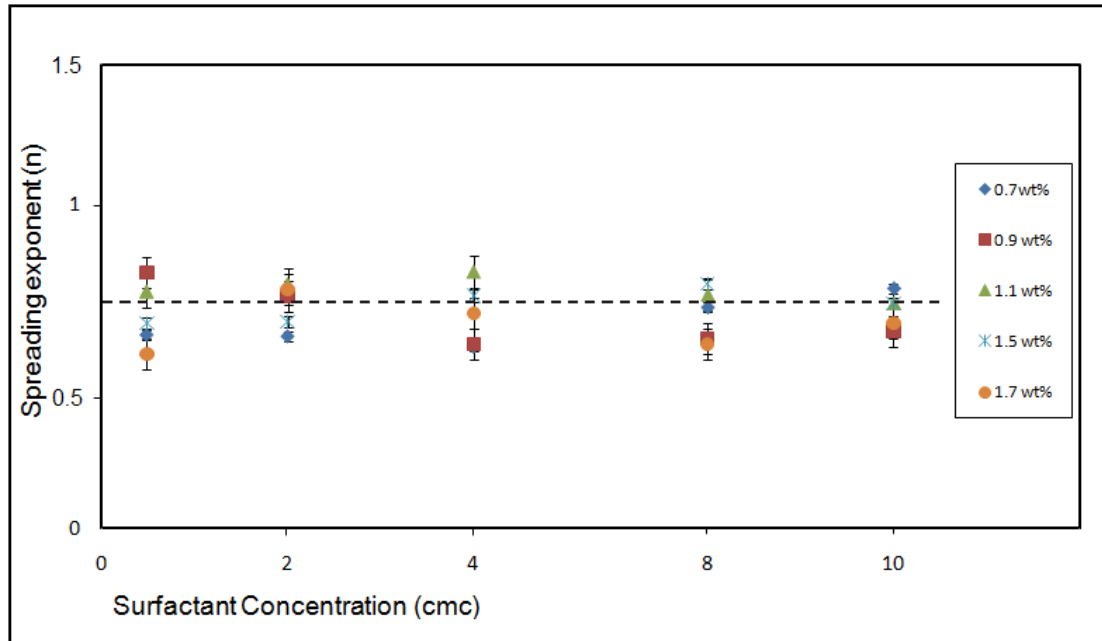


Figure 5.20: Variation of the spreading exponent with Silwet L-77 concentrations, for spreading on gelatine gel layers of different concentrations. These points represent the average of multiple runs. The dashed line is the theoretically predicted value of $3/4$ which is characteristic of Marangoni-driven spreading on thick layers (Fay 1969, Hoult 1972, Jensen 1995).

The crack propagation speeds observed for the spreading on gelatine, are the slowest reported in this study. This is demonstrated by the values of k measured that are smaller than those measured for the spreading on agar. Figure 5.21 summarises the different values of k found for different gelatin gel and Silwet L-77 concentrations. The minimum value of k is observed for a 4 cmc Silwet L-77 drop spreading on a 1.7 wt% gel, and the maximum value of k is reported for a 8 cmc Silwet L-77 drop spreading on a 0.7 wt% gel. Therefore, the velocities related to spreading on gelatine are slightly smaller than those related to SDS spreading on

agar, and much smaller than those related to Silwet L-77 spreading on agar. Similarly to the previous cases, it is observed that k decreases with increasing gel concentration and strength.

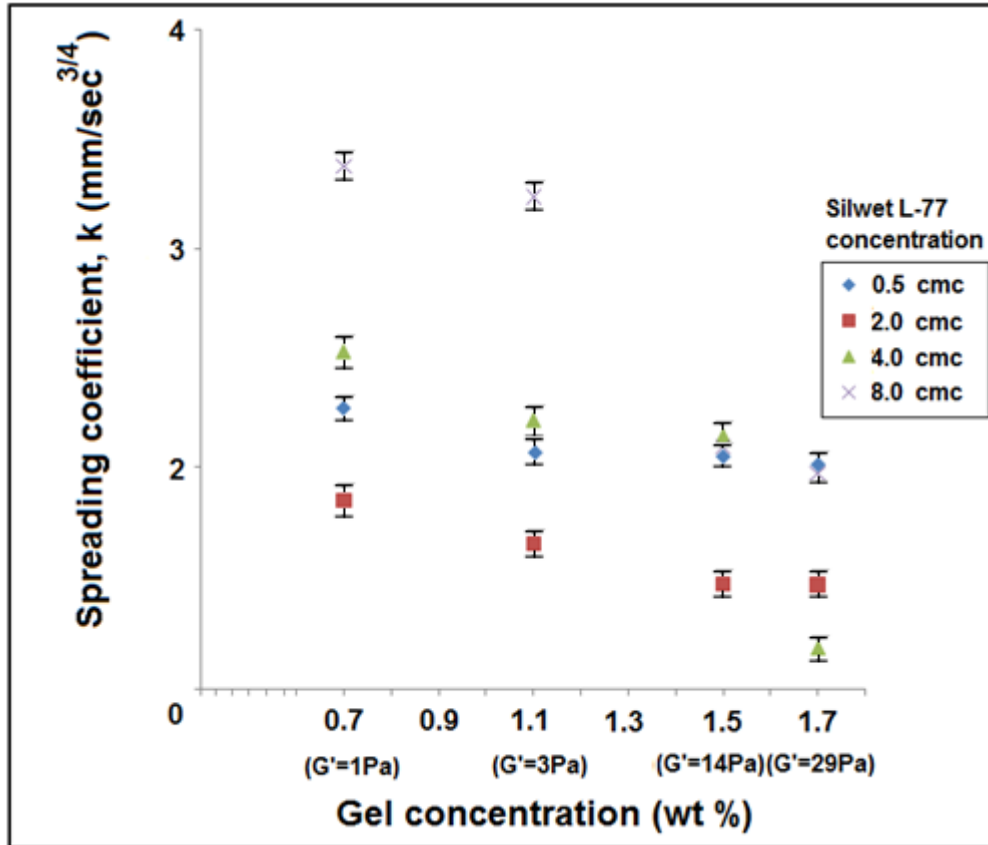


Figure 5.21: The dependence of the spreading coefficient on gelatine gel concentration for spreading of Silwet L-77 droplets.

The evolution of the “arms” seems to be faster for substrates of lower concentrations, while it is faster for highly-concentrated substrates. This is demonstrated in Figure 5.22 where dL/dt is plotted against time for different gelatine gel concentrations. It is observed that dL/dt is decreasing with increasing gel concentration and that it has its higher values for early times in each case, and decrease afterwards.

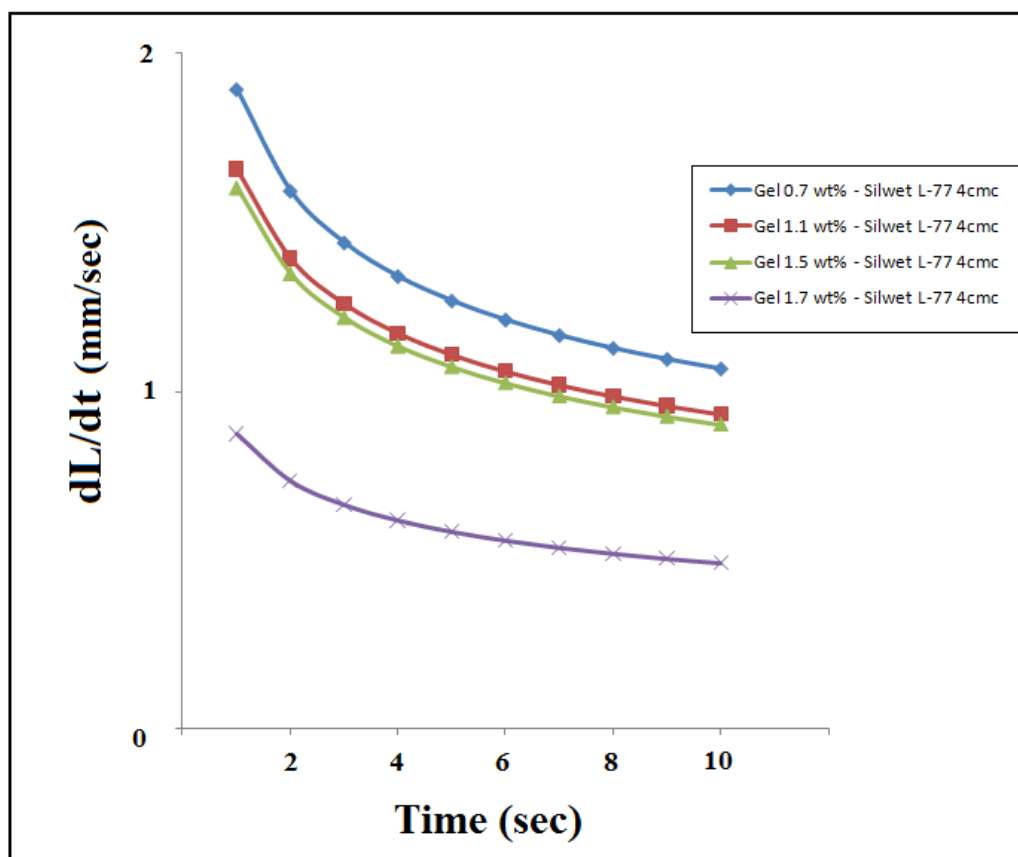


Figure 5.22: Plot of dL/dt against time for spreading of an Silwet 4 cmc droplet on gelatine gels of varying concentrations

Neither increased Silwet L-77 concentration nor increased gelatine concentration seem to affect the number and the length or the “arms” formed. Table 5.7 below shows the number of major spreading “arms” formed across a range of gelatine gel and Silwet-L77 concentrations tested. What characterizes the spreading on gelatine substrates, is that most of the patterns formed have numerous “arms”. It is not possible to see a pattern with less than 3 “arms”, even though it was common for the spreading on agar. There are many patterns with 10 “arms” or more, and the maximum number of “arms” observed is 13.

Table 5.7: Number of major “arms” formed in patterns across the range of gelatine gel and Silwet L-77 concentrations tested. These values represent the average of multiple runs, with typical standard error values varying from ± 0.5 to ± 1 .

Gelatine gel conc. (wt%)	Silwet L-77 concentration						
	0.5 cmc	2 cmc	4 cmc	8 cmc	10 cmc	50 cmc	100 cmc
0.7	6	8	8	7	8	11	10
0.9	4	3	6	7	7	8	10
1.1	7	4	9	12	7	10	13
1.3	7	5	5	7	7	7	8
1.5	3	5	6	6	5	7	8
1.7	3	2	6	4	10	2	5

The number of “arms” is scattered fairly evenly across the concentration ranges, and there seems to be no “peak” surfactant concentration where the number of arms has a maximum. Table 5.8 summarizes the minimum and maximum “arm” lengths observed. The minimum length is 0.54 cm for an 8 cmc Silwet L-77 drop spreading on a 1.5 wt% gelatine gel, and the maximum length is 4.62 cm for a 0.5 cmc drop spreading on a 0.9 wt% gel. These values show that, compared to the spreading of Silwet L-77 and SDS on agar gels, “arms” longer than 4 cm are very rare for spreading on gelatine.

