EFFECT OF COMPOSITION ON EMPIRICAL STABILITY TRENDS FOR OIL-IN-WATER EMULSIONS

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ABSTRACT

Relative stabilities of paraffin oil-in-water emulsions were determined empirically as a function of increasing ionic strength, surfactant type or concentration, droplet size, pH and calcium(II) concentration. Stabilities were measured by droplet size changes, planar interface oil droplet coalescence times, creaming rates and photography. Stability trends between methods were compared. Conclusions were derived in terms of creaming and coagulation. The trends below were discussed in terms of theories of emulsion stability.

1. Increased surfactant concentrations stabilised the emulsions against creaming. Coalescence trends were complex: an optimal cetylpyridinium chloride concentration stabilised the emulsions. Beyond that concentration, stability was reduced. Because of its low HLB, increased sorbitan sesquioleate concentrations destabilised emulsions towards coalescence.
2. Smaller droplets stabilised all the emulsions despite the increased polydispersity.
3. Increased ionic strengths accelerated creaming. Coalescence was faster for cetylpyridinium chloride because of reduced droplet repulsion. Sodium dodecyl sulphate resisted coalescence at all ionic strengths due to the restabilisation predicted by the Stochastic model.
4. pH did not affect emulsions containing a pH-stable surfactant (sodium dodecyl sulphate). Emulsion stability was reduced with acid- or base-labile labile surfactants (sorbitan sesquioleate, cetylpyridinium chloride) due to reduced ability to lower the surface tension during emulsification, or hydrolysis.
5. Ca^{+2} destabilised emulsions containing anionic surfactants (sodium dodecyl sulphate and laurate) by co-ordination, but had little effect on a cationic emulsifier

(cetylpyridinium chloride) to which it did not co-ordinate. The destabilisation of anionic-based emulsions was due to the formation of oil-wettable solid salts and the removal of the o/w surfactant.

6. Low stabilities of sorbitan sesquioleate-based emulsions were attributed to Bancroft's rule and the low hydrophile-lipophile balance of sorbitan sesquioleate.

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PHYSICAL CONSTANTS, SYMBOLS & ABBREVIATIONS

L (Avogadro's number)	6.023×10^{23} mole^{-1}
k (Boltzmann constant)	1.381×10^{-23} JK^{-1}
ϵ (Permittivity of a vacuum)	8.854×10^{-12} C^{2}N^{-1}m^{2}
e (charge of an electron)	1.602×10^{-19} C
T	Kelvin temperature
o/w emulsion	oil-in-water emulsion
w/o emulsion	water-in-oil emulsion
HLB	hydrophile-lipophile balance
s.d.s.	sodium dodecyl sulphate
c.p.c.	cetylpyridinium chloride
s.s.o.	sorbitan sesquioleate
c.c.c.	critical coagulation concentration

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SECTION A

LITERATURE REVIEW

A1. INTRODUCTION[1]

Emulsions are colloidal dispersions of a liquid in another mutually-insoluble liquid. They usually contain a surface-active agent ("surfactant") and/or solid particles to stabilise the liquid-liquid interface of the (usually poly-) dispersed droplets. There are two inverse types of emulsions: oil-in-water (o/w) emulsions and water-in-oil (w/o) emulsions. O/w emulsions consist of droplets of a dispersed, internal (discontinuous), hydrophobic phase that is suspended in an external (continuous) hydrophilic phase, e.g. milk. In w/o emulsions, the discontinuous phase consists of aqueous droplets dispersed in an oil matrix, e.g. oil field emulsions. The dispersed phase droplet diameter of emulsions is usually between 0.1-100 μm. Micro-emulsions have droplet diameters less than 1 μm. The study of microemulsions, w/o emulsions and complex emulsions-within-emulsions differs from that of coarser, simple o/w emulsions and is beyond the scope of the study. This dissertation focuses on coarse o/w emulsion stability. Some of the principles in this report pertain only to o/w emulsions.

Emulsions are extremely important for a variety of industrial applications including oil recovery, coating-, food- and polymerisation processes, cosmetics, commercial explosives, pharmaceuticals, textiles, cleaning agents and agricultural sprays.

In an emulsion, hydrophilic and lipophilic phases are in intimate contact. Consequently, the system is metastable thermodynamically and/or kinetically. By various mechanisms, the phases separate from each other. Emulsion stability is a critical property for all applications, making an understanding of the decay process a subject of practical and fundamental importance. Unfortunately, the stability of emulsions depends on a diverse array of experimental parameters, so that the prediction of stability of a given system from basic principles is difficult. The control of emulsion stability is largely an empirical art. The development of models to provide the formulator with rapid stability predictions, prior to formulation, lags behind practical evaluations.

This report investigates the factors that influence the empirical stability of o/w emulsions.

A2. MECHANISMS OF EMULSION DECAY[1, 4-6, 9, 10, 13-29]

A2.1. INTRODUCTION & DEFINITIONS

When an emulsion is formed, the interfacial area of the mutually-insoluble liquid phases increases dramatically. Phase separation therefore occurs by various mechanisms with time in order to minimise the thermodynamically-unfavourable hydrophobic-lipophobic interactions. The time scales for coarsening of emulsion droplets span a wide range from seconds to several years. Ultimately, the two phases will be separated by one interface. Some emulsions restabilise after initial decay into a larger average droplet size and size distribution and then remain indefinitely stable.

There is a distinct difference between the ease of formation of an emulsion and its subsequent stability[2, 3]. An emulsion may form faster than another emulsion because the kinetics of its formation require less activation energy, but it may be thermodynamically less stable than the other emulsion once it has formed.

Emulsion decay occurs by one or more of the following mechanisms: sedimentation; flocculation; coalescence; inversion; Ostwald ripening. The decay is often a kinetic combination of these events, e.g. coagulation or sedimentation-flocculation. These mechanisms are defined below.

- **Sedimentation**: Separation of the phases, without breaking of the droplets, is called sedimentation. Creaming is a type of sedimentation. It is the rise of oil droplets to the top of an emulsion when the hydrophobic phase has a lower density than the hydrophilic phase.

- **Flocculation (aggregation)** : This is the (usually reversible) sticking together of droplets with the formation of three-dimensional clusters, without coalescence of the individual droplets. Normal flocculation results from decreased repulsive interactions.

In Brownian flocculation, droplets undergoing Brownian motion collide with each other to form larger droplets.

- **Coalescence (breaking)**: This is the spontaneous, irreversible joining of small (flocculated) droplets to form larger droplets, which leads ultimately to two liquid phases that are separated by a single interface.

- **Coagulation**: This is the combination of flocculation followed by coalescence. Coagulation is aggregation into the primary-minimum energy well (Sec. A3), whilst flocculation involves only aggregation into the secondary minimum. "Irreversible" coagulation can thus occur only after "reversible" coagulation has taken place.

- **Sedimentation-flocculation**: This refers to the simultaneous flocculation and creaming of oil droplets, in which creaming droplets undergoing Brownian motion collide to form larger particles whilst creaming[4]. Emulsion decay is accelerated by the different creaming rates of different-sized aggregates, which collide with slower, smaller droplets.

- **Inversion**: It is the process of the discontinuous phase droplets becoming the external -phase and the continuous phase becoming the droplet phase, e.g. the formation of a w/o emulsion from the o/w emulsion.

- **Ostwald ripening (molecular diffusion)**: This refers to the preferential molecular diffusion of smaller droplets into the larger droplets. This decay process may be accelerated by surfactant micelles.

Unstable emulsions are characterised by fast rate constants in one or more of the decay mechanisms. To characterise the stability of an emulsion, it is important to consider all the emulsion-breaking mechanisms. The origins and outcomes of these decay mechanisms are detailed below.

A2.2. CREAMING[1, 5-8, 33]

Creaming originates from gravitational effects due to a density difference between the two phases. From Stokes law[1, 5] for individual droplets, an average mass creaming rate, V, can be predicted[6]:

$$V=\Sigma\frac{8\pi g n_i r_i^5 \Delta\rho}{27\eta_e M} \quad \ldots\ldots \quad \text{Equation 1}$$

where:

- g is the gravitational constant
- n_i is the number of droplets with radius r_i
- $\Delta\rho$ is the density difference between the external and internal phases
- η_e is the viscosity of the external phase
- M is the volume of the internal phase.

There are four important consequences of Stoke's law and Eq. 1 in terms of instability as a result of creaming. These are:

1. Smaller density differences result in slower creaming rates[6] ($V \propto \Delta\rho$).

2. Smaller droplets cream much more slowly than larger droplets[4] ($V \propto n_i r_i^5$). Flocculation accelerates creaming of smaller droplets since an aggregate creams as a single, larger droplet.

   The differential creaming rate results in a Boltzmann distribution of droplet sizes in the creamed layer[1]:

$$n_h = n_0 e^{\frac{-4\pi r_i^3 \Delta\rho g h}{3kT}}$$ . . . . . . Equation 2

where:

- n_h is the number of droplets with radius r_i at height h in the creamed layer
- n_0 is the droplet concentration at the bottom of the creamed layer.

In the creamed emulsion zone, the droplets are close-packed. The emulsion is referred to as a high internal phase emulsion. In typical polydisperse emulsions, smaller droplets fill the interstitial spaces between larger droplets. This results in a packing efficiency of between 0.74 and unity in the creamed layer, depending on the phase volume and polydispersity of the droplets.

3. Higher external phase viscosities retard creaming[7] ($V \propto 1/\eta_e$) .

4. Creaming is insignificant, even at low external (aqueous) phase viscosities, if the gravitational potential energy is much less than the thermal energy that retains the droplets in suspension[1, 8]:

$$\frac{4}{3}\pi r^3 \Delta\rho g h \ll kT$$ . . . . . . Equation 3

where h is the total emulsion height.

Typical examples in Table 1 (25°C, 20cm high emulsion) show that the average droplet size has a much greater effect on the creaming rate than density differences. Creaming is significant for all normal density differences, but becomes insignificant as the droplet sizes are reduced to the microemulsion regime.