Table 5.8: Minimum and maximum “arm” lengths (in cm) across the gelatine and Silwet L-77 concentrations tested. These are measured using the software of the microcamera with an error of ± 0.01 .

Gelatine gel conc.(wt%)	Silwet L-77 concentration													
	0.5 cmc		2 cmc		4 cmc		8 cmc		10 cmc		50 cmc		100 cmc	
0.7	Min	0.77	Min	0.85	Min	0.99	Min	0.97	Min	1.05	Min	0.91	Min	1.14
	Max	1.34	Max	1.43	Max	1.30	Max	1.41	Max	1.46	Max	1.31	Max	1.81
0.9	Min	2.51	Min	3.04	Min	1.61	Min	0.94	Min	0.78	Min	1.14	Min	1.00
	Max	4.62	Max	3.58	Max	2.91	Max	2.79	Max	1.40	Max	2.14	Max	1.62
1.1	Min	1.60	Min	2.29	Min	2.00	Min	1.13	Min	1.36	Min	0.90	Min	1.12
	Max	2.94	Max	4.22	Max	3.85	Max	3.19	Max	2.63	Max	2.16	Max	2.06
1.3	Min	1.50	Min	1.43	Min	1.18	Min	0.89	Min	1.04	Min	0.90	Min	0.94
	Max	2.18	Max	1.74	Max	2.06	Max	2.11	Max	2.40	Max	2.09	Max	1.86
1.5	Min	1.37	Min	1.62	Min	1.36	Min	0.54	Min	0.96	Min	0.65	Min	0.90
	Max	2.63	Max	3.08	Max	2.83	Max	2.63	Max	1.90	Max	1.88	Max	1.82
1.7	Min	2.70	Min	2.20	Min	0.62	Min	0.41	Min	0.75	Min	2.55	Min	1.22
	Max	3.08	Max	3.27	Max	2.66	Max	2.81	Max	2.68	Max	4.18	Max	5.56

Figure 5.23 shows the dependence of the width of the “arms” on the storage modulus of the substrate. It is clear that the width decreases with increasing gelatine gel concentration (strength). For gel concentrations of 1.7 wt% ($G'=29$ Pa), the “arm” widths are the smallest reported in this study.

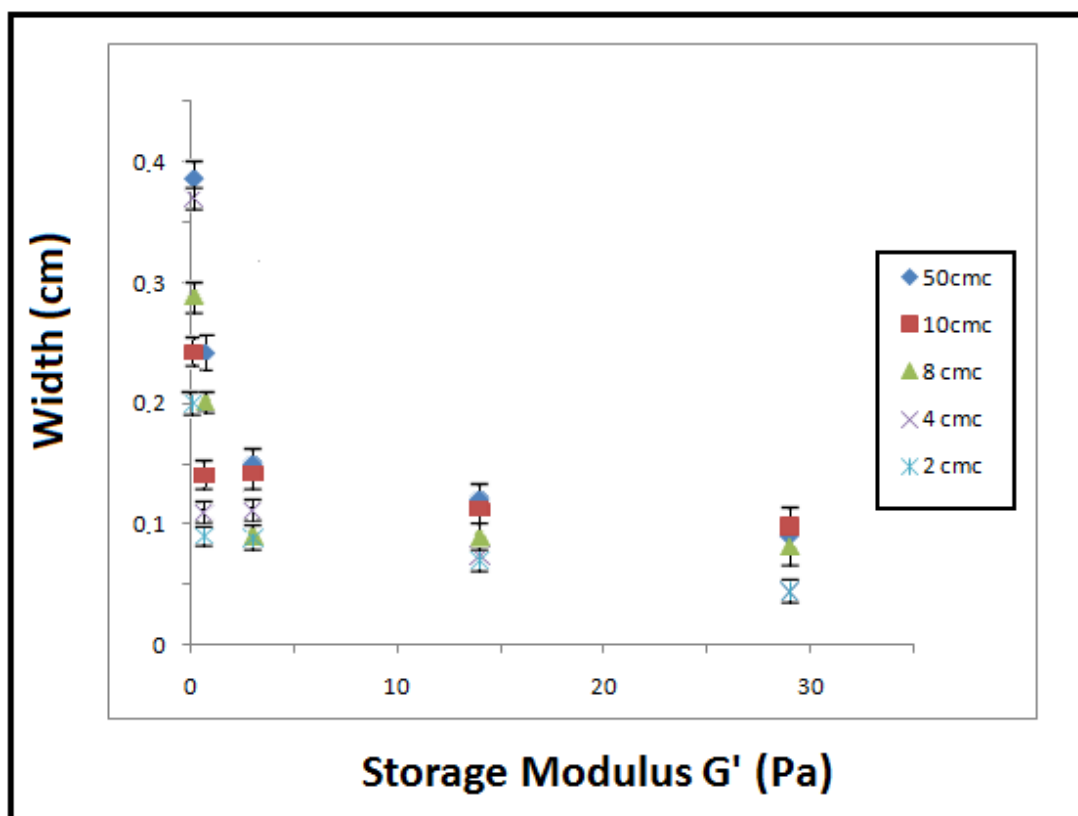


Figure 5.23: *Dependence of the width of the pattern “arms” on storage modulus of gelatine. Each point represents the average of multiple runs $G' = 0.1$ Pa corresponds to 0.7wt% gelatine, $G' = 0.65$ Pa corresponds to 0.9wt% gelatine, $G' = 3$ Pa corresponds to 1.1 wt% gelatine, $G' = 14$ Pa corresponds to 1.5 wt% gelatine and $G' = 29$ Pa corresponds to 1.7 wt% gelatine.*

5.3.3 Relative Strength of Forces

Marangoni stresses were found to be dominant for the spreading on gelatine and, since the parameters remain broadly similar to those on the spreading on agar, their relevance to other participating forces is expected to be similar to what was determined in sections 5.1.3 and 5.2.3. For the different combinations of gelatine and Silwet L-77 concentrations examined, S was found to have values from 33 mN/m to 45 mN/m, and L varies from 0.005 m to 0.046 m (table 5.8). The time scale over which Marangoni stresses act, t_m , varies from 10^{-4} s to 10^{-2} s. The surface Peclet number, Pe_s , is in the order of 10^8 , and the ratio of Marangoni to surface

diffusion time scales, t_m/t_{Ds} is of the order of 10^{-6} , indicate the dominance of Marangoni stress over surface diffusive effects. The bulk Peclet number, Pe_b , is in the order of 10^6 and the ratio of Marangoni to bulk diffusive time scales, t_m/t_{Db} , achieves values from 10^{-9} to 10^{-8} , indicating that bulk diffusive effects are more significant. The Bond number achieves values from 3.5 to 4.8 indicating that the significance of gravitational forces is the same as in the case of Silwet L-77 spreading on agar, and slightly less significant than in the spreading of SDS.

5.3.4 Summary of Silwet L-77 spreading on Gelatine Gels, and comparison with Silwet L-77 spreading on Agar Gels.

The spreading of aqueous Silwet L-77 solution droplets on gelatine gels can lead to the formation of propagating cracks on the gel surface. Compared to the spreading of the same surfactant on agar, the most evident difference is that the cracks can now be seen for gel concentrations one order of magnitude higher than agar. However this is to be expected, since these gelatine concentrations (0.7 wt% to 1.7 wt%) have associated storage modulus values similar to the ones attributed to the agar concentrations tested (0.04 wt% to 0.14 wt%), suggesting that both substrates are broadly of the same strength for the relevant concentration limits and therefore offer similar resistance to spreading and crack formation. The only exception is the 1.7 wt% gelatine concentration, where the value of the storage modulus is somewhat higher ($G' = 29$ Pa) than the ones observed usually on agar, and in this concentration region the thinnest “arms” are reported.

Other notable differences include a “self-healing” tendency of the gelatine, with the cracks being able to close even before the pattern has been fully developed. In addition, the evolution of the cracks is much smaller in the case of gelatine, and it can last for times up to $t = 100$ seconds. Patterns with large number of “arms” (even more than 10) are quite common, which

was not the case on agar. Similarities include the fact that the spreading exponent values are found to be within the same limits as in the spreading on agar, suggesting that the spreading is Marangoni driven. The values of the length or the “arms” are broadly similar, and their width seems to increase while the gel concentration increases (also evident on agar).

5.4 Preliminary Observations with 2 mm-thick Substrates

All the patterns presented above were the result of surfactant spreading on approximately 4 mm-thick gel substrates. This choice was conducted by the fact that, as described in Section 2.4, due to the wettability of the gel, 4mm is the minimum thickness of a gel layer that could be formed by pouring the polymer solution inside a Petri dish of 14 cm in diameter. However, in order to have an indication of the role of the layer thickness, an additional set of experiments that featured spreading on layers of slightly smaller thickness was conducted. A smaller thickness was achieved by using a pipette to remove a quantity of the solution that was already poured inside the dish. In this way, the smallest thickness that could be achieved without causing dewetting of the layer was approximately 2mm. Figure 5.24 below shows a pattern map depicting a summary of the observed behaviour corresponding to the spreading of droplets of Silwet L-77 solutions of varying concentrations on approximately 2mm-thick gel layers of varying concentrations.