TABLE 1: EFFECT OF DROPLET SIZE & DENSITY DIFFERENCE ON CREAMING

AVERAGE DROPLET RADIUS (μm)	DENSITY DIFFERENCE $\Delta\rho$ (g.ml^{-1})	$\dfrac{\frac{4}{3}\pi r^3 \Delta\rho g h}{kT}$	RELATIVE CREAMING RATE
50	0.1	24.9×10^9	FAST
	0.2	50.0×10^9	
	0.3	74.6×10^9	
	0.4	100×10^9	
50	0.1	24.9×10^9	FAST
5		24.9×10^6	SLOWER
1		20.0×10^4	SLOW
0.05		24.9	VERY SLOW

A2.3. FLOCCULATION[9-12, 33]

The origins of flocculation are described by the DLVO theory[9, 10] (Sec. A3). If the electrical repulsive and kinetic energies between droplets are less than the van der Waals attractive energies, flocculation will ensue. Flocculation is at least a second-order process since two or more droplets are involved. The flocculation rate is influenced by the viscosity[11] of the medium and by droplet interactions[12], which are determined by particle size, aqueous phase dielectric constant and ionic strength.

Flocculation causes two effects which are detrimental to emulsion stability:

1. an increase in the effective size of the particles. This accelerates the creaming rate.
2. an increase in the probability of coalescence, since flocculation (reversible coagulation) precedes coalescence (irreversible coagulation).

A2.4. COALESCENCE[1, 3, 13-25]

In o/w emulsions, when two oil drops have flocculated into the primary minimum energy barrier (Sec. A3), a thin film of aqueous phase is formed and trapped between them. Under the kinetic and gravitational forces acting on the film, which are the sum of attractive and disjoining forces, it drains to a critical thickness and then ruptures, resulting in coalescence of the drops. Droplet coalescence is usually a first-order process. In highly concentrated emulsions, instability is often dictated by the coalescence rate[13].

The main stages in the formation, evolution and rupture of the film between two droplets are[14]:

1. Two oil droplets approach each other.

2. Both droplets deform at their touching interface into bell-shaped dimples.

3. The dimples disappear, a plane-parallel film forms and drains under the combined action of gravity, suction at the Plateau borders and the disjoining pressure. Disjoining pressure is the isotropic pressure difference between the film meniscus and that in the bulk aqueous phase. The liquid from the central part of the film flows out more slowly than that from the edges. A very thin Newtonian black film is formed.

4. When the film thickness is reduced to ca. 1000Å, other forces influence the draining. Corrugations grow by a stochastic process into a nucleated "hole" due to inhomogeneities in the film thickness[15]. The inhomogeneities are caused by random thermal fluctuations, dust, vibrations, defects in the surfactant monolayer[1] and concentration gradients which induce convective instabilities. Rupture of the metastable film occurs at a critical thickness due to these small, spontaneous surface perturbations. The rupture begins at the thinnest part of the film.

Metastability is reached when border suction, van der Waals attraction and double-layer repulsion equilibrate, whereas instability results when the attractive forces predominate[16]. When the film is thick, draining proceeds rapidly and the fluctuations grow slowly or not at all. When the film becomes thinner, the drainage rate slows down, whereas the fluctuations grow faster and faster. This occurs until a critical thickness is attained, at which one of the fluctuations grows so fast that the film breaks[16]. Interface coalescence generally does not occur at a film thickness of greater than 300 Å[17].

The rate of drainage of the intervening thin film is critical to the stability of the emulsion and is the rate-determining step of the coalescence process[11, 18, 19]. The rate of film thinning is influenced by the following factors:

- The rate decreases with an increase in interfacial curvature (film area)[15, 20], -viscosity[14, 21, 22], -elasticity[22], -tension gradient (Gibbs-Marangoni effect)[18] and interdroplet repulsion[23]. The critical thickness is also decreased as the radius of the film is decreased. According to the Reynold's equation, the rate of film thinning varies inversely with the square of the film radius[24]. In practice, the rate is usually several times greater than the equation predicts[18].

- The rate increases with an increased force pressing on the film[3], increased van der Waals attraction (larger droplet sizes), high surface diffusion coefficients[22] and with respect to surface fluctuations with wavelengths larger than a critical wavelength.

- Forces of interaction: capillary pressure (suction at the Plateau borders) and the disjoining pressure[20]. Disjoining pressure consists of the electrostatic repulsive forces between ions on the two surface layers, the attractive van der Waals forces among all the molecules of the film, and the steric forces due to steric hindrance in closely-packed monolayers.

- The following surfactant parameters (Sec. A4.1)[20]: adsorption-desorption and diffusion kinetics; aqueous bulk concentration[25] and concentration gradients[22]; selective solubility.

A2.5. INVERSION[1, 6, 26-28]

The inversion of an o/w emulsion into a w/o emulsion occurs because of surfactants with unsuitable HLB (hydrophile-lipophile balance, Sec. A4.1.2) values, oil-wettable solids (Sec. A4.7.1), unsuitable temperatures (Sec. A4.9) and aqueous phase pH's (Sec. A4.10). Altering the latter two parameters can alter the hydrophile-lipophile balance[26] (HLB) of the surfactant, which will determine the type of emulsion that is favoured at the new HLB value:

- When the phase-inversion temperature is transgressed, the emulsion inverts[6, 27].

- Co-ordination by H^+ or other counterions to the surfactant head group(s) can alter the surfactant HLB and result in inversion. When steric stabilisers (Sec. A4.7) are present, a change in pH may change the wettability characteristics of the solids. This can also result in inversion[28].

A2.6. OSTWALD RIPENING[1, 23, 29, 48]

Ostwald ripening is a second-order process driven by the higher Laplace pressure in smaller oil droplets. As a consequence of the Kelvin effect and Raoult's law, small droplets have higher solubilities in the external phase, and higher vapour pressures, than the larger droplets or a bulk amount of that phase. Consequently, the smaller droplets diffuse at the expense of their own size into the larger droplets. The decrease in size of the smaller droplets increases the vapour pressure difference between these and the larger droplets and accelerates the decay.

Ostwald ripening is important only for emulsions with small droplet sizes (< 1 μm diameter), made with a chemically homogeneous droplet phase of significant solubility in the continuous phase[29]. In o/w emulsions, the nature of the oil phase (Sec. A4.11) therefore influences the extent of this instability. However, an excess of a surfactant may assist Ostwald ripening even in large droplets by solubilising and transporting fractions of the droplet by encapsulation in micelles. This process is not dependent on the Laplace pressure of the droplet and hence it may occur for relatively large droplets (above the microemulsion regime).

Since it will be central to the discussion of the factors affecting the stability of emulsions, attention is now directed to the DLVO theory of droplet coagulation (Sec A3).

A3. DLVO THEORY FOR EMULSION COAGULATION[9, 10, 28, 30 - 32, 37]

A3.1. PREDICTING COAGULATION

The DLVO theory[9, 10, 30] of colloid coagulation can mathematically quantify the effect of oil droplet interactions on the coagulation of o/w emulsions. The acronym "DLVO" refers to the first letters of the surnames of four prominent researchers that developed this model for colloid stability in general. These researchers were Derjaguin, Landau, Verwey and Overbeek. The theory determines the effects of ionic strength and particle size on emulsion stability by calculating the total interaction energy (V_T) between two oil droplets as a function of interdroplet distance (H). This is achieved by summing the repulsive (V_R) and attractive (V_A) energies at each distance[a]:

$$V_T = V_R + V_A \qquad \text{. . . . . . . Equation 4}$$

The attractive and repulsive terms are calculated from Eq's 5 (or 6) and 7 respectively. The transition between stability and coagulation occurs when $V_T = 0$ and $\partial V_T / \partial H = 0$. The latter condition defines an energy minimum ("well") in the interaction function. Coagulation will occur when the attractive term predominates, but if the repulsive forces outweigh V_A, the emulsion will be stable against coagulation. Various scenarios are thus possible as the droplets approach:

1. a positive energy barrier (several multiples of the kinetic energy kT) prevents coagulation entirely.

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[a] For emulsions that are stabilised by steric stabilisers, a steric repulsive term (V_s) must be included[37].

2. a very deep primary-minimum energy barrier prevents coalescence, but a shallow secondary-minimum (which occurs at larger interdroplet separation) is sufficient for flocculation to ensue.
3. there is no energy barrier and an attractive energy at all droplet separations results in coalescence.

The origins and mathematical description of the attractive (V_A) and repulsive (V_R) terms, that are used to calculate the total interaction function (V_T) in Eq. 4, are outlined below.

A3.2. ATTRACTIVE INTERACTIONS[32]

The attractive energy arises from van der Waals forces. The calculation of V_A depends upon the interdroplet distance (H). Two scenarios are considered:

1. For H < 150 Å, V_A is given by:

$$V_A = \frac{Aa}{12H'}\left[\frac{\lambda}{\lambda + 3.54\pi H'}\right] \quad \ldots\ldots \quad \text{Equation 5}$$

where:

- A is the van der Waals constant of the droplet
- a is the radius of the droplet
- H' is a number referred to in literature as the Hamaker constant (varies between 10^{-19} - 10^{-20} J)
- λ is the wavelength of the London frequency of the droplet.

2. For H > 150 Å, V_A is approximated by:

$$V_A = \frac{Aa}{\pi}\left[\frac{2.45\lambda}{120(H')^2} - \frac{\lambda^2}{1045(H')^3} + \frac{\lambda^3}{5.62 \cdot 10^4 (H')^4}\right] \quad \ldots\ldots \quad \text{Equation 6}$$

A3.3. REPULSIVE INTERACTIONS[32, 61]

The repulsive component of the interaction function is caused by electrostatic, (steric) and kinetic forces. The overlap of diffuse electrical double layers, which surround each droplet, causes the droplets to repel each other. The double layer originates from a residual surface charge on each oil droplet. O/w emulsion stability is controlled by the potential drop of the double layer at the aqueous side of the interface.

The repulsive force (Φ_R) due to double layer effects is calculated from Eq. 7:

$$\phi_R = \frac{4\pi\epsilon a_1 a_2}{a_1 + a_2}\psi^2 \ln[1 + e^{-KH'}] \qquad . \; . \; . \; . \; . \; . \quad \text{Equation 7}$$

where:

- Ψ is the surface potential at the Stern radius[b]
- a_1 and a_2 are the radii of the droplets
- κ is the Debye-Huckel inverse length given by:

$$\kappa = \sqrt{\frac{2e^2 L I_m}{\epsilon k T}} \qquad . \; . \; . \; . \; . \; . \quad \text{Equation 8}$$

where I_m is the total ionic strength due to the electrolytes ($I_m = \frac{1}{2}\Sigma c_i z_i^2$). Since the inverse length is proportional to the square root of the ionic strength, droplet repulsion is reduced as electrolyte is added and coagulation ensues at higher ionic strengths (Sec. A4.8.1).

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[b] Zeta potential (ξ) is a direct estimate of the electrical repulsion between droplets as it is a rough measure of the electrical potential at the Stern radius. The larger the magnitude of the zeta potential, the less likely are the drops to flocculate and the more stable is the emulsion. Zeta potential is dependent upon pH; the use of its magnitude and sign for estimating stability is meaningless without a corresponding associated pH. However, flocculation generally ensues between a zeta potential of $|30|$ mV at any pH.

The predictions of the DLVO theory, that relate ionic strength to stability, have been experimentally verified[28, 31 - 33].

The mechanisms of emulsion decay (Sec. A2) and the interparticle interactions that affect the decay (Sec. A3) have been defined. We will next discuss the physico-chemical parameters that determine emulsion stability.

A4. FACTORS AFFECTING EMULSION STABILITY

The integrity of an o/w emulsion depends on the preparation method and the physical and chemical properties of all the components. The variables which determine o/w emulsion stability are:

1. Surfactant type, concentration and solubility in the two phases (HLB).
2. Density difference between the aqueous and oil phases.
3. Droplet size, droplet size distribution and droplet concentration (phase volume) of the oil phase.
4. Viscosities of the aqueous and oil phases, the bulk emulsion and the interface.
5. Steric stabilisers.
6. Ionic strength of the aqueous phase, incl. the type of electrolytes in that phase.
7. Temperature.
8. pH of the aqueous phase.
9. Oil type.
10. Shear forces during and after emulsification.

The stability of a given emulsion depends on the above inter-dependent variables. However, one or more of these parameters may over-ride the others. The dominant variable(s) will then largely dictate the stability. For example, high aqueous phase viscosities will stabilise o/w emulsions due to a "freezing" effect on the decay mechanisms, despite other factors in the system which would predispose the emulsion to rapid instability in the absence of a high external-phase viscosity. The effects of the above variables on stability are detailed below.

A4.1. SURFACTANT[1, 3, 6, 7, 14, 18, 20, 22, 23, 28, 31, 34-38, 40-49]

A4.1.1. INTRODUCTION

Surfactants are emulsifier molecules or ions which partition their hydrophilic "head" group(s) at the phase boundary and thereby lower the interfacial tension between the phases. This facilitates emulsion formation and stabilises the emulsion kinetically and thermodynamically. Creaming is reduced by the attainment of smaller droplet sizes. Decreased interfacial tension reduces capillary suction of the thin liquid film in the coalescence step and hence increases the coalescence time[18]. Coalescence of droplets is extremely sensitive to surfactant congregation at the interface. Surfactants reduce the drainage rate of thin films by increasing the surface- and shear dilational viscosities[18], which retards the wave motions that cause film rupture. They also increase the tangential mobility of the interface, which leads to a slower rate of film thinning[14, 34].

Since the surface tension is lowered by surfactants, kinetic emulsification is facilitated by their presence. Consequently, as their concentration is increased, smaller droplet sizes are obtained for the same amount of shear. Smaller droplets result in more stable emulsions (Sec. A4.3). The droplet size distribution depends upon the type and concentration of emulsifier and the presence of a co-emulsifier[35].

Mixtures of emulsifiers (co-emulsifiers) often form more stable emulsions than the individual surfactants[36 - 38]. The degree of increased stability will depend on the ratio of the two emulsifiers that are employed[38]. The enhanced stability when co-emulsifiers are used is due to surfactant complex formation at the interface, which results in a stronger interfacial film. For example, in apparent contrast to the HLB concept (Sec. A4.1.2), o/w emulsions can sometimes be stabilised by using a w/o emulsifier in conjunction with the o/w emulsifier due to complex formation[38]. However, bridging flocculation can occur with a two-component emulsifier mixture, whereas this destabilisation mechanism may be absent when only either pure emulsifier is used[23].

A4.1.2. SURFACTANT TYPE[1, 3, 32, 37 - 43]

Emulsion stability depends on the structure of the surfactant that is used and the ionic category to which it belongs. The ionic nature of the hydrophilic "head" group(s) enables categorisation into four types of surfactant, viz. anionic, non-ionic, cationic and zwitterionic emulsifiers.

Suitable non-ionic surfactants are often less sensitive than ionic surfactants to destabilising variables because:

- the head group(s) are not sufficiently ionic to be bound tightly by electrolytes[39].
- if they have long hydrocarbon chains, they can form entropically-stabilised[32] gel-like emulsions due to stratification[40], or overlapping and interpenetration, of the chains[38]. The gel network retards creaming and is a primary (steric) barrier to coagulation. Emulsions that are stabilised by simple, low-molecular weight non-ionic emulsifiers are characterised by slow coalescence rates because of steric hindrance by the bulky non-ionic chains at the interface[3, 32]. This steric repulsion can considerably outweigh and assist double layer repulsion and over-rule van der Waals attractive forces[37].

The stability a given surfactant will confer upon an o/w emulsion can be estimated from its hydrophile-lipophile balance (HLB)[1, 41, 42]. The HLB is related to the overall polarity and solubility of the surfactant. Higher solubility of the surfactant in water implies a higher HLB value. The HLB ratio normally ranges between 0 - 40. O/w emulsions require an HLB between 8 - 18, but lower values between 3 - 6 are optimal for w/o emulsions[1]. Surfactants with low HLB values will therefore break or invert o/w emulsions[1], unless complex formation can occur[38]. A surfactant combination with the optimal HLB for a given emulsion will form the smallest droplets and attain the highest viscosity, both of which are stabilising effects[43].

A4.1.3. SURFACTANT CONCENTRATION[1 - 3, 6, 7, 14, 20, 22, 27, 28, 31, 34, 35, 37, 40, 43 - 48]

A surfactant with an HLB that is too low for an o/w emulsion can break the emulsion. The extent to which it does so will increase as its concentration is raised[1].

There are two concentration regimes that are separated by an optimal value in which emulsifiers, with suitable HLB values for an o/w emulsion, either stabilise or destabilise the emulsion[7, 44, 45]. The two scenarios are discussed below.

A4.1.3.1. SUB-OPTIMAL SURFACTANT CONCENTRATIONS

Below the optimal concentration, emulsions are progressively stabilised by adding surfactant because the interfacial tension between the phases is reduced and the interfacial film is strengthened[7]. The concentration corresponding to the maximum film drainage time corresponds to the critical micelle concentration (c.m.c.[c])[20]. The drainage time increases with an increase in surfactant concentration partly because of an increase in the bulk viscosity of the surfactant-soluble phase[14] and a lengthening of the thinning stage. Evidence for this trend includes the following:

- Droplet lifetimes at a planar o/w interface[2, 14, 46]

Droplet lifetimes at planar o/w interfaces were measured to increase roughly with the cube root of the surfactant concentration[46]. However, over a wider range, the coalescence time increases with increasing surfactant concentration, reaches a maximum value and then decreases[14]. The stability increases up to a maximum because of an increase in the bulk viscosity of the surfactant-soluble phase and a lengthening of the thinning stages. At low surfactant concentrations, the amplitude of the surface waves, which causes the thin film to rupture, is large. Low surfactant concentrations thus result in film rupture at a large critical film thickness. As the surfactant concentration increases, the waves are damped, causing the films to drain to lower thicknesses before rupture occurs. At the surfactant c.m.c, the surface film is completely saturated with the surfactant and the elasticity is at a maximum[14].

- Increase in droplet size on storage[3]

Up to the optimal concentration, mean droplet sizes in emulsions increase less as a

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[c] The c.m.c. is the threshold concentration above which surfactant exists in the surfactant-soluble phase primarily as micelles and not as free units.

function of time as the surfactant concentration is increased[3].

- Coalescence pressure[3]

In creamed- or high-internal phase emulsions, the minimum centrifugal pressure that is required to enforce coalescence of the close-packed droplets increases with higher surfactant concentrations[3].

- Viscosity[14, 22, 34, 37, 40, 43, 47]

The viscosity of emulsions (Sec. A4.6) increases, for a fixed shear time, with increasing surfactant concentration up to the optimal concentration[37, 43, 47]. The stabilising increase in viscosity is partially due to immobilisation of the more surfactant-soluble continuous phase by the formation of a micellar or gel network[37, 47]. At high surfactant concentrations below the optimum concentration, mesomorphic liquid crystals may be formed by the surfactant. These have very high viscosities and inhibit the film drainage rate[40]. Surfactants strongly influence the tangential mobility of the liquid interfaces[34]. An increase in the interfacial viscosity number results in an increase in interfacial mobility and hence higher film drainage times[14]. Film thinning rates are fastest when the interfaces are fully mobile and slowest when the interfaces are immobile[22].

- Increased refinement[3, 27, 35, 40, 43]

A stabilisation arises from smaller droplet sizes, which have an associated larger electroviscous drag[3, 27, 40]. For an equivalent amount of shear using the same emulsifier, a model predicts that a higher emulsifier concentration will give a smaller average droplet diameter and distribution width[35, 40, 43]. As the emulsifier concentration is increased, the most frequently occurring droplet diameter decreases, but assumes a limiting value that cannot be reduced by further increases in emulsifier concentration or homogenisation period[35]. It can be shown mathematically that all droplet size distribution parameters depend on the emulsifier concentration[35].

- Stability at high ionic strengths[31]

Addition of a sufficient amount of soluble soap to an emulsion can prevent coalescence, even at high ionic strengths[31].