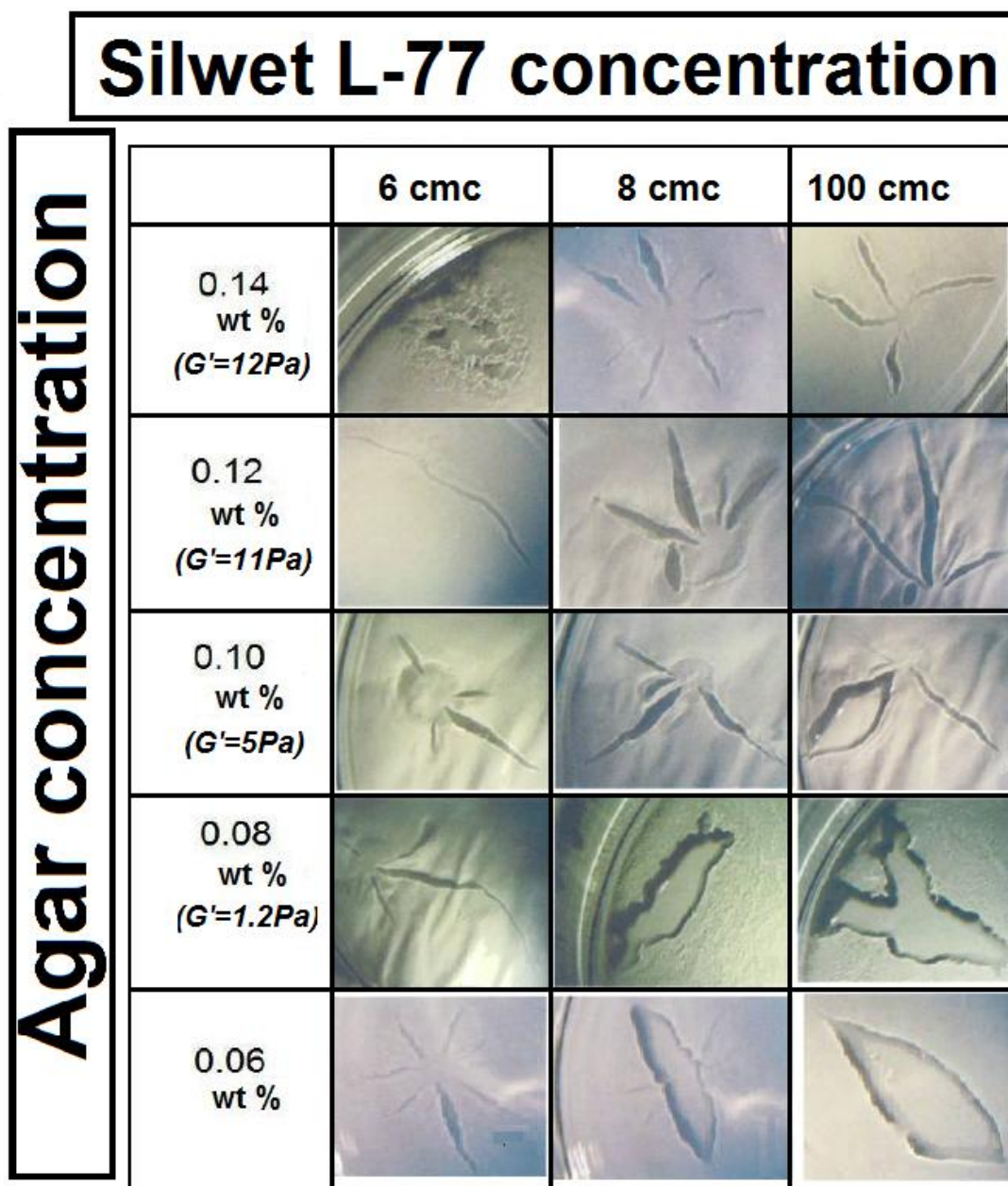


Figure 5.24: Pattern map showing fully-developed patterns from Silwet L-77 droplets of different concentrations which have spread on approximately 2 mm-thick agar gel layers of varying concentrations.

Compared to previous observations on the 4 mm layers, the striking difference here is what initially seems to be a “dewetting” behaviour that accompanies the formation of the cracks and that manifests itself by the opening of “holes” on the gel surface. This is more evident on lower gel concentrations (0.06 wt% to 0.08 wt%) and on higher surfactant

concentrations (8 cmc and above). In these cases, the “holes” open from the spot of the droplet deposition and seem to reach the glass substrate below the gel layer, at the same time that cracks are formed. For intermediate gel concentrations of 0.10 wt%, these holes are only observed on very high surfactant concentrations. For gel concentrations of 0.12 wt% and above no such “holes” are observed.

However, there is no evidence that the “dewetting” observed here is the equivalent of similar examples of autophobing and dewetting behaviour described in the literature, for example in Birch *et al.* 1994, in Woodward and Schwartz 1997 and in Afsar-Siddiqui *et al.* 2004 (see also Section 3.3); these works feature the spreading of cationic surfactants, however the surfactant used here is non-ionic. In addition, it is not clear whether this observation corresponds to complete dewetting or not. These “holes” seem to reach the glass substrate, however one can argue that there could be a very small, invisible to the eye, liquid layer that still remains on the bottom of the Petri dish. For the above reasons, the term “severe thinning” seems more appropriate to describe the behaviour shown in Figure 5.24.

This severe thinning might be the result of a de-bonding of the gel from the glass due to the propagation of cracks; the cracks have a depth that penetrates the gel further while they propagate. For very thick layers (of thickness near and above 4 mm), this depth does not visibly affect the main bulk of the gel, however for less thick layers the formation of the cracks causes gel to move away from the region of their propagation, leaving behind what seems to be a hole. The fact that “holes” open at the same time that the cracks propagate does not allow precise measurement of the spreading exponent, n , in such layer thicknesses. However, the observations summarised in Figure 5.24 can be useful in providing an indication of the scale of the crack depth, which should be in the region of millimetres since the gel surface profile is affected in this way. Since the holes are

observed in low gel concentrations and high surfactant concentrations and are absent elsewhere, one can suggest that the depth of the cracks seems to increase with decreasing gel concentration or with increasing surfactant concentrations. Finally, it should be noted that a decrease of the gel layer thickness from 4 mm to 2 mm results in a decrease of the value of the Bond number, Bo . However, this decrease is not significant and the resulting values of Bo in the specific set-up are near and above 1, indicating that gravitational forces are not negligible.

Summary

The spreading of SDS and Silwet L-77 droplets on both types of approximately 4mm-thick gel layers was found to be accompanied by the formation of cracking patterns, which are similar morphologically to those observed by Daniels *et al.* (2007). The typical pattern observed constitutes mainly of crack-like projections emanating from the location where the surfactant droplet is deposited on the gel layer. These projections can be described as spreading “arms” with well-defined edges, which grow to resemble asymmetrical “starburst” formations. It is evident that the patterns can be formed only inside a “window” of surfactant and gel concentrations, which represents an “intermediate” state of the gel, where it has neither a dominant solid-like nor a dominant liquid-like behaviour. At sufficiently high or low gel concentrations for which the gel exhibits solid-like or liquid-like behaviour, respectively, the possibility of such starburst formation is very small. Strong Marangoni stresses are identified to be the driving force behind the pattern formation, with gravitational forces also playing an important role. Preliminary observations on surfactant spreading on 2mm-thick layers show severe thinning and forming of “holes” in the surface of the gel.

Chapter 6

Discussion

Synopsis

Possible explanations of the intriguing experimental results presented in the previous Chapter, are given herein. Of central importance is the understanding of the spreading mechanism that is responsible for the observed phenomenon of the pattern formation on the gel surfaces. In particular, the factors that determinate the initiation and the hindering of the pattern formation are examined. The findings on the spreading exponent are further analysed and compared with the theoretical and experimental results of other researchers. This is followed by an attempt to quantify the Marangoni stresses that are identified to be responsible for the formation of the cracks, and to compare them against the rheological characteristics of the gels. The different roles of the adsorption of the superspreading surfactants and the effects of gravitational forces are highlighted and conclude this Chapter.

6.1 Spreading exponent –Identification of Marangoni forces

In order to determine the value of the spreading exponent, n , for the power law $L(t) \sim kt^n$, logarithmic plots of the evolution of the length of the “arms” that form a “starburst” were constructed. In the same pattern, not all “arms” were shown to grow following the same scaling relationship, therefore an average value of the exponent for every specific pattern was determined. Figures 5.4, 5.11 and 5.20 show that the power-law scaling varies from $L \sim t^{1/2}$ to $t^{0.85}$, with the majority of the spreading patterns being found to grow with time as $L \sim t^{3/4}$, independently of the gel type and concentration and of the surfactant type and concentration. Daniels *et al.* (2007) confirms values close to $n = 3/4$ for the spreading of PDMS and Triton X-305 on agar gels, and in a geometry similar to the one used in our experiments. The $t^{3/4}$ scaling is characteristic of Marangoni-driven spreading on thick films, suggesting that Marangoni stresses are dominant for the cases examined here and in the spreading of both types of surfactants on both types of gel substrates that have a thickness of 4 mm. The theoretical argument behind the $t^{3/4}$ power-law for Marangoni dominated spreading is presented here (See also Fay 1969): For a spreading of a droplet on a deep fluid layer, and under the assumption that the surface tension gradient is balanced by the viscous stress of the underlying layer, the Marangoni stress balance at the air-liquid interface is given by:

$$\frac{\partial \sigma}{\partial r} = \mu \frac{\partial u}{\partial z}, \quad (6.1)$$

where σ is the local surface tension, u is the tangential velocity and μ is the film viscosity. A simple scaling of (6.1) gives:

$$\frac{S}{R} \sim \mu \frac{U}{\delta}, \quad (6.2)$$

where S is the spreading parameter, R is the radial extent of the spreading of the drop, U is a characteristic velocity, and δ denotes the thickness of the viscous boundary layer with density ρ and viscosity μ , and is given by

$$\delta = (\mu T / \rho)^{1/2} \quad (6.3)$$

where T denotes a characteristic time-scale. Substituting (6.3) into (6.2) gives:

$$\frac{S}{R} \sim (\rho\mu)^{1/2} \frac{U}{T^{1/2}} . \quad (6.4)$$

$$\text{Now } U \sim \frac{R}{T}, \quad (6.5)$$

and substituting (6.5) into (6.4) and re-arranging gives

$$R^2 \sim \frac{S^{1/2}}{(\mu\rho)^{1/4}} T^{3/4} \quad (6.6)$$

The general scaling relation for a deep viscous fluid support, first mentioned in section 2.2.2 is given by Jensen (1995):

$$L(t) \sim \left(\frac{\alpha^2 M^2 t^3}{\mu\rho} \right)^{\frac{1}{2(n+2)}} \quad (6.7)$$

where α is the surface activity ($-d\sigma/d\Gamma$) and M the total mass of spreading material. For a uniform front of an infinite transverse extent, $n = 0$, and the value of the exponent is $3/4$.

The same time dependence has been both theoretically predicted (Joos and Pintens 1977; Foda and Cox, 1980) and experimentally confirmed in the literature, for instance in a recent study by Berg (2009) on the spreading of SDS and DTAB surfactants along the interface between thick layers of water and decane. It has been also confirmed in the case of oil and silicon oil spreading on water (Hoult 1972, Foda and Cox 1980, Camp and Berg 1987, Dussaud and Troian 1998, Svitova *et al.* 1999), and on surfactant solutions (Bergeron and

Langevin 1996), and on the surfactant-induced fracture of a particle raft (Vella *et al.* 2006). It should be noted, however, that in the previous studies of Fay (1969) and Hoult (1972), the spreading rates depend on viscosity, which is not the case in this work.