A4.1.3.2. ABOVE OPTIMAL SURFACTANT CONCENTRATIONS

Above the optimal concentration, addition of surfactant can destabilise the emulsion by:

- solubilising and transporting small oil drops, by diffusion in micelles, into the larger drops. A surfactant micelle can encapsulate oil molecules located at the surface of a smaller oil droplet. The smaller droplet decreases in size as the surfactant micelles transfer the oil molecules in small quantities to larger droplets. This process is called surfactant-aided Ostwald ripening[48]. Ostwald ripening in the absence of surfactant requires droplet sizes in the microemulsion regime. This is so because only very small droplets have significantly high Laplace pressures to dissolve in the aqueous phase. However, when surfactant is present, the oil is transferred to larger droplets not by dissolution in the aqueous phase but by micellisation by surfactants. Solubilisation of oil molecules at the surface of a droplet by micellisation can occur for relatively large droplets because the mechanism of transfer to larger droplets differs from that of normal Ostwald ripening. In surfactant-assisted Ostwald ripening, the diffusing oil molecules are protected from the lipophobic aqueous phase due to the disguise offered by the surfactant micelle.

- inversion[1, 28].

- increasing the flocculation or coalescence rates[6, 7, 45].

A4.1.4. <u>PARTITIONING OF SURFACTANT BETWEEN PHASES</u>[1, 14, 18, 22, 49]

The film-thinning rate during coalescence depends upon selective partitioning of surfactant between the two phases[14] and upon surfactant adsorption kinetics.

- Selective solubility

Emulsions in which the surfactant is soluble in the film phase are more stable than those in which it is soluble in the drop phase[14, 18]. This is due to Bancroft's rule[49], which states that the phase of greater surfactant concentration tends to be the continuous phase. Therefore, in o/w emulsions, surfactants that dissolve in the aqueous phase confer greater stability than those that are partitioned in the oil drop phase. Low HLB values imply high lipophilicity, i.e. greater solubility in the oil phase and vice versa[1]. Surfactants with low HLB's (< 6) are therefore expected to form less-stable o/w emulsions than those with higher HLB values (8 - 18).

- Adsorption kinetics

If the bulk concentration of surfactant is high, but its adsorption onto the interface is relatively weak, faster coalescence occurs[14]. The amount of surfactant that is present at the interface depends on the rate of diffusion or emulsification-induced transfer from the bulk to the interface, which depends on the viscosity of the phase that contains the bulk of surfactant. The amount of surfactant in the interfacial region decreases with time[22]. As the amount of surfactant at the interface is reduced, the mobility of the interface decreases, thereby increasing the rate of film thinning.

A4.2. DENSITY DIFFERENCE BETWEEN AQUEOUS & OIL PHASES[1, 5-8, 33, 50]

Eq. 1 shows that more stable emulsions are formed when the density differences between the aqueous and oil phases are minimised. When the density between the phases increases, gravity causes the less dense phase to rise to the surface of the emulsion by the decay mechanism known as creaming. The origins and effects of creaming were explained in Sec. A2.2.

A4.3. DROPLET SIZE[2, 4, 32, 46, 51 - 60, 62]

Generally, more stable emulsions are formed if the droplets are smaller, since a longer period is required for creaming and complete breakage into separate phases to occur. Droplet size affects the creaming, coalescence and flocculation rates:

- The average mass creaming rate is proportional to the fifth power of the droplet radius (Eq. 1). Smaller droplets, which have a larger surface area-to-volume ratio, exert more electroviscous drag than larger droplets. This results in a higher emulsion viscosity that stabilises the emulsion.

- Lifetimes of thin films, which determine the coalescence rate, are dependent on the film radius[51]. However, although mathematical treatments[52] suggest that smaller droplets are more stable than larger ones (Sec. A2.4), droplet lifetimes from interface coalescence studies have not revealed a consistent trend[2, 46, 52 - 60]. Larger droplets have a smaller surface area-to-volume ratio, which is thermodynamically more favourable. Conversely, the film-thinning rate increases with an increase in the van der Waals attractive forces, which increase with larger droplet sizes.

- Electrostatic effects influence large and small droplets differently[61]. Stability against flocculation increases exponentially with increasing particle size[4]. The secondary minimum region for flocculation depends upon attractive and repulsive terms (Eq. 5, 6 and 7), which vary with particle size[32]. The larger the particle size, the larger is the secondary minimum. However, the coagulation rate decreases with increasing initial droplet concentration[13, 31]. This is because for equivalent phase volumes, a larger initial droplet concentration implies a decreased droplet size. A mathematical model predicts that smaller droplets give slower coalescence rates during coagulation[52].

A4.4. DROPLET SIZE DISTRIBUTION[3, 7, 23, 31, 62]

Narrow distributions give more stable emulsions due to a reduction of Ostwald ripening, accelerated coalescence and differential buoyancies during sedimentation-flocculation.

- In o/w emulsions with submicron-size drops and a pure, volatile oil phase, Ostwald ripening occurs particularly with broad distributions, but is reduced by narrow distributions[62]. Since larger droplets are thermodynamically more stable than smaller droplets, they grow at the expense of the latter. Therefore, an emulsion in which the distribution is small tend to be more stable than those in which there is high polydispersity.

- Broad distributions result in an increased flocculation rate[31], which in turn accelerates creaming. Calculations suggest that the flocculation rate may increase by 15 % if the distribution is symmetrical and up to 50 % if assymetrical[31].

- The creaming rate increases if the $n_i r_i^5$ term (polydispersity) is increased (Eq. 1)[7].

A4.5. DROPLET CONCENTRATION (PHASE VOLUME)[13, 31, 37, 52, 63]

Changing the phase volume can affect stability by altering the factors which determine stability[13]:

- For a low internal-phase volume and a rapid coalescence rate, coagulation is determined by the flocculation rate.

- In concentrated emulsions[13], coalescence is the rate-determining step, especially if this rate is decreased by a suitable emulsifier.

- When o/w emulsions are diluted with water, the bulk viscosity (which influences overall stability) can decrease due to a reduction in the viscoelastic drag component of the total viscosity[37]. With non-ionic surfactants, a high viscosity indicates the development of a gel network in the continuous phase which can act as a primary barrier to coagulation[37]. A similar gel-like structure has been proposed for o/w emulsions stabilised by polyelectrolytes[63]. Dilution of this gel reduces the effectiveness of the primary barrier. Creaming can also occur more easily if the gel is diluted.

A4.6. VISCOSITY[11, 18, 22, 23, 37, 43, 46, 47, 51 - 53, 64 - 69]

Viscosity influences stability by rendering the droplets more or less mobile and subject to flocculation, creaming or coalescence.

The viscosities of the external phase[11, 37, 51, 52], the internal phase[18, 52], the interface[22, 46, 53, 64 - 67] and the bulk emulsion[37, 43, 68] all influence the stability of o/w emulsions.

A4.6.1. BULK VISCOSITY[37, 43, 47]

High bulk viscosities reduce kinetic causes of instability such as creaming and flocculation by preventing free motion of the droplets[43].

Bulk viscosity, which often correlates with overall emulsion stability[43], depends on the viscosity of the hydrophobic and hydrophilic phases, the nature of the oil phase[47], the phase ratio[37], the amount and type of surfactant[37, 43] and the droplet size.

A4.6.2. EXTERNAL (HYDROPHILIC) PHASE VISCOSITY[6, 11, 37, 51, 52,.64]

Higher external phase viscosities stabilise an emulsion by reducing flocculation[11, 37, 51], coalescence[52, 64] and creaming[6] (Eq. 1). In o/w emulsions, the hydrophilic external-phase viscosity depends on temperature and the amount and type of surfactant.

A4.6.3. INTERNAL (HYDROPHOBIC) PHASE VISCOSITY[18, 52, 69]

An increase in the viscosity of the oil droplets was not observed empirically to influence stability[52]. However, models[18] show that a higher drop-phase viscosity stabilises an emulsion towards coalescence by decreasing the film drainage rate.

A4.6.4. INTERFACIAL VISCOSITY[6, 18, 22, 46, 53, 64 - 67]

Decreased interfacial viscosity has been correlated with increased coalescence rates of thin liquid films and therefore decreased emulsion stability[6, 18, 22, 46, 53, 64 - 67]. A transient fluctuation in interfacial viscosity can also lead to instability[46].

A4.7. STERIC STABILISERS[2, 3, 23, 28, 39, 40, 46]

Certain solid particles, non-ionic surfactants, polymers and macromolecules constitute an important class of emulsifying agents. They function by a mechanism called steric stabilisation. If their properties are unsuitable, they may also destabilise emulsions.

A4.7.1. COLLOIDAL SOLIDS[2, 28]

Insoluble colloidal particles that are partially wetted by both the aqueous and oil phases can stabilise emulsions by adsorbing at the interface to form a mechanically-rigid barrier which modifies the rheological properties at the interface[28]. This barrier retards the rupture of the thin liquid film in the coalescence step. Coalescence can occur if the solids are displaced along the interface.

The effectiveness of suitable solid particles in stabilising an emulsion depends on the following:

- Size

The particles must be much smaller than the droplets in order to be properly located around the interface. Emulsion stability increases as the solid particle sizes are decreased.

- Charge and electrostatic interactions

Charged colloidal solids may cause electrostatic repulsion between droplets, which will reduce coagulation. If the charge is unsuitable, the solid can destabilise the emulsion.

- Concentration

Emulsion stability increases as the particle concentration increases[28]. Viscoelasticity of the interfacial film is attained if the concentration of solids is sufficiently high[28].

- Surface tension ("wettability")

Water-wettable particles stabilise o/w emulsions whilst oil-wettable particles stabilise w/o emulsions[28]. Adsorbing solids can cause inversion of an o/w emulsion if they are preferentially oil-wettable.

A4.7.2. POLYMERS & MACROMOLECULES[3, 23, 40, 46]

Certain macromolecules (e.g. proteins, carbohydrates) and polymers can wrap around emulsion droplets to form mechanically-rigid or viscoelastic barriers to coalescence. Adsorbing macromolecules may, however, destabilise emulsions by attachment to more than one droplet at a time (bridging flocculation)[23]. Destabilisation by non-adsorbing polymers may also be induced by depletion flocculation[23].

Proteins stabilise emulsions optimally when they are close to the pH at which they are precipitated, e.g. gelatin at its isoelectric point[46]. They cause a large increase in the interfacial viscosity which inhibits film drainage[40]. The viscoelasticity and resultant dampened surface fluctuations accounts for their efficacy.