In the case of gels, Szabó *et al.* (2000) and Kanenko *et al.* (2005) report a $R \sim t^{1/2}$ scaling in the studies involving the spreading of different liquids on the surface of PAMS (2-acrylamido-2-methylpropanesulfonic acid) gels. More specifically, Kanenko *et al.* (2005) found values of the spreading exponent for a polymer gel underlying layer of $n = 0.45$ and $n = 0.3$ for miscible and immiscible spreading liquids, respectively. Large Marangoni stresses are absent in those studies, and it is argued that the spreading on gel substrate is very similar to that on a solid surface, therefore equation (6.6) cannot be applied, since the assumption which takes into account the effect of the viscous drag of the underlying fluid is not applicable to solids. However, the gels that we examine in this study are of very small concentrations and largely composed of water, therefore it may not be entirely appropriate to characterise their behaviour as mainly solid-like.

The fact that not all “arms” of the same pattern were shown to grow following the same scaling relationship can be explained by the high degree of local heterogeneities on the surface of a gel. These arise from the fact that a gel consists of heterogeneous populations of molecules that can have different physico-chemical properties (Lahaye and Rochas 1991). Therefore, on a local level, concentration and surface tension gradients can arise between different regions of the same gel surface. Weaker gels can exhibit more heterogeneities than stronger gels (Boyne *et al.* 2008). In the surfactant-induced gel fracture studied here, concentration and surface tension gradients can affect the crack propagation phenomenon in terms of the size and the shape of the “arms” and in terms of the propagation velocities. The non-uniformities on the surface are also responsible for the fact that the “starbursts” are asymmetrical and that the patterns of the same “starburst” are not morphologically identical to

each other. Furthermore, the conditions in a specific region of the gel surface can be different from those in a neighbouring region. Therefore, the conditions for one potential “arm” may be different and more conducive to growth from those of another. In addition, as an “arm” grows it may “shield” and hinder the growth of a neighbouring arm by making the conditions less conducive to growth (smaller concentration gradients for instance).

The large opportunity for discrepancies in the rheology of the gel can also increase the degree of local heterogeneities, since even small disturbances to the gel surface during its preparation, storage or usage can change its rheological properties.

6. 2 Mechanism

The droplet spreading mechanism is different on rigid solids as compared to liquids. Gels are elastic/viscoelastic materials with behaviour intermediate between solid and liquid substrates. Varying and studying different combinations of the gelatine and surfactant concentrations provides insight into the liquid–solid substrate spreading behaviour. The experimental findings of Chapter 6 show that the presence of surfactant-driven “starburst” crack-like patterns can be observed on the surface of both major gel types, polysaccharide-based and protein-based. This indicates that it is possible for the phenomenon to be observed over a wide range of different types of compliant substrates, characterised by the gel concentration, provided the surfactant concentration is sufficiently high.

Given the dominant presence of Marangoni stresses in the SDS-agar, Silwet L-77 -agar and Silwet L-77- gelatine systems, it can be suggested that the formation of the “starburst” patterns is the result of the competition between those stresses and the gel strength, and that the main driving force behind the fingering instability that manifests itself via the formation of these patterns, is the surface tension gradients generated between the surfactant and the gel.

Whether a droplet spreads on a gel surface is thermodynamically determined by the spreading coefficient (Harkins 1952):

$$S = \sigma_g - \sigma_d - \sigma_{gd} \quad (6.8)$$

with σ_g , σ_d and σ_{gd} being the interfacial tensions for gel-air, droplet-air and gel-droplet respectively. The droplet will spread if $S \geq 0$. Equation (6.8) is equivalent to the general equation (2.1) mentioned in section 2.2. Under the assumption that σ_{gd} is negligible (Daniels *et al.* 2005, 2006), since both the droplet and the gel are composed mainly of water, the spreading parameter is defined as $S \equiv \sigma_g - \sigma_d$. The crack-like patterns can be formed when the surface tension gradients are sufficiently large to generate Marangoni stresses strong enough to overcome the resistance of the rigidity of the gel and to form cracks on its surface. This explains the observation of higher probability for cracks to occur in cases where the surfactant concentration is large and the gel concentration is small. Since the length scales along the direction of propagation are longer than those perpendicular to it, one expects the largest surface tension gradients to be in the latter direction. Hence, one also expects, therefore, that this will lead to an “unzipping” of the gel in a manner perpendicular to the direction of the largest surface tension gradient, as shown in the schematic depicted in Figure 6.1. This mechanism highlights the width of the “arms” as an important parameter that can characterize this spreading instability.

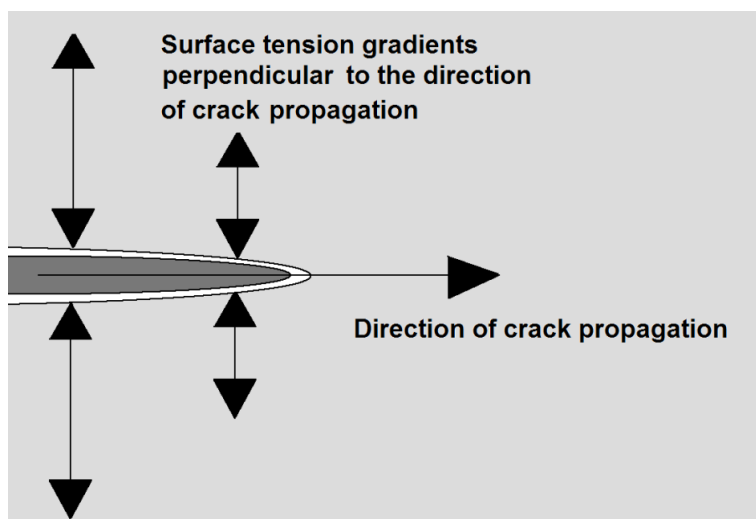


Figure 6.1: “Unzipping” of a crack, perpendicular to the direction of surface tension gradients

It is easier to visualise this assumed “unzipping” mechanism by creating a small artificial crack of known size on the surface of the gel with a needle, and then depositing a droplet of surfactant inside the crack, and measuring its increased width, as it is illustrated in Figure 6.2. The way that the crack opens during its propagation gives an impression of “unzipping” to the observer.

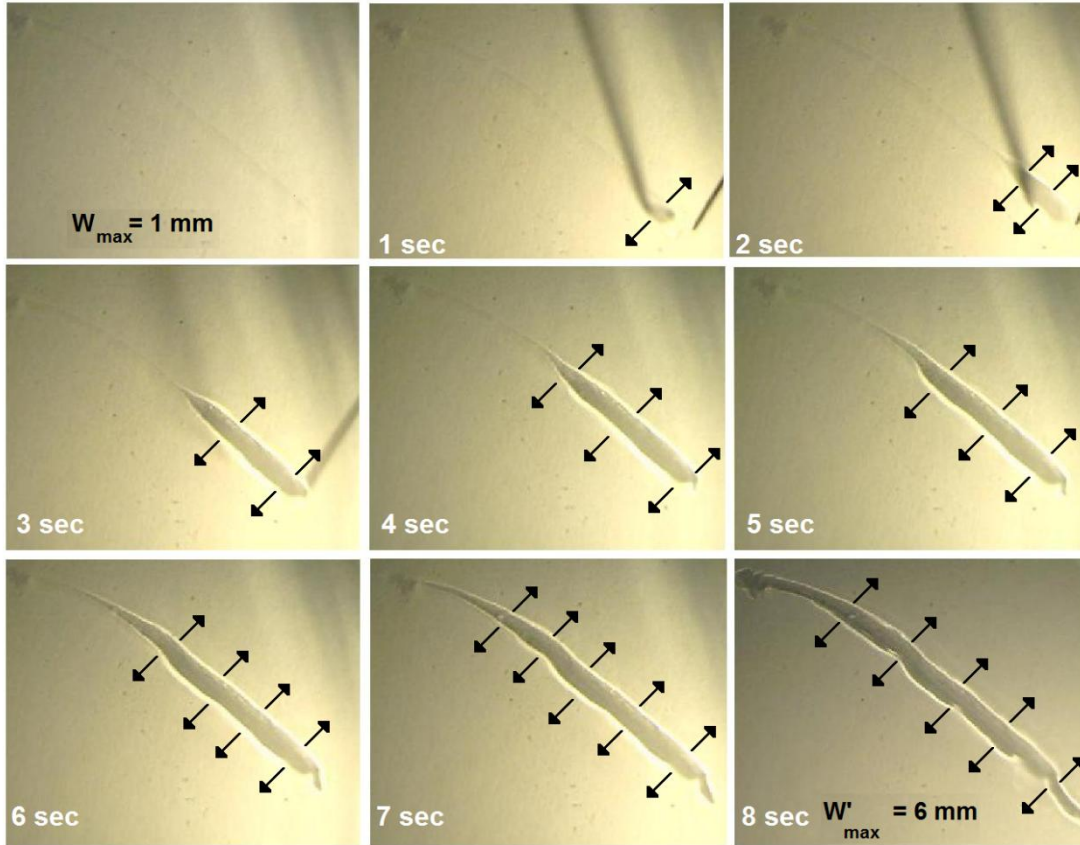


Figure 6.2: An artificial crack, 1mm in width created on the surface of a 0.10 wt% agar gel. 8 seconds after the deposition of a 6cmc Silwet L-77 droplet the width of the crack increases to a maximum of approximately 6 mm. The directions of the arrows show how the crack “unzips”.

Since the width of the cracks can be associated with the shear modulus of the gel (Figures 5.7, 5.14 and 5.23), a change of the width (Δw) together with the difference in surface tensions can quantify a stress that can be compared with the storage modulus. Therefore, a crack-like “arm” will be formed on the surface of the gel if:

$$\frac{S}{\Delta w} \geq G' \quad (6.9)$$

Inequality (6.9) is similar to the one suggested by Daniels et al. (2007) in order to characterise the Marangoni instability and to associate it mainly with the number of “arms” that can form.

Our findings show that even though there is a higher propensity for the formation of patterns with a larger number of “arms” when the surfactant concentrations increase, or when the gel concentration decreases, a clear trend cannot be discerned for either of the two cases, and the distribution in the number of “arms” is scattered fairly evenly across the range of the cases studied (Tables 5.1, 5.3 and 5.5). Therefore, the number of “arms” parameter is not taken into consideration in inequality (6.9).

The validity of inequality (6.9) inside the surfactant and gel concentration limits where the pattern formation is obvious is tested herein. For agar concentrations near 0.12 wt%, the value of $S/\Delta w$ is very close to the associated values of G' , that is why for the higher concentration of 0.14 wt% no patterns are formed. More specifically, for the pattern shown on Figure 6.3.1, $S = 20\text{mN/m}$, and the maximum width found here is 0.0016 m. This gives $\frac{S}{\Delta w} = 12.5\text{ Pa}$ which is greater than $G' = 11\text{ Pa}$. Similarly, for the pattern shown on Figure 6.3.2, $S = 25\text{mN/m}$, the maximum width is 0.0022 m, giving $\frac{S}{\Delta w} = 11.3\text{ Pa}$. At low agar concentrations, the larger widths are counterbalanced by the smaller values of the storage modulus, so that $\frac{S}{\Delta w}$ is consistently greater than G' . Figures 6.4 and 6.5 show similar considerations for other characteristic patterns observed in agar and gelatine substrates near the limits of pattern formation.