Polymers (e.g. polyvinyl alcohol and polyvinyl acetate) stabilise emulsions, especially in combination with surfactants, due to the formation of polymer-surfactant complexes[3]. Ionic surfactants can associate with p.v.a. to form polyelectrolyte-like complexes at the interface.

A4.8. ELECTROLYTES & IONIC STRENGTH[6, 13, 28, 30-32, 70-72]

A4.8.1. TOTAL IONIC STRENGTH[28, 30-32]

The DLVO theory (Sec. A3) explained the electrostatic origins of interdroplet repulsion in terms of the electrical double layer. Equations 7 and 8 showed that double layers, which push the droplets apart and prevent flocculation, are compressed as electrolyte is added. The repulsive force and decrease in electrical potential between droplets is therefore reduced as the ionic strength is increased[70]. This leads to faster coagulation. The flocculation and coagulation rate constants usually increase with increased ionic strength[31, 32]. However, restabilisation can occur after a certain degree of coagulation has ensued (Sec. A5.3). The concentration at which coagulation becomes significant is called the critical coagulation concentration (c.c.c.). The increase in the coalescence rate with increased electrolyte concentration is due to neutralisation of the surface charge.

The magnitude and sign of the charge (z) of an electrolyte has a profound effect on coagulation (Eq. 8). Since the inverse length (κ) of the double layer is proportional to $(\sum c_i z_i^2)^{1/2}$, trivalent droplet counterions flocculate emulsions more than divalent ions and much more than monovalent ions[32, 70]. Empirically, this order (lyotropic series) is observed as the Schulze-Hardy rule[6, 31, 32, 70]. This rule states that the concentration of an ideal electrolyte that is needed to coagulate an emulsion depends to the reciprocal sixth power on the charge number of the droplet counterions, but not on the specific nature of the counterions and only moderately on the nature of the emulsion.

Droplet surface charge is often determined by the charge of the surfactant head group(s) if the surfactant is ionic. If the droplet has a net negative charge, cationic droplet counterions will induce flocculation, whereas anionic counterions will flocculate positively-charged droplets. The destabilisation occurs particularly with higher valencies of the counterions.

A4.8.2. CO-ORDINATING IONS[31, 71]

Co-ordination of certain ions to oppositely-charged head groups of ionic surfactants can precipitate (inactivate) the surfactant and thereby destabilise the emulsion. The precipitate may, however, act as a steric stabiliser against coalescence if its wettability is suitable. For example, for certain anionic surfactants that are precipitated by trace amounts of some cations, the solid salt which is formed increases the rigidity of the interfacial film and retards the coalescence rate[31].

Inversion may occur if certain ions convert the surfactant into a form which favours the inverse emulsion. For example, solid particles of calcium alkanoates favour water-in-oil emulsions, whereas alkanoates of Group I metals favour oil-in-water emulsions[71].

A4.8.3. SURFACTANT COUNTERION[31, 70, 72]

The counterion (gegenion) of an ionic surfactant in the double layer influences the interfacial surface area that is occupied by the surfactant head group. The surface tension and droplet size, which influence stability, are thus affected by the gegenion. This occurs because gegenions have characteristic hydrated radii[72].

A4.9. TEMPERATURE[6, 7, 26, 27, 46, 53, 73]

An increase in temperature decreases the viscosity of the external phase and affects the HLB of emulsifiers. Reduced viscosity can result in increased sedimentation (Eq. 1), flocculation, sedimentation-flocculation[73] and coalescence[46, 53], whilst an altered HLB will invert the emulsion beyond its phase-inversion temperature[6, 26, 27].

The coalescence time of droplets decreases when the temperature is increased[46, 53] because of increased molecular motion at the interface. This results in a perturbation of the thin liquid film and the creation of a hole, which leads to film rupture (Sec. A2.3).

Storage at elevated temperatures (~ 70°C), or subjecting the thin films of the emulsion to perturbations by temperature cycling, breaks many emulsions[7] and is used to predict long-term emulsion stability.

A4.10. pH OF AQUEOUS PHASE[28, 46, 75, 76]

The pH can influence emulsion stability by affecting the stability and HLB of surfactants, the droplet surface charge and the wettability or charge of steric stabilisers.

- Emulsions which contain non-ionic surfactants that are not pH-labile are less affected by pH than those which are prepared from protonable ionic surfactants[75]. The stability of o/w emulsions that contain suitable anionic surfactants are affected at lower pH regimes by protonation of the head group[76]. Protonation of the anionic head group lowers the emulsifier's HLB, which may cause stabilisation or inversion, depending on the required[1] HLB for the emulsion. Non-ionic surfactants which have pH-labile functional groups (e.g. esters) may be hydrolysed at pH extremes.

- The droplet surface charge may be affected by pH changes. This can alter the flocculation and creaming rates.

- An altered pH may change the wettability of solid stabilisers, which can result in inversion[28] or enhanced stabilisation. Macromolecular steric stabilisers such as proteins function optimally at their isoelectric point, which corresponds to an associated pH[46].

A4.11. TYPE OF HYDROPHOBIC PHASE[17, 29, 43, 46, 52, 69, 77, 79 - 85]

The hydrophobic phase usually consists of hydrocarbon oils. The vapour pressure, polarity and hydrocarbon chain length of the oil(s), which are related parameters, can affect the stability by influencing the solubility of the oil in the hydrophilic phase. If the droplets are sufficiently small (< 1 μm in diameter), solubility can influence the extent of Ostwald ripening.

A4.11.1 VAPOUR PRESSURE & BOILING POINT[18, 29, 46, 78]

Coalescence times of oil droplets with high vapour pressures are less than those of droplets with lower vapour pressures[46]. If Ostwald ripening is operative, hydrocarbons with lower boiling points (higher vapour pressures) therefore give less stable emulsions than those with higher boiling points[29]. Addition of a small quantity of an oil that has a low vapour pressure to the dispersed phase retards Ostwald ripening by reducing the total vapour pressure (Raoult's law)[78]. A model suggests that low oil-phase diffusivity decreases coalescence rates by decreasing film drainage rates[18].

A4.11.2. POLARITY[17, 52, 80 - 85]

Droplet coalescence times at a planar o/w interface decrease if the polarity of the oil is increased. If Ostwald ripening occurs, polar hydrocarbons will therefore form more stable emulsions than less-polar analogues because the former are more soluble in the hydrophilic phase[52, 80]. Unsaturation, aromaticity or cyclic structures therefore decrease the droplet stability[52] of o/w emulsions and the effect of added electrolyte on instability is greater for more polar oils[17]. Emulsions that are stabilised by hydrocolloids[82 - 85] are less stable with higher oil polarities, unless the oil can undergo a specific interaction with the surfactant to form a complex film at the interface[81].

A4.11.3. HYDROCARBON CHAIN LENGTH[29, 43, 47, 52, 69, 77 - 80]

If Ostwald ripening occurs, droplets that are comprised from longer-chain alkanes are more stable than those made with shorter-chain length alkanes. This is due to Raoult's law[29, 52, 69, 78 - 80] (longer-chain alkanes have smaller vapour pressures). With longer-chain hydrocarbons (e.g. liquid paraffin[d]), Ostwald ripening is inoperative unless it is assisted by surfactant micelles. The instability of emulsions that are prepared from such oils occurs by coalescence[29]. In smaller hydrocarbons (e.g. hexane), instability is due to Ostwald ripening[29]. However, in emulsions comprised of larger droplets, where Ostwald ripening is not a mode of instability, larger hydrocarbons may form less stable emulsions than smaller homologues[52].

Besides having an influence on Ostwald ripening, the oil phase can affect the bulk viscosity[47] (Sec. A4.6.1) and the properties of the interfacial film[52]. Longer-chain alcohols (C_{12} - C_{16}) in the oil phase increase the stability of o/w emulsions by interactions of the head group at the interface[52] or by forming a complex condensed film[29]. Stability also depends on the emulsifier's HLB. This is influenced by the solubility of the surfactant in the oil, which depends on the nature of the oil[43, 77].

A4.12. SHEAR FORCES[23, 35, 40, 43, 86]

The shear forces (shear method, rate and time) which are applied to form an emulsion will influence its formation and subsequent stability. Gentle shear can also break pre-formed emulsions by accelerating the film-thinning stage during coalescence.

Small drops confer greater stability (Sec. A4.3) and size distributions are influenced by the energy input upon emulsification[23]. Geometric mean drop diameters[35] and deviations[86] decrease to equilibrium values with increased impeller rotational speeds, mixing intensity or time.

Higher emulsifier levels reduce droplet sizes much faster than longer homogenisation times[35]. Optimal homogenisation times may be calculated for different emulsifier concentrations[35]. Efficient emulsifiers (in terms of the ease of emulsion formation, but not

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[d] This is the hydrophobic phase that was used in this report.

necessarily the storage stability) can be selected by monitoring changes in droplet size distribution for a set homogenisation time[35].

Knowledge of emulsion stability, as detailed above, has largely been derived from empirical measurements. The prediction of stability by modelling is outlined in the next section (Sec. A5).

A5. MODELLING EMULSION STABILITY[1, 4, 13, 18, 31, 33, 51, 70, 77, 87 - 94]

A5.1. INTRODUCTION

Modelling of emulsion decay depends on the operative type(s) of instability for a given emulsion. For example, there is no creaming or flocculation in close-packed, high internal-phase emulsions. Different models can predict instabilities that arise from creaming, flocculation, sedimentation-flocculation or coalescence, or a combination of these, and some can predict a shift in the rate-determining instability. For example, the coagulation rate is determined by either a rate-limiting flocculation or coalescence rate[13, 31, 51].

Modelling of stability is based on the simple mathematical expressions[87 - 89] of the DLVO theory (Sec. A3), von Smoluchowski[11] and van den Tempel[13, 51, 70] and on a recursive stochastic approach to coalescence[90, 91]. A recursive stochastic process is one in which the same calculation is repeated but with changing numbers such that the results that are obtained become smaller until a limit is reached. This is comparable to a bouncing ball which finally comes to rest. Models that were based upon simple mathematical expressions[28, 77, 92 - 94] could only describe the coalescence of monodisperse distributions and predict the critical aggregation ionic strength, which describes the transition between stability and instability. The Stochastic model[90] accomodates polydisperse emulsions and can determine the extent of coalescence beyond the critical coagulation concentration (Sec. A4.1). An important prediction of the Stochastic model is that emulsions may coalesce to a new distribution which is indefinitely stable, i.e. complete separation of the phases does not always occur.

A5.2. MODELS BASED ON SIMPLE MATHEMATICAL EXPRESSIONS[4, 11, 13, 33, 51, 70]

Von Smoluchowski's treatment for the coagulation of hydrophobic sols[11] can be used to predict the flocculation of emulsions. Van den Tempel extended von Smoluchowski's theory to include the kinetics of coalescence[13, 70]. A recent model has corrected for van den Tempel's overestimated rate of increase in aggregate size by taking an overall balance on all particles in the emulsion instead of a balance on each aggregate[51] and also for the underestimation of the coalescence rate in flocculated aggregates[4]. The contemporary model can predict:

1. the dynamic behaviour of polydispersed emulsions in which Brownian flocculation, sedimentation-flocculation and creaming occur simultaneously[4, 33].
2. a change in the rate-controlling decay mechanism[51].
3. limiting cases, such as negligible creaming or flocculation and varying degrees of electrostatic stabilisation.

However, shortcomings in these models occur because of oversimplifications. There are three main reasons that these derivations are not useful in evaluating emulsion aggregation:

1. The expressions consider only the interaction between identically-sized and -charged particles and assume only weak electrostatic interactions and high interfacial potentials. Approximations that are valid for high surface potentials are difficult to reconcile with the aggregation of low-potential particles.
2. Coalesced droplets may be sufficiently stable to not undergo further coalescence.
3. Aggregation that leads to coalescence does not give rise to a readily-determinable empirical observation.

These shortcomings are overcome in the Stochastic model.

A5.3. THE STOCHASTIC MODEL[90, 91]

The Stochastic model[90, 91] is based upon Smoluchowski's coagulation equation[18]. The model determines the evolution of the droplet distribution by calculating the recursive interactions between pairs of differently-sized and differently-charged droplets. The procedure is outlined below.

The model treats the emulsion as a droplet distribution which is described by a two-dimensional array of particle radius and Stern potential. The value of each array element denotes the number of droplets within a given radius and potential (or channel). A monodisperse emulsion is thus represented by a single nonzero value in this array. The model is primed with values for droplet size and potential distribution, ionic strength and the attractive force based on the Hamaker constant (Sec. A3.2). A common value for the Stern potential is initially assigned to all particles. Providing that the initial number of particles is greater than several thousand, the model is independent of the number of droplets in the discontinuous phase.

Coalescence is simulated by randomly selecting pairs of droplets sequentially from the radius axis, with statistical weighting of the total volume of droplets within each radius interval. The Stern potential for each droplet is chosen randomly, with linear weighting from the potential distribution for the appropriate radius interval. The net energy of interaction of the droplets is determined as a function of separation if no energy barrier is calculated or, if it is less than the thermal energy (kT), the droplets are predicted to coalesce. Upon coalescence, the array is modified to account for removal of the interacting particles and formation of a new droplet. The radius and potential of the larger droplet is calculated assuming conservation of charge and volume. The repetitive simulation is interrupted periodically to inspect the array or terminated when no further coalescence is predicted.

The gross effect predicted by the simulation of coalescence is that the size distribution is shifted to larger droplet sizes with increasing ionic strength and Hamaker constants (i.e. increased attractive forces and less repulsion) and decreasing charge densities (reduced repulsive forces). The effect is greater for small values of interfacial charge density.

A restabilisation of the emulsion, after a certain degree of coalescence has occurred, may be predicted. This prediction is due to an increase in electrostatic repulsion that is caused by increasing electrical potentials which progressively overtake the increase in van der Waals attraction associated with increases in particle volume. For the nth generation of coalesced droplets, the critical aggregation ionic strength (I^{n}_{ca})[e], is given by[94]:

$$I^{n}_{ca}=I_{ca}\cdot 2^{\frac{4[n-1]}{9}} \qquad \text{. . . . . . . Equation 9}$$

Eq. 9 shows that most emulsions (except those with very low interfacial charge density) are expected to restabilise, preventing complete breaking and separation into two phases. The increase in charge density is due to a decrease in surface area-to-volume ratio as one goes to larger spherical particles[94].

In the Master equation[91], a probabilistic analysis derives the daughter size distribution from knowledge about breakage probabilities of individual droplets. The equation is valid for binary or higher-order breakage and any combination thereof.

The evidence that is presented in Sec. A4 on the factors that influence the stability of emulsions is largely empirical. Modelling of stability (Sec. A5) must also be validated experimentally. Therefore, Sec. A6 therefore outlines how to assess emulsion stability in practice.

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[e] This is related to the c.c.c. (Sec. A4.8.1).

A6. MEASUREMENT OF EMULSION MORPHOLOGY & STABILITY

A6.1. OVERVIEW OF TECHNIQUES[1, 7]

In order to assess emulsion stability, it is first necessary to establish the morphology. Four methods are used to differentiate between o/w and w/o emulsions[1, 37]:

1. Conductometry. O/w emulsions conduct more electrical current than w/o emulsions, in which the continuous oil phase has low conductivity.

2. Staining. If the droplets are coloured upon microscopic examination, the phase to which the dye was added, prior to emulsion formation, is the internal phase and vice versa.

3. Dilution. If pure external phase is added, the emulsion is diluted but remains homogeneous. If internal phase is added, it forms a separate layer that will not mix into the emulsion without agitation.

4. Direction of sedimentation. The relative phase densities determine the direction of sedimentation of the internal phase (Eq. 1). The external phase separates as a clear layer, whilst the droplets that comprise the internal phase form a close-packed emulsion. If the external phase is more dense than the internal phase, it will separate below a creamed, high internal-phase emulsion.

Once the morphology has been established, the most rapid decay mechanisms must be identified. Methods must then be chosen to assess the decay mechanisms. It is sometimes necessary to use the methods to identify the decay mechanisms if these are not readily apparent. In order to assess overall stability it is best to use two or more techniques. This is so since instability may be influenced by more than one decay mechanism, each of which may be revealed by a different method. The methods that are chosen will depend on the type of instabilities that are present. The time that is required for instabilities to manifest themselves is often experimentally inconvenient. Accelerated ageing tests (identified by * in the list below) are then used to hasten the decay. Such tests are often used prior to, and in conjunction with, another method.

Methods that are used for estimating emulsion stability, as a function of time, are listed below.

1. Creaming or flocculation rate[7, 28, 37, 43, 45].

2. Droplet size distribution changes using microgranulometric techniques: low-angle laser diffraction, Coulter® instruments[37], photomicroscopy[32, 95], microscopy coupled to data image analysis[29] or photography of the bulk emulsion.

3. Decrease in the total number of droplets[31, 32, 43, 64] using turbidimetry, microscopy[31, 32, 40, 51] or Coulter® instruments[43, 64].

4. Droplet coalescence at a planar oil-water interface[2, 17, 28, 46, 52, 54 - 60, 96].

5. Turbidimetry[31, 43, 44, 97, 98].

6. Viscometry[7, 37, 43].

7. Electrical properties: zeta potentials[32, 37, 95, 99], dielectric constant, conductance[27, 50] conductivity[7], capacitance and resistance.

8. Centrifugation* (accelerated coalescence)[1, 3].

9. Densitometry[37, 45].

10. Freeze-thaw temperature cycling[*7] or storage at elevated temperatures[*7].

11. Pulsed nuclear magnetic resonance[7].

12. Differential scanning calorimetry and differential thermal analysis[7].

13. Mechanical agitation[*1].

14. Ultrasound[23].

The emulsions that were studied in this report were investigated by measuring droplet size distribution changes, coalescence times at a planar o/w interface, creaming rates and by photography. The application of these methods in interpreting emulsion stability is therefore outlined below.

A6.2. DROPLET SIZE DISTRIBUTION CHANGES

Measurements of changes in the total number of droplets, or of the mean droplet volume and distribution of sizes with time, are the only fundamental means of evaluating emulsion decay. The best parameters to use in order to characterise the size distribution are the volume mean diameter (D[4,3]) and the distribution width (span). The stability parameter d_t/d_0 is the ratio of the average droplet diameter after a storage time t (d_t) to the average diameter immediately after preparation (d_0)[29]. This stability parameter is precarious for estimating stability unless it is accompanied by meaningful shifts in the corresponding spans[61].

An increase in d_t/d_0 correlates with a decrease in the number of droplets per unit volume. Measuring the latter is a much more sensitive method, since a 10 % decrease in the interfacial area is accompanied by a 27 % decrease in the number of particles[13]. For measuring the total number of droplets per unit volume, Coulter® counters are ideal. However, there are practical complications in measuring the number of particles per unit volume in emulsions by this technique. These include the adherence of oil droplets to the conductance orifice walls, erroneously-low particle concentrations due to flocculation of droplets and the necessity of diluting the droplets in saline media, thereby changing the ionic strength. For these reasons, the Coulter® technique was not employed and less-sensitive low-angle laser diffraction was chosen.

A6.3. DROPLET COALESCENCE AT A PLANAR INTERFACE[2, 17, 18, 28, 46, 48, 52, 54 - 60, 96, 100]

The experimental configuration for this method is detailed in Sec. C3.2. The earliest models of emulsion stability were concerned with the coalescence of single droplets at a planar liquid-liquid interface[18]. The rate of thin-film drainage and rupture in the coalescence step (Sec. A2.4) may be approximated by measuring the time required for half of a sampling population of equal-sized drops to coalesce at a planar oil-water interface. This method has contributed towards an understanding of variables such as droplet size[2, 46, 52, 54 - 60], temperature[46], surfactant[2, 46, 48], electrolyte[17] and the prediction of emulsion stability[2, 46, 52, 100 - 102]. It is only an approximation of coalescence in real emulsions because in this method:

1. droplets larger than those found in most emulsions must be used for practical reasons.
2. surfactant concentrations that are used are normally much less than in emulsions.
3. the assumption of a flat interface only approximates film rupture of spherical droplets.