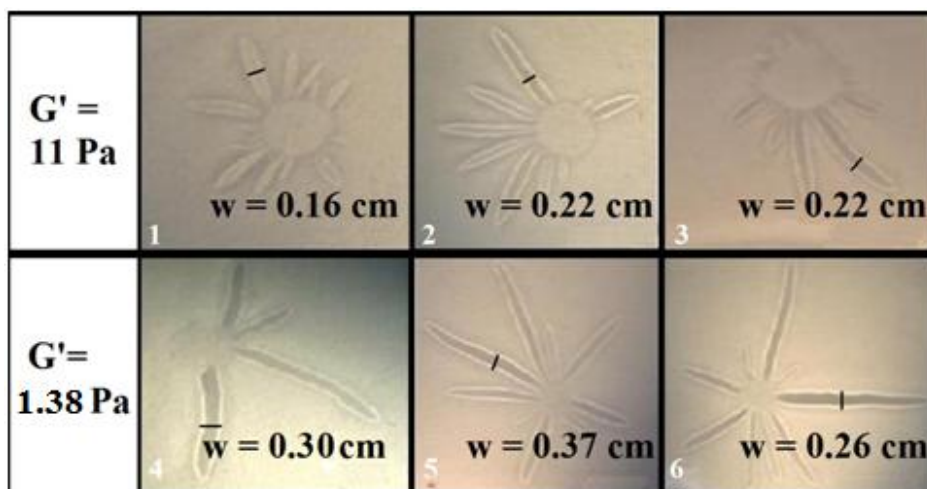


Figure 6.3: The maximum “arm” width of various patterns observed near the limits of the concentration “window” where the cracking formation occurs, for SDS droplets spreading on agar gels of concentrations 0.12 wt% (top row) and 0.08 wt% (bottom row). **1:** $S=22\text{mN/m}$, and $S/\Delta w = 13.75 \text{ Pa}$. **2:** $S=27\text{mN/m}$, $S/\Delta w = 12.2 \text{ Pa}$. **3:** $S= 28\text{mN/m}$, $S/\Delta w = 12.7 \text{ Pa}$. All these are greater than, but very close to $G'=11\text{Pa}$. **4:** $S=27.5\text{mN/m}$, and $S/\Delta w = 9.16 \text{ Pa}$. **5:** $S=32.5\text{mN/m}$, $S/\Delta w = 8.78 \text{ Pa}$. **6:** $S= 33.5\text{mN/m}$, $S/\Delta w = 12.8 \text{ Pa}$. All these are greater than $G'=1.38 \text{ Pa}$.

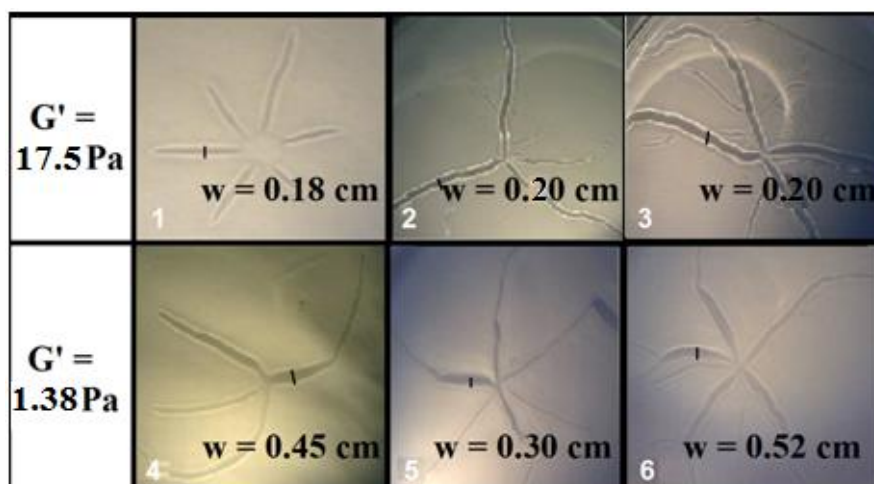


Figure 6.4: The maximum “arm” width of various patterns observed near the limits of the concentration “window” where the cracking formation occurs, for Silwet L-77 droplets spreading on agar gels of concentrations 0.14 wt% (top row) and 0.08 wt% (bottom row). **1:** $S=36\text{mN/m}$, and $S/\Delta w = 20 \text{ Pa}$. **2:** $S=39 \text{ mN/m}$, $S/\Delta w = 19.5 \text{ Pa}$. **3:** $S= 40\text{mN/m}$, $S/\Delta w = 20 \text{ Pa}$. All these are greater than, but very close to $G'=17.5\text{Pa}$. **4:** $S=43.5\text{mN/m}$, and $S/\Delta w = 9.6 \text{ Pa}$. **5:** $S=44.5\text{mN/m}$, $S/\Delta w = 14.8 \text{ Pa}$. **6:** $S= 45.5\text{mN/m}$, $S/\Delta w = 8.75 \text{ Pa}$. All these are greater than $G'=1.38\text{Pa}$.

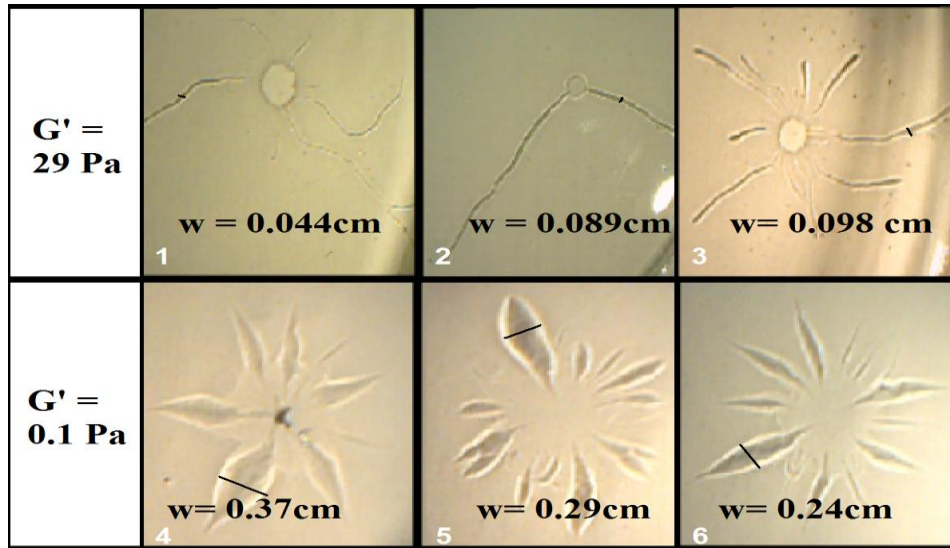


Figure 6.5: The maximum “arm” width of various patterns observed near the limits of the concentration “window” where the cracking formation occurs, for Silwet L-77 droplets spreading on gelatin gels of concentrations 1.7 wt% (top row) and 0.7 wt% (bottom row) . **1:** $S=33 \text{ mN/m}$, and $S/\Delta w = 75 \text{ Pa}$. **2:** $S=35 \text{ mN/m}$, $S/\Delta w = 39.3 \text{ Pa}$. **3:** $S= 35 \text{ mN/m}$, $S/\Delta w=35.7 \text{ Pa}$. All these are greater than, but close to $G'=29 \text{ Pa}$. **4:** $S=43 \text{ mN/m}$, and $S/\Delta w = 11.62 \text{ Pa}$. **5:** $S=45 \text{ mN/m}$, $S/\Delta w=15.5 \text{ Pa}$. **6:** $S= 45 \text{ mN/m}$, $S/\Delta w=18.75 \text{ Pa}$. All these are greater than $G'=0.1 \text{ Pa}$.

A comparison of $S/\Delta w$ against G' for all the cases studied here, is illustrated in Figures 6.6, 6.7 and 6.8 below:

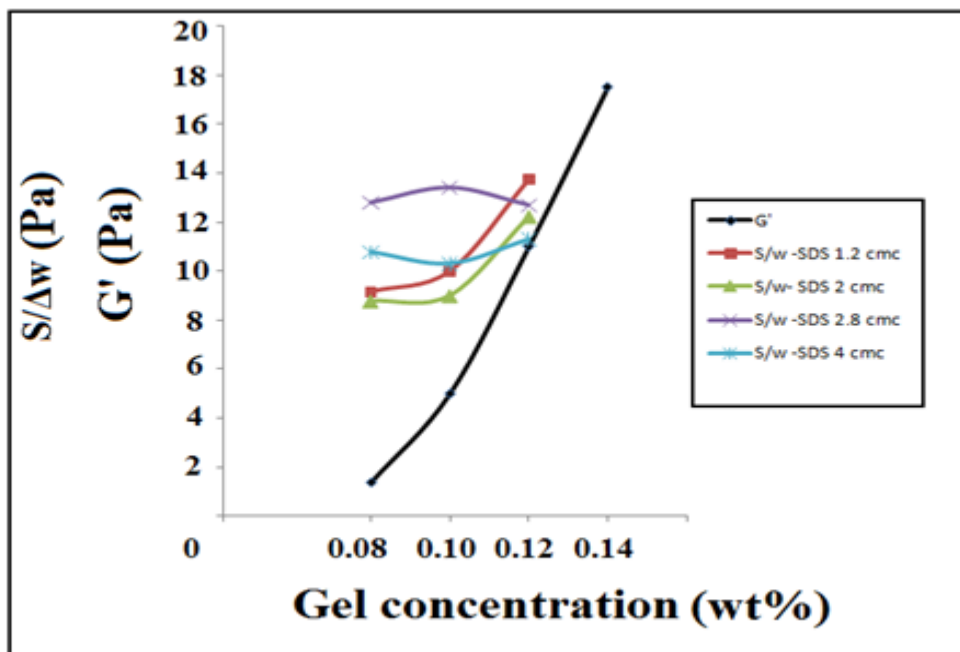


Figure 6.6: $S/\Delta w$ and G' against agar gel concentration, with SDS concentration varying parametrically. $S/\Delta w$ is constantly greater than G' wherever cracking patterns are observed.

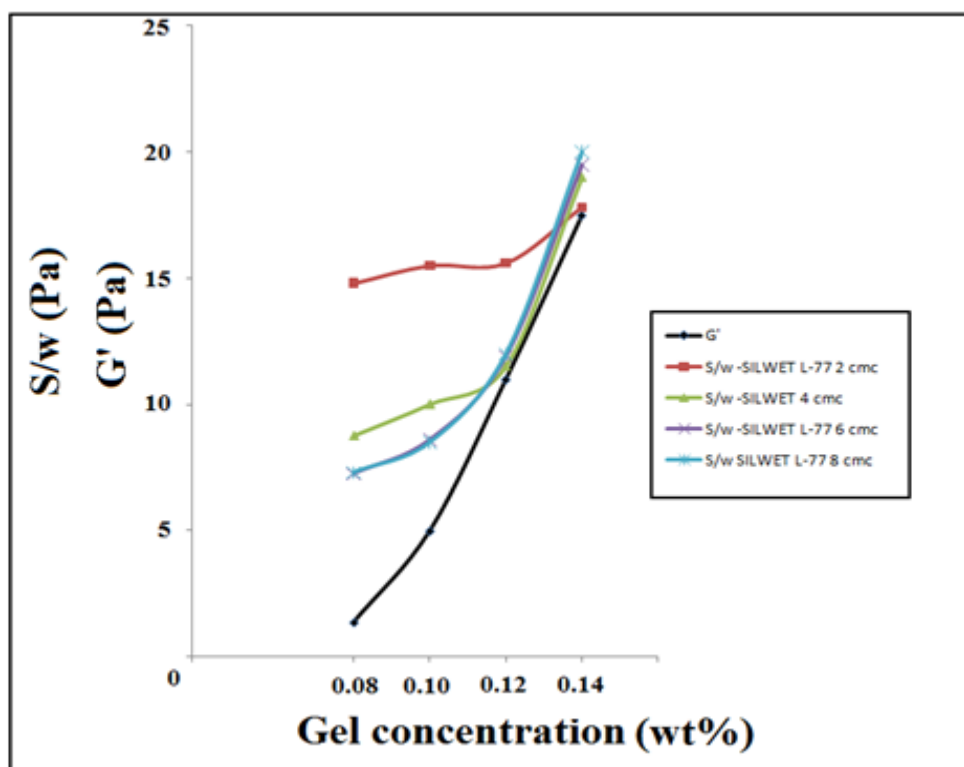


Figure 6.7: $S/\Delta w$ and G' against agar gel concentration, with Silwet L-77 concentration varying parametrically. $S/\Delta w$ is constantly greater than G' wherever cracking patterns are observed.

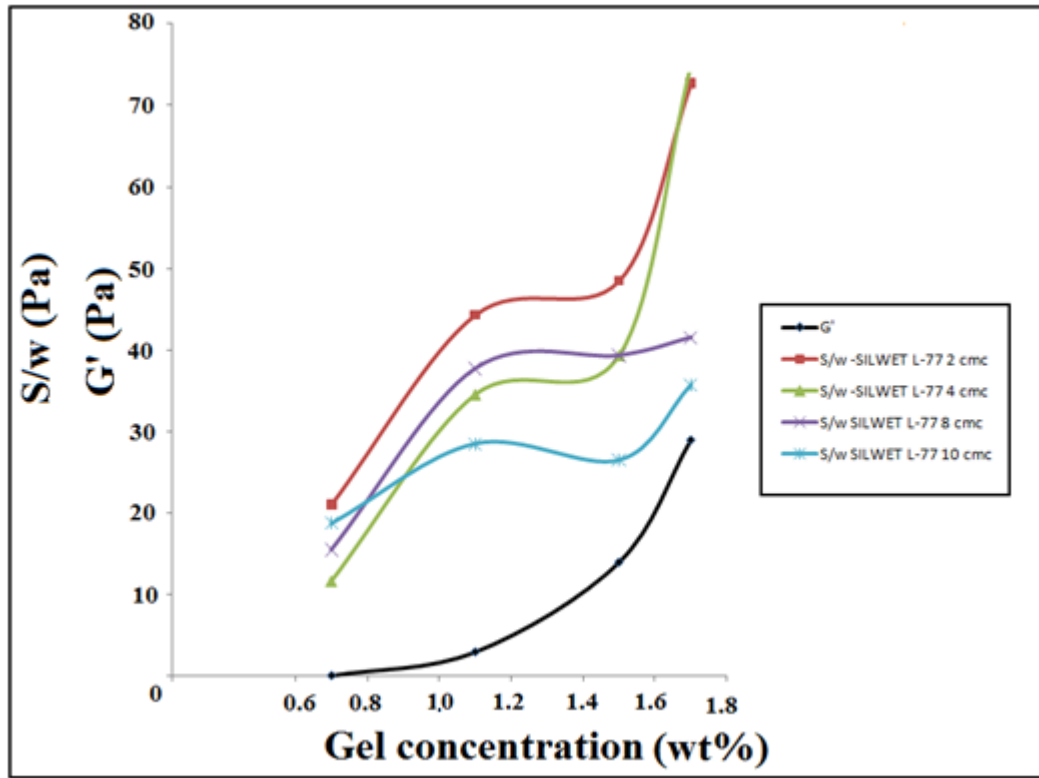


Figure 6.8: $S/\Delta w$ and G' against gelatine gel concentration, with Silwet L-77 concentration varying parametrically. $S/\Delta w$ is constantly greater than G' wherever cracking patterns are observed.

Figures 6.3-6.8 show that inequality (6.9) is valid for all types of surfactants and of gels, for the concentrations where there is pattern formation. For lower gel concentrations, $\frac{S}{\Delta w}$ is much greater than G' and this results in the formation of very wide “arms”. For very high gel concentrations, $\frac{S}{\Delta w}$ is greater but very close to G' and this results to the formation of very narrow arms. Further concentration increase does not allow any “arm” formation. Thus, it may be possible using (6.9) to get an estimate of the arms’ width by dividing S by G' , both of which are *a priori* measurable quantities.

For the agar and gelatine concentrations where the cracks were observed (from 0.04 wt% to 0.14 wt% for agar and from 0.7 wt% to 0.17 wt% for gelatine), the gel is in an “intermediate” situation, and can behave both like a solid and a liquid. For the high concentrations within

these limits, the substrate starts to behave more like a solid, even though this behaviour is not as dominant as in even higher concentration (where eventually there would be no crack formation). Therefore, the characteristics of spreading on both solid and liquid substrates can be attributed here, and adsorption and diffusion of the surfactant can both be participating in the spreading process.

The high crack propagation speeds indicated from the findings illustrated in Figures 5.12 and 5.13 are indicative of very high Marangoni stresses that can promote very rapid “arm” growth. In order to get such high Marangoni stresses, and especially in the concentrations much higher than the cmc examined here, it is essential for the accumulation of the surfactant at the contact line to be prevented. This can be possible by adsorption of the surfactant at the substrate, that induces high surface tension gradients, and in turn, generate high Marangoni stresses. For spreading on solids, the unique behaviour of superspreaders has been associated with their ability to adsorb at the substrate. The adsorption of a surfactant at the substrate has been considered as an important factor by researchers (Rafai *et al.* 2002, Kumar *et al.* 2002, Clay and Miksis 2004, Kim *et al.* 2006, Karapetsas *et al.* 2011a) in the spreading process and in other phenomena like the autophobic effect (Craster and Matar 2007). Karapetsas *et al.* (2011a) suggests that a soluble superspreading surfactant can adsorb at the solid surface through two mechanisms; either the surfactant monomers that reside in the bulk can freely adsorb/desorb at the substrate, or the surfactant monomers in the liquid-air interface can adsorb/desorb directly at the substrate through the contact line.

For Silwet L-77, the ability to adsorb significantly at the substrate has been attributed to the intriguing “T” shape structure of the trisiloxane molecule and the large area of the hydrophobic trisiloxane group (Anathapadmanabhan *et al.* 1990, Kumar *et al.* 2003, Radulovic *et al.* 2010). The structure of trisiloxane surfactants allows them to adsorb directly onto a solid surface, when dissolved in an aqueous phase, and to assemble into bilayers at the

contact line. On the contrary, for a non-superspreading surfactant (such as SDS for instance), adsorbed at the air/liquid interface, it is less possible to transfer directly onto the surface of the underlying substrate, but tends to accumulate in front of the contact line (Maldarelli 2011). In addition, since a gel consists of a network of polymer chains, adsorption of the surfactant on the liquid-gel interface could possibly occur in the form of an entanglement of the surfactant molecules to the polymer chains. In this case, the hydrophobic part of the surfactant molecule would be attached to the polymer chain and the hydrophilic part would be attached to the aqueous phase. Due to its “T” shaped structure, a Silwet L-77 molecule would be more favourable to entangle in a polymer chain and to provide better packing, compared to an SDS molecule. In order to support the latter theory, however, more information of the molecular structure and the molecular dynamics of the materials involved here needs to be obtained, since one has to investigate whether the size of the surfactant molecules and of the polymer chains would allow such entanglement.

A combination of different effects might be responsible from preventing further growth of the “arms”. The relaxation of the surface tension gradients due to accumulation of surfactant when the initial surfactant concentration is high, or at later times during the spreading of surfactant of intermediate concentration, is the most obvious one; at low surfactant concentrations, the surface tension gradients are not sufficiently large to give rise to pattern formation. At very large surfactant concentrations, surfactant might accumulate at the contact line, resulting in the reduction of surface tension gradients, or even in the generation of reverse Marangoni forces. At intermediate concentrations, large surface tension gradients can be generated and maintained, and the formation of the crack occurs. However, in this case, the surface tension gradients can relax with time, when the rate of surfactant transport near the contact line is higher than the rate of its removal. At this stage, the significant gravitational forces can increase further.

An indication of the nature of the cracks can be given by mixing the surfactant with a small quantity of methylene blue dye before the spreading. In both types of gels, it was observed that, even though there is formation of “arms” once again, the dyed surfactant was not observed to reach the end of the “arms”. The “arms” propagate ahead of the point up to which the dyed surfactant goes instead, thus leaving a coloured and an uncoloured region within each crack. This could suggest that the surfactant does not reach the end of the cracking arms, and that the crack can propagate further ahead from the area where the stress is generated. In other words, the stress is being relieved by the crack propagation ahead from the area of its application, showing that the spreading “arms” observed here are genuine cracks, and not indentations.