Consequently, emulsion stability does not necessarily correlate with the method[52, 100]. However, it is useful in interpreting the dependence of droplet stability against coalescence on the stability-influencing variables that were discussed in Sec. A4.

A6.4. CREAMING RATE[7, 28, 37, 43, 45]

The origins, consequences and measurement of creaming are detailed elsewhere (Sec. A2.2 and C3.3). Faster creaming rates imply greater instability due to coagulation (i.e. a larger effective droplet size) or larger actual droplet diameters. For emulsions in which sedimentaton occurs significantly, creaming rates are useful in demonstrating the effects of any variable which alters the actual droplet size or external phase viscosity (Eq. 1). Examples of this type of variable are the surfactant type and surfactant concentration. Variables that increase the flocculation rate will also cause the droplets to cream more rapidly, since the effective size of a coagulated droplet is larger than the constituent droplet sizes. Consequently, factors which alter the repulsive and attractive forces (i.e. effective droplet size) between droplets may be studied by this method. Examples of such factors include ionic strength and pH.

A6.5. PHOTOGRAPHY

A qualitative assessment of emulsion stability may be obtained from the bulk appearance. Unstable emulsions will exhibit greater phase separation, due to creaming, and/or breaking as a result of droplet coalescence. The extent of these instabilities for a given storage time is a qualitative indication of relative stability. Photographs serve as permanent records of the observations.

SECTION B

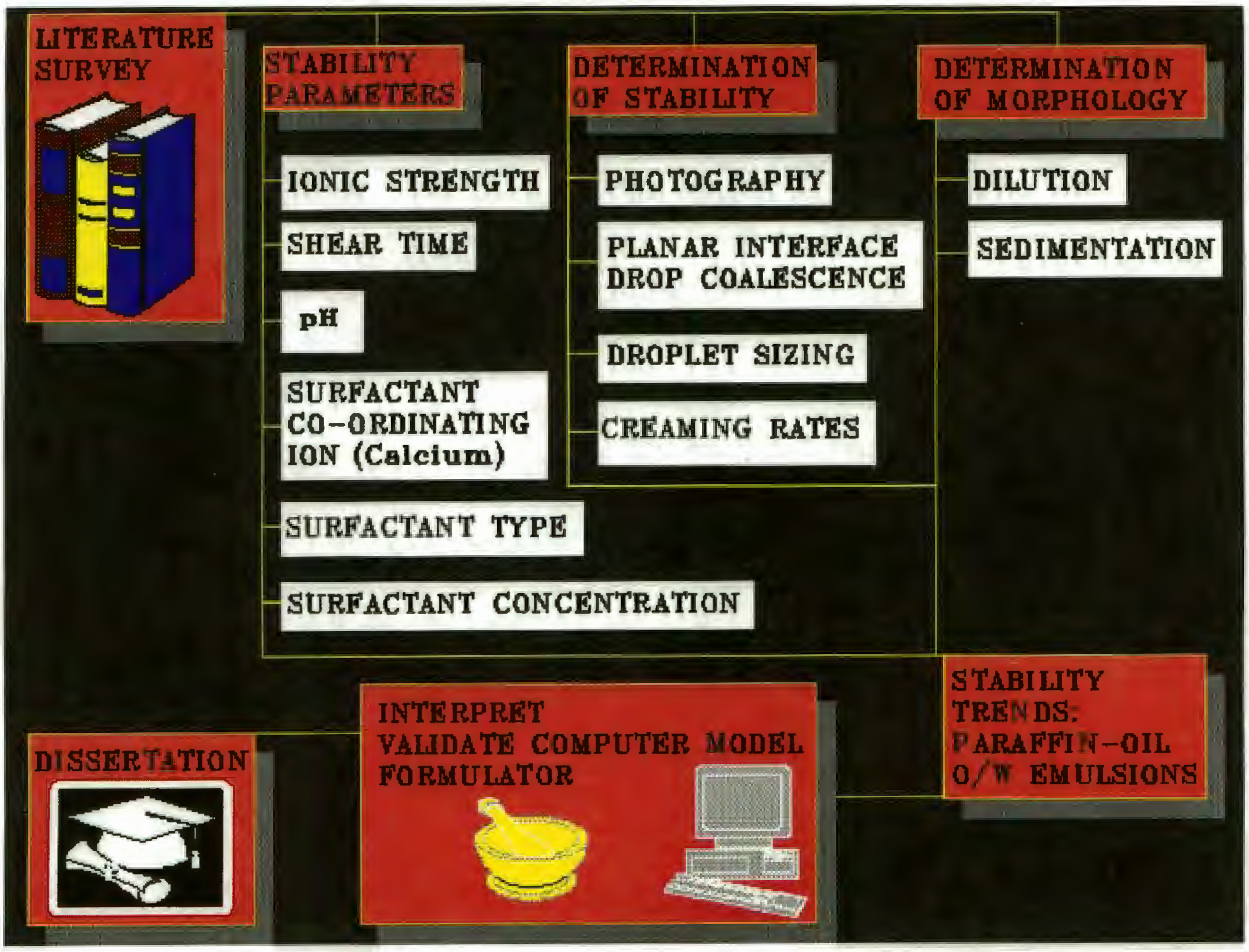
RESEARCH OBJECTIVES

The broader scope of the study was structured to accomplish the following:

1. A greater insight into emulsion chemistry, particularly regarding o/w emulsion stability as a function of ionic strength, surfactant concentration and type, shear time (droplet distribution), pH and the presence of surfactant co-ordinating ions such as calcium(II).
2. An ability to formulate optimally-stable o/w emulsions, or to destabilise such emulsions by manipulation of the practical and theoretical principles of emulsion formation and stability.
3. The possibility of validating a stochastic computer model of stability in future work from the experimentally determined stability trends that result from this study.

The approach to achieve these objectives is illustrated schematically by the flow diagram (p. 42). The strategy was as follows:

1. Conduct a literature survey to establish the variables that affect stability and how the stability is measured.
2. Define both the o/w emulsion under investigation and the selected parameters that may influence its stability.
3. Develop suitable methods for establishing the morphology, kinetic- and thermodynamic stability.
4. Experimentally evaluate the stability trends.
5. Interpret the trends in terms of theoretical and experimental knowledge that was acquired from the literature survey and laboratory evaluations.
6. Conclude the principles for formulating a stable emulsion and evaluating its stability.


LITERATURE SURVEY
STABILITY PARAMETERS
IONIC STRENGTH
SHEAR TIME
pH
SURFACTANT CO-ORDINATING ION (Calcium)
SURFACTANT TYPE
SURFACTANT CONCENTRATION
DETERMINATION OF STABILITY
PHOTOGRAPHY
PLANAR INTERFACE DROP COALESCENCE
DROPLET SIZING
CREAMING RATES
DETERMINATION OF MORPHOLOGY
DILUTION
SEDIMENTATION
STABILITY TRENDS: PARAFFIN-OIL O/W EMULSIONS
INTERPRET
VALIDATE COMPUTER MODEL
FORMULATOR
DISSERTATION

SECTION C

EXPERIMENTAL

C1. REAGENTS

Chemically-pure liquid paraffin (0.84 $g.ml^{-1}$) was obtained from Holpro Analytics. Saarchem supplied sodium dodecyl sulphate (> 98 % pure), sodium chloride (> 99.5 % pure), calcium chloride dihydrate (> 99 % pure) and h.p.l.c.-grade n-heptane (0.69 $g.ml^{-1}$, > 99.8 % pure). Sigma supplied sorbitan sesquioleate, sodium laurate (sodium dodecanoate, > 99 % pure) and cetylpyridinium (1-hexadecylpyridinium) chloride monohydrate (purity unspecified). The sorbitan sesquioleate had a fatty acid composition of ca. 70 % oleic acid (C18:1). The balance was primarily palmitic acid (C16:0), stearic acid (C18:0) and linoleic acid (C18:2). The surfactants and reagents were not further purified.

The emulsions were prepared from deionised, glass-distilled water which had a conductivity less than $0.5\times10^{-6}\ \Omega^{-1}\ cm^{-1}$. Glassware for the preparation and storage of emulsions was thoroughly cleaned with commercial detergent, then rinsed repeatedly with running tap water followed by deionised, distilled water. Ionic strengths were calculated by assuming ideality of electrolytes ($I = \frac{1}{2}\Sigma c_i z_i^2$) and neglecting surfactant ions and their counterions. The pH of aqueous phases was adjusted with aqueous sodium hydroxide or hydrochloric acid prior to final dilution of that phase, such that the ionic strength, surfactant concentration, etc. were as indicated.

C2. EMULSION PREPARATION

Volumetric phase ratios of paraffin oil (or heptane) and water were 50 %. The emulsions were prepared by layering 6 ml of the oil phase onto 6 ml of the aqueous phase in cylindrical 20 ml borosilicate glass bottles (internal diameter = 25 mm) and shearing at ca. 6200 r.p.m. using a flat metal impeller (diameter = 18 mm; width = 5 mm) that was attached via a metal shaft to a Moulinex Turbomix blender. The shear rate was optimised such that adequate emulsification was achieved, but that the formation of foams was minimised or eliminated. This was accomplished by connecting the blender to the mains via a rheostat and reducing the shear rate to the optimum. No compensation was made for any drift in the electric current.

Loss of emulsion, due to vortex formation or splashing, was avoided by using screw-on plastic lids that had a hole for the impeller shaft. The blender was modified to screw directly onto the lids. The quoted impeller shear rate was measured in an air medium by using a revolution counter which functioned on the principle of a reflected laser beam coupled to a timer. It was assumed that any reduction in shear rate due to the (low) viscosity of the emulsions would be virtually identical for all samples.

Except for experiments that investigated the effects of shear time on stability, a standard shear time of 60 seconds was used. Similarly, 1 % m/v of surfactant was used as the standard concentration except for experiments that tested the effects of surfactant concentration on stability. The concentration refers to the percentage of surfactant (m/v) in the phase into which it was dissolved. For cetylpyridinium chloride monohydrate, the concentration refers to the cetylpyridinium chloride component of the hydrated surfactant. The surfactants were dissolved in the aqueous phase prior to emulsification, except sorbitan sesquioleate, which was dissolved in the paraffin.