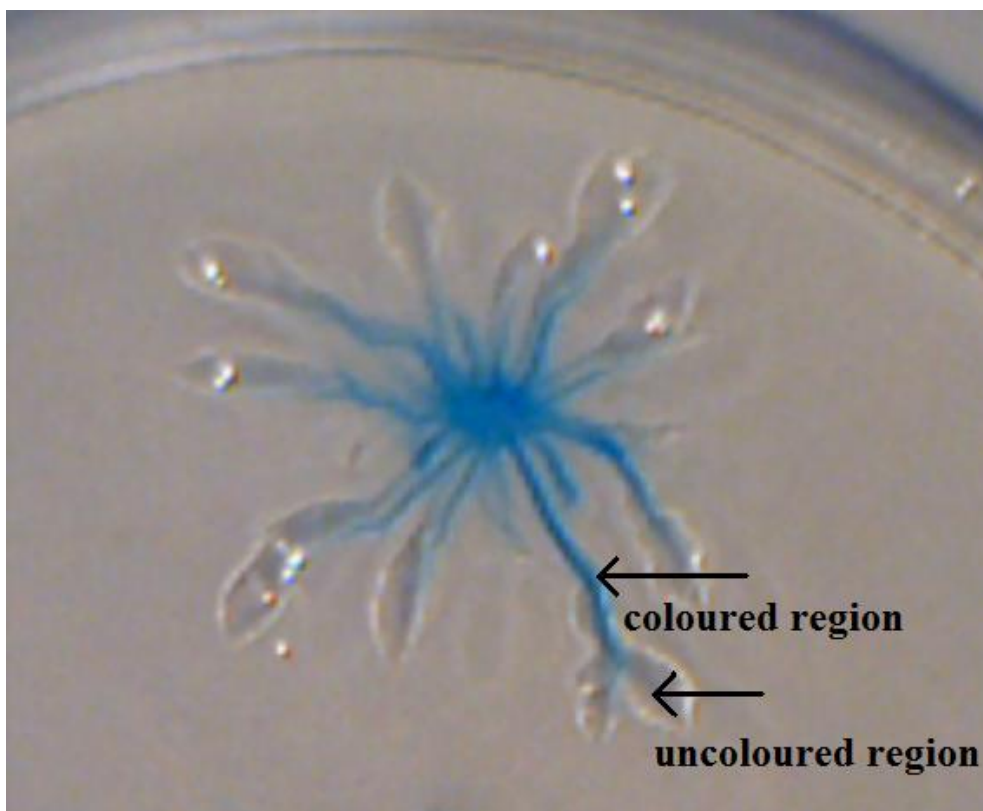


Figure 6.9: Pattern formed after the deposition and spreading of a droplet of 8 cmc Silwet L-77 mixed with methylene blue, on a 1.1 wt% gelatine layer.

All the cracks of the patterns shown in Figures 5.1, 5.8 and 5.15 seem to have a central darker region, which is surrounded by a brighter border. The latter represents the contact line

between the crack and the uncontaminated gel. This indicates that the crack has a depth and it penetrates into the surface of the gel, and that region between the crack and the uncontaminated gel surface is slightly elevated (Figure 6.10).

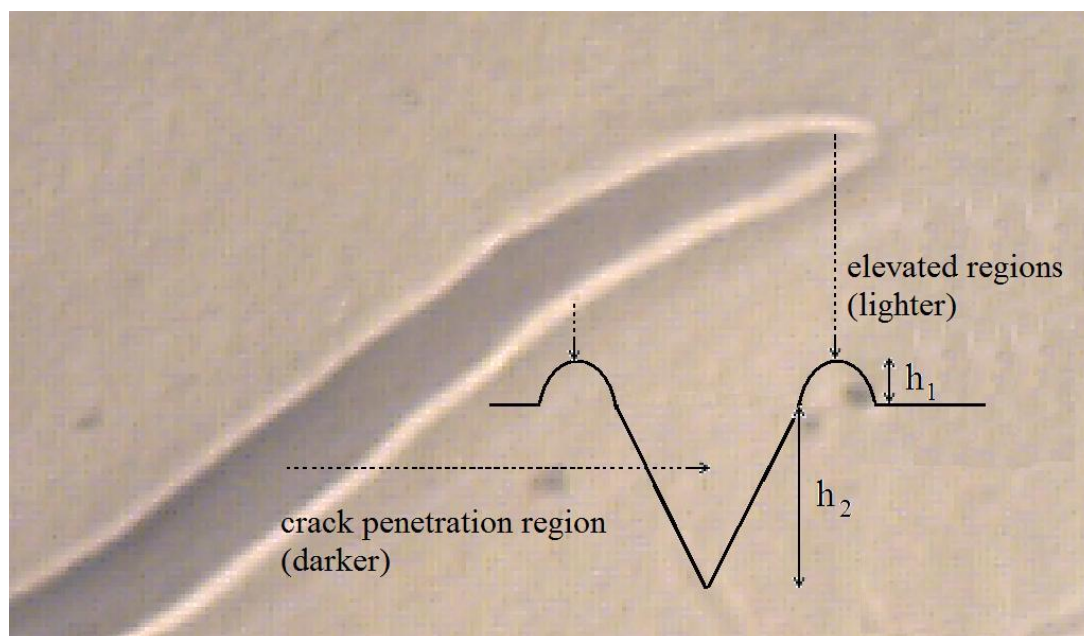


Figure 6.10: The elevated and the crack penetration regions of the gel surface near the contact line of the crack and the uncontaminated area. This crack is formed on the surface of a 0.12 wt % agar gel after the deposition of a 2 cmc Silwet L-77 solution droplet.

This elevated region in the contact line can be linked with the thickening regions that can be created locally at the surfactant leading edge from the disturbance in the film height caused by Marangoni spreading on liquids (Afsar-Siddiqui *et al.* 2003, Edmonstone *et al.* 2006). It could also be considered as the analogue of the raised rim that is observed during the surfactant superspreading on solids (Rafai *et al.* 2002, Beacham *et al.* 2009, Karapetsas *et al.* 2011a). In the region very close to the contact line, the surfactant concentration is reduced due to the adsorption of the surfactant. The high surface tension generated locally resists the deformation of the interface and allows the contact angle to retain high values, leading to the formation of this elevated rim.

The significance of gravitational forces highlighted by the high values of the Bond number found in Sections 5.1.3, 5.2.3 and 5.3.3 has an effect on preventing the “arms” from propagating further on the surface of the gel. With time, gravitational effects increase while the surface tension gradients are relaxed. Gaver and Grotberg (1990) suggested that, whenever hydrostatic forces overwhelm Marangoni stresses, a flow reversal effect can arise. This will move fluid from the thickened or elevated regions back to the thinning regions (cracks) of the substrate, diminishing the original substrate height disturbance. An assumed height profile of the droplet spreading and the formation of the crack is depicted in Figure 6.11.

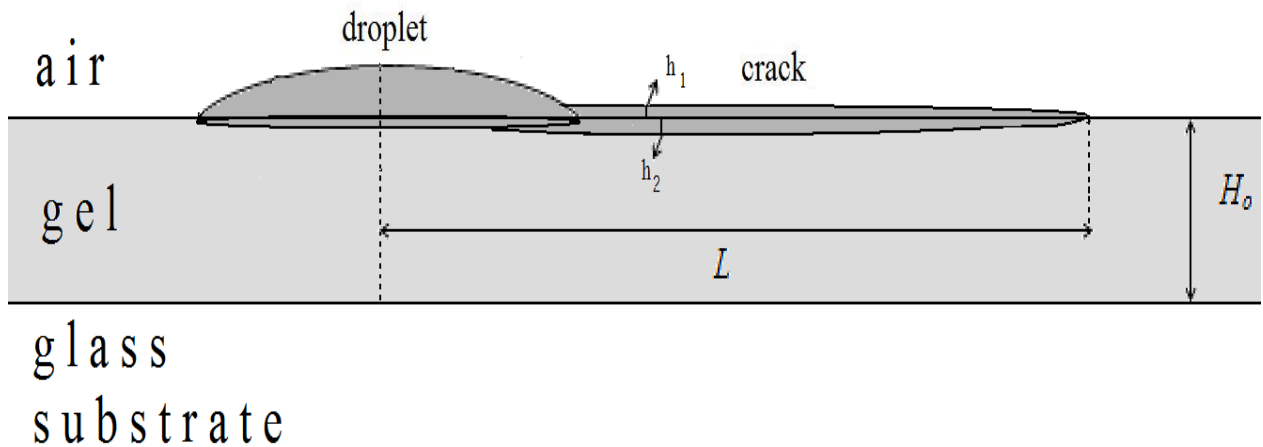


Figure 6.11: Schematic diagram of the height profile during a crack formation. h_1 is the height of the elevated area and h_2 is the depth of the crack.

Summary

It is proposed that the formation of the cracking patterns on the surface of a gel is the result of the competition between Marangoni stresses and the gel strength, and that the surface tension gradients generated between the surfactant and the gel drive the process. It has been observed that a crack is formed within the experimental conditions that allow $S/\Delta w$ to be greater than G' , where S is the spreading coefficient, Δw is the change of the width of the crack and G' is the storage modulus of the substrate. In the same approach, it is possible to get an estimate of the width of the cracks by dividing S by G' .

The existence of an “unzipping” mechanism that is responsible for the crack formation and propagation on the surface of the gels is suggested. There is evidence that the surface tension gradients are larger in the direction perpendicular to crack propagation, thus allowing an “unzipping” of the gel. A typical crack has a depth that is assumed to be in the range of millimetres, and an elevated region that surrounds it. Due to the significance of gravitational forces in the experimental set-ups examined here, flow reversal is expected to occur and to move fluid from the elevated region towards the interior of the crack, preventing further growth.

Chapter 7

Conclusions

Synopsis

The main findings of this work that has been detailed over the last two chapters are summarised herein. This study aimed to present the experimental qualitative and quantitative results obtained from the spreading of droplets of aqueous SDS and Silwet L-77 solutions on underlying thick agar and gelatine gel layers. Possible explanations on the observed phenomenon of the formation of the cracking patterns on the surface of the gels were given, together with suggestions on the spreading mechanism and the relative significance of forces that play a role in the process. Suggestions for future continuation of this study conclude this Chapter and the present thesis.

7.1 Contribution and Summary of Findings

Overall, the results of the present thesis provided insight into the interactions between spreading surfactant-laden liquids and underlying gel substrates. This can contribute to the control and improvement of large number of processes that involve systems of gel-like materials and liquids. Towards this direction, the intriguing rapid “self-healing” phenomenon of gelatine, which is reported in this work for the first time, might be an additional useful consideration.

To further enhance the speed and the effectiveness of such processes, superspreading surfactants can be used. The concept of superspreading on solids and liquids which has been very popular among researchers recently, has never been considered in the case of gels up to date. Our results demonstrated that the superspreading behaviour of the relevant group of surfactants becomes evident during their interaction with gels, by observing their ability to fracture gel surfaces that could not be fractured with convectional surfactants, and to promote very high crack propagation velocities, even when used in very small quantities.

The present thesis also demonstrates the universality of the surfactant-driven gel fracture. Due to the spreading of superspreading and convectional (non-superspreading) surfactants, crack-like patterns can appear on the surface of different types of gels. It is therefore possible that such instabilities can occur on any gel-like material of any type, including the mucus-laden films in the human lung. By using surfactants, it could be possible to crack such mucus and release the airways of the lung, improving respiration.

The suggested mechanism of “unzipping” of the gel in a manner perpendicular to the direction of crack propagation highlights the importance of the width of the cracks in the process. Via the suggested inequality $\frac{S}{\Delta w} \geq G'$ it may be possible to control the width of the cracks by changing S and G' .

In addition, the results of the rheological characterisation presented in section 4.6.2 of Chapter 4, are expected to be put to immediate use by other scientists and be beneficial for future research that will be conducted in the field.

A detailed summary of the experimental findings presented in this thesis follows.

- The spreading of SDS and Silwet L-77 droplets on both agar and gelatine gel layers was found to be accompanied by the formation of cracking patterns, which are similar morphologically to those observed by Daniels *et al.* (2007). The typical patterns observed comprises mainly crack-like projections emanating from the location where the surfactant droplet is deposited on the gel layer. These projections can be described as spreading “arms” with well-defined edges, which grow to resemble asymmetrical “starburst” formations. They all seem to have a central darker region that corresponds to the “interior” of the crack, and a brighter region that surrounds it corresponds to a slightly elevated area that represents the contact line between the crack and the uncontaminated gel.
- It is evident that the patterns can be formed only inside a “window” of surfactant and gel concentrations, which represents an “intermediate” state of the gel, where it exhibits both solid-like and liquid-like behaviours. At sufficiently high or low gel concentrations for which the gel exhibits solid-like or liquid-like behaviour, respectively, the possibility of such starburst formation is very small. For SDS spreading on agar, the patterns are observed for gel concentrations from 0.06 wt% to 0.12 wt%, and for surfactant concentrations above 0.4 cmc. It should be noted that these are the same SDS concentration limits within fingering is visible for spreading on thin liquid substrates (Affsar-Siddiqui *et al.* 2003). For Silwet L-77 spreading on agar, the “window” is wider, and patterns are observed for gel concentrations from 0.04 wt% to 0.14 wt%, and for surfactant concentrations above 0.3 cmc. Finally, for

Silwet L-77 spreading on gelatine layers, the gel concentration limits are very different, namely from 0.7 wt% to 1.7 wt%, and the surfactant concentrations where the patterns can be seen start from 0.5 cmc and increase up to several times the cmc. However, beyond 10 cmc the qualitative and quantitative characteristics of the pattern formation seem to remain the same.

- Marangoni stresses are dominant during the spreading in all cases examined, since the spreading exponent, n , of the $R(t) \sim kt^n$ power-law was found to have values between 1/2 and 0.85, with values close to 3/4 being the majority. Hence, there is an agreement with the $t^{3/4}$ scaling prediction, characteristic of Marangoni-driven spreading of a finite mass of surfactants on thick films. Therefore, the surface tension gradients generated between the surfactant and the gel can be identified as the main driving force behind the observed pattern formation.
- During the spreading exponent measurements it was observed that different “arms” of the same pattern could grow following different scaling relationships. This is due to the heterogeneities that occur on the surface of all the gels which make the conditions for growth different from one region of the gel surface to another. That is also why the patterns are not symmetrical and the “arms” of the same patterns are not identical to each other.
- Marangoni stresses dominate over surface and bulk diffusion phenomena. However, the high Bond numbers found here, highlight the importance of gravitational forces. More specifically, the Bond number takes values from 4.6 to 7.2 for SDS spreading on agar, from 3.3 to 4 for Silwet L-77 spreading on agar, and from 3.5 to 4.8 for Silwet L-77 spreading on gelatine. Therefore, in all cases gravitational forces are significant, but they are somewhat more significant when a non-superspreading surfactant is used.

- The morphologies of the patterns formed due to the spreading of Silwet L-77 droplets on agar, are much more complicated compared to those formed by SDS spreading on the same substrate. In the latter case, the “arms” of the patterns are mainly straight, while in the former case the “arms” very curved, and they can have ridges along their edges. Smaller “arms” emerging from the main ones are also reported. The spreading on gelatine also reveals a “self-healing” property of the substrate that allows the cracks to close even before the pattern has been fully developed. In this case, patterns with large number of “arms” are very common. The largest and wider “arms” are reported in the case of Silwet L-77 spreading on agar. The shortest “arms” reported are found in the case of SDS spreading on agar, and the thinnest are found in the case of Silwet L-77 spreading on gelatine. In all three cases, the number and length of the “arms” seem to change randomly while the surfactant and gel concentrations meters change. There is only a slightly higher propensity for a larger number of “arms” to be formed with increasing surfactant concentration. In all cases examined, however, the “arm” width clearly decreases while the substrate gel concentration increases.
- The spreading of Silwet L-77 results in higher crack propagation speeds, as it is reflected by the higher values of the spreading coefficient, k , measured for Silwet L-77, compared to the ones for the spreading of SDS. The rapid crack propagation promoted by Silwet L-77 is even more intriguing given the fact that in this study Silwet L-77 was used in much smaller quantities compared to SDS. Thus, the superspreading behaviour of Silwet L-77 is evident. This behaviour is usually linked with the “T” structure of the trisiloxane molecule that allows the superspreading surfactant to adsorb onto the substrate and to assemble into bilayers at the contact line. The adsorption onto the substrate prevents the accumulation of the surfactant in the contact line and generates very high Marangoni stresses. On the other hand, the adsorption of SDS is not very significant. This behaviour of Silwet L-77 is not obvious in gelatine, where

the smallest values of maximal crack propagation speeds are reported. For all the cases examined, the evolution of the “arms” is faster for weaker gels and slower for stronger gels.

- The existence of a mechanism where the basic feature is the “unzipping” of the gel in a manner perpendicular to the direction of the largest surface tension is possible. This is indicated by the fact that the length scales along the direction of crack propagation are longer than those perpendicular to it, hence the surface tension gradient is expected to be larger in the latter case. Therefore, the width of the “arms” seems to be a significant characteristic of the spreading process. It is possible to estimate the width by dividing the spreading parameter, S , with the storage moduli that characterises the gel substrate, G' . It can be suggested that a cracking “arm” can be formed on a gel surface only if $\frac{S}{\Delta w} \geq G'$.
- Further growth of the “arms” is prevented when the Marangoni stresses are initially weak due to very high surfactant concentration, or when they relax with time when the rate of surfactant transport near the contact line becomes higher than the rate of its removal. At the same period of time, gravitational forces become more significant, and flow reversal is possible. While the latter occurs, fluid is moved from the elevated regions back to the “interior” of the cracks, levelling the original height disturbance of the substrate. It is also possible for an “arm” to hinder the growth of another neighbouring “arm” by making the conditions in the specific region of the gel surface less conducive to growth.

7.2 Recommendations for Future Work

The images presented in this work provide qualitative information on the different morphologies observed, and quantitative data on the length and the width of the spreading “arms”. However, it would be useful to construct a height profile and measure the different height variations, by determining the depth of the cracks and also the height of the elevated regions that surround them. Using a profilometer in order to obtain 3-D profiles and surface topography information could be useful in the measurement of the depth of the cracks and of the elevated regions height. This could also be helpful in quantifying the roughness of the gel profile. Such measurements were attempted using a profilometer, however, they were not successful at this point, since there was lack of reflectivity of white light from the gel surface, and also because very large scan areas were required in order to obtain details of the height variations within a crack. A possible way to address this problem is to mix the gel with small polystyrene spheres (Wright *et al.* 1996, Daniels *et al.* 2007).

In addition to visualising the surfactant surface distribution by mixing surfactant with a dye (methylene blue), the bulk surfactant distribution within the gel could be obtained by using fluorescently tagged surfactant molecules with the aid of fluorescent microscopy (see also Fallest *et al.* 2010).

It would also be important to model the spreading of surfactants on gel substrates in order to obtain accurate predictions of the flow which will be validated against the experimental findings. The physical properties associated with a gel of given thickness and rheological characteristics and a drop of known surfactant concentration can be used to construct the various dimensionless groups which would appear in the model equations. The two-dimensional governing equations can then be integrated numerically to yield predictions of the flow characteristics. Detailed comparisons between theory and experiment can be carried out in terms of the spatio-temporal evolution of the flow profiles. Since the gels used here are

viscoelastic materials, a hierarchy of mathematical models of viscoelasticity can be adopted, ranging from simple Maxwell models to the more complicated Oldroyd-B models. The theoretical work by Zhang *et al.* (2002) on the spreading of surfactant on thin viscoelastic films can be a good starting point for this. Discrepancies between the predictions and the experimental data found here can be used to revise the models as necessary.

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APPENDIX

Error Analysis

During the experimental processes related to the present work, the following errors were taken into consideration:

Systematic errors

These occur due to the experimental set-up and/or methods. Provided the same apparatus and methods are used to obtain all results, they will be present to the same degree in all the obtained results. To minimize the impact of experimental errors, the same methods and materials were used throughout the experiments. For instance, when pouring out the hot agar or gelatin gel into the Petri dishes, this was done with the Petri dishes already in place instead of first pouring it out and then moving the dishes. Therefore, any distortion in results obtained is likely to be small and constant throughout.

Random errors

These arise from random fluctuations in measurements. Measurements could be affected by changes in the temperature, humidity or other conditions in the lab which could not be perfectly controlled. To minimise the effect of random errors, measurements were repeated several times (usually 3) when applicable and a mean value was taken.

Instrumental errors

These arise from the lack of mathematical accuracy in an instrument.

The Wilhelmy plate apparatus measures the surface tension with an accuracy of $\pm 0.001 \text{ mN/m}$. However this error is not taken into consideration, since it is much smaller than the standard error that occurs when taking the average of 3 runs. For a typical measurement, the latter is $\pm 0.5 \text{ mN/m}$.

The Dino X-Lite digital microcamera AM-413M has a resolution of 1.3 Megapixel. Using this to measure a distance (e.g. 10cm), one should consider the number of square boxes which corresponds to each pixel, by taking into consideration the following:

$$1\text{box/pixel} = (10 \times 10 \text{ mm}) / 1.3 \times 10^6 \text{ pixel} = 7.69 \times 10^{-5} \text{ mm/pixel}.$$

The Pioneer OHAUS scale measures weight in g with four decimals. A typical measurement of 0.08 g of agar powder can result in an actual measured value of 0.0803 g. Therefore the value can be expressed as $0.0800 \pm 0.0003 \text{ g}$ or $80.0 \pm 0.3 \text{ mg}$.

Standard deviation

When taking the average of values for a number of experimental runs, or when taking the average value of the spreading exponents for each single “arm” of a single pattern, the standard deviation was determined, as in the example shown below:

Spreading exponent for the pattern formed during the spreading of 2 cmc SDS on a 0.08 wt% agar gel:

Leg	n
1	0.7371
2	0.7685
3	0.7522
4	0.7379
5	0.7438
6	0.7718

Mean: 0.751883

Standard deviation: 0.015181

Therefore, for this pattern, $n = 0.75 \pm 0.02$