For studies of the effect of calcium(II) on stability, 1 ml of aqueous calcium chloride, which contained the required amount of Ca^{+2}, was rapidly added to 11 ml of emulsion (comprised from 5 ml aqueous phase and 6 ml oil phase) which had been blended for 40 seconds. The interruption of mixing during addition of the Ca^{+2} solution was minimised. The emulsions were then blended for another 20 seconds so that the total mixing time was the standard 60 seconds.

C3. STABILITY EVALUATIONS

C3.1. DROPLET SIZING

Droplet size distributions were determined in duplicate or triplicate using a Malvern® 2600 B0 Series low-angle laser diffractometer. The lens had a focal length of either 63 mm or 100 mm, depending on the size of the droplets. In most experiments, a 100 mm lens was used.

This lens measures between 1.9 - 181 µm. The path length of the quartz sample cell was 14.3 mm. An aligned helium-neon laser beam (2 mW, 633 nm) was used. The optical path was cleaned before each measurement such that the background reading of each detector channel was less than 30. For this purpose, filtered (dust-free > 4 µm) deionised water was used in the sample cell.

Except for preliminary experiments, where the Boltzmann distribution of droplet sizes in the creamed layer was revealed, the emulsion bottles were gently inverted several times prior to sampling with a clean Pasteur pipette. The narrow pipette tip was removed so that the minimum diameter of the glass capillary greatly exceeded that of the measured droplet diameters. Aliquots of the homogenised samples were rapidly transferred to the sample cell via the pipette. The tip of the pipette was protruded half-way into the total depth of magnetically-stirred water in the cell. Sufficient sample was added to the cell to obtain an obscuration between 0.1 - 0.5, thereby avoiding low signal-to-noise ratios or multiple scattering. The cell was always located within the focal length of the lens. Care was exercised to ensure that the stirrer bar did not adhere to the walls of the cell during stirring, during which oil drops were trapped between the stirrer bar and the cell. If this occurs, it could lead to preferential creaming of the larger droplets, which could result in erroneously-low droplet sizes and spans[33]. Between measurements, the cell, windows and stirrer were therefore cleaned with ethanol and detergent, rinsed thoroughly with distilled water and were dried.

A Gallenkamp centrifuge was used at maximum speed for experiments that investigated accelerated ageing by centrifugation. The magnitude of the centrifugal force ($\omega^2 r$)[1] was not determined. After centrifugation of 12 ml of each emulsion for the stated time, the centrifuge tube and contents were gently inverted several times. Thereafter, an aliquot was sampled by laser diffractometry.

In order to calculate scattering matrices, relative refractive indices were derived by measuring the refractive indices (${}^{D}_{20}n$) of each oil and aqueous phase that were used with an Abbe refractometer. These appear in the Appendix (Sec. G1). However, the droplet sizes that are quoted were obtained from the standard particle-in-liquid scattering matrix presentation and were not corrected for the actual refractive index ratios in the emulsions. The correction was not made for three reasons:

1. Results obtained using n-heptane in w/o emulsions showed that, at our relative refractive indices, these corrections were unnecessary (Appendix G1).
2. In the distribution frequency histograms, no significant Fraunhofer "ghost peaks" were seen.
3. The droplets were much larger than the laser wavelength (633 nm).

C3.2. PLANAR INTERFACE DROPLET COALESCENCE

The apparatus that was used for these experiments (Fig. 1) was originally described by Cockbain and McRoberts[2]. The internal bulb in Fig. 1 contains the upper oil- and lower water phases. At the base was a rubber septum through which a microsyringe needle, which contained paraffin oil, penetrated into the aqueous phase. The inner bulb was protected from

Fig. 1: thermostatted cell for measuring coalescence times of oil droplets at a planar oil-water interface.

dust by a loosely-fitted glass stopper that was located above the oil phase. This bulb was jacketed by an outer bulb. Water was circulated between the bulbs via a water bath which was maintained at 25°C. The water outlet nozzle faces the observer at the oil-air interface in Fig.1.

The inner bulb was cleaned before each experiment by rinsing repeatedly with Teepol® detergent and water, followed by soaking with chromic acid cleaning mixture. It was then rinsed with distilled water more than ten times to remove traces of adsorbed Cr^{+3}, which can destabilise droplets (the Schulze-Hardy rule). The bulb was rinsed twice with the appropriate surfactant solution and was filled with 20 ml of that solution. A clean oil-water interface was formed by layering 20 ml of paraffin oil onto the aqueous phase and by sucking off a part of the dirt-contaminated interface with a pipette. The interface was equilibrated for 1 hour. The o/w interface was curved concave downwards and the interfacial diameter was 6 cm.

A 10 μl Hamilton microsyringe and needle (internal diameter = 22S gauge, point style 3[f]) were purged repeatedly with paraffin oil prior to each experiment by attachment of the syringe neck to a vacuum pump via rubber tubing. The syringe was then filled with paraffin. Drops (2 μl) were formed at the tip of the needle, which was located 1.5 cm below the oil-water interface. Each droplet was allowed to age for 60 seconds on the tip and then was detached by a gentle tap. The time between the droplet reaching the interface and its disappearance was recorded as the coalescence time. This was repeated for a number of droplets at each surfactant concentration.

C3.3. CREAMING RATES

12 ml of each emulsion was prepared by the method described in Sec. C2. The moment when emulsification was complete was considered as the onset of creaming (ageing time = o). Just over 10 ml of each emulsion were rapidly transferred into graduated (to 0.1 ml) 10 ml measuring cylinders. Any foam that resulted from the emulsification was removed from the

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[f] Other needle apertures were found to be unsuitable.

surface by a Pasteur pipette. If necessary, the final volume was then adjusted rapidly with un-foamed emulsion up to 10 ml. The position of the interface between the separated aqueous phase and the milky-white emulsion, as a volume on the cylinder, was recorded as a function of time. The time intervals were chosen as 1, 2, 3, 4, 5, 10, 30, 60 and ca. 1440 minutes. The volume that had separated was converted into a volume percentage of the total aqueous phase[43, 103] (5 ml = 100 % separation). The measurements were performed at ambient temperature (15 - 25°C) without thermostating.

C3.4. PHOTOGRAPHY

12 ml of each emulsion was prepared by using the method described in Sec. C2. These emulsions then were stored at ambient temperature (15 - 25°C). When the stability trend for a series of samples was considered visually to be most resolved, they were photographed. The optimal storage time varied, depending on the parameters for each series of emulsions with a given variable.

SECTION D

RESULTS & DISCUSSION

D1. EMULSION TYPE & INSTABILITIES

D1.1. COMPOSITION

The emulsions were defined as 1:1 phase volumes of liquid paraffin[g] and water with increasing pH's, ionic strengths, surfactant[h] or calcium concentrations and droplet sizes. Liquid paraffin is a highly-refined oil that consists of a mixture of medium-chain aliphatic hydrocarbons. The four surfactants that were used had either anionic, cationic and non-ionic head groups (Fig. 2). Sorbitan sesquioleate is a mixed ester comprised on average of 1½ oleate moeities per sorbitol residue. Fig. 2 indicates one pyranoside monoester of sorbitan sesquioleate.

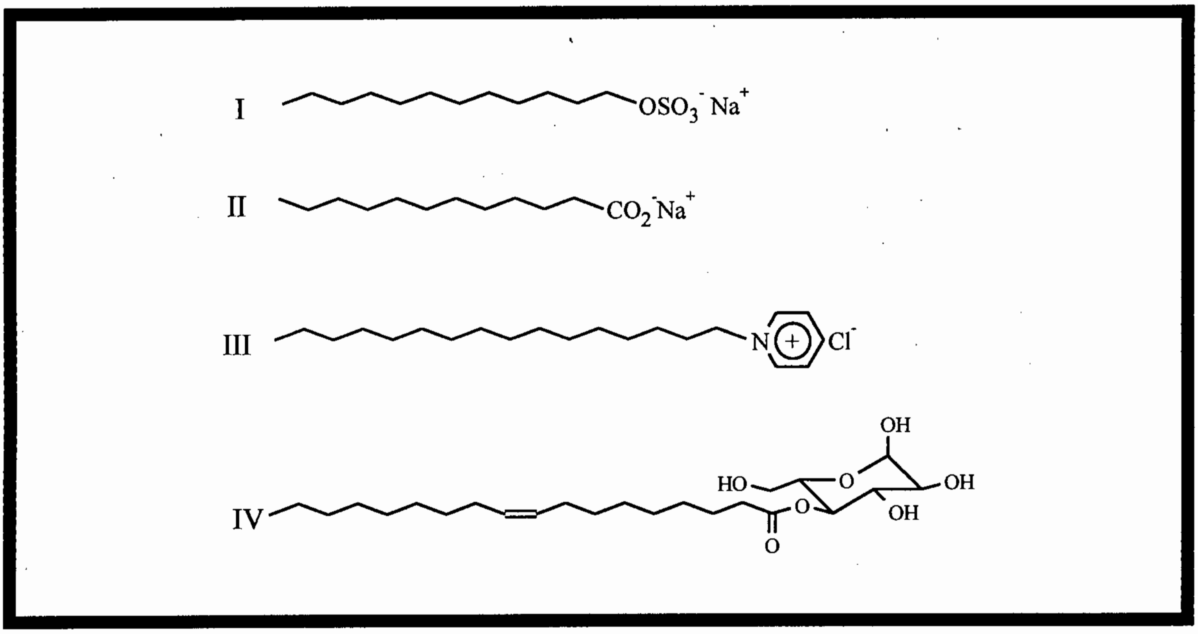

Fig. 2: surfactants used in the study. I: sodium dodecyl sulphate; II: sodium laurate; III: cetylpyridinium chloride; IV: sorbitan oleate.

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[g] In initial droplet sizing experiments, n-heptane was used as the oil phase because it is chemically homogeneous. However, rapid separation of the emulsions then occurred prior to significant coalescence, although the upper milky layer was not broken. This separation was subsequently identified as creaming. However, a change to paraffin oil was made since the smaller density difference (Sec. C1) between paraffin oil and water, relative to that of heptane and water, was expected to reduce the creaming rate (Eq. 1). Initial droplet sizing results therefore apply to heptane-water emulsions. Subsequent results apply to paraffin oil-water emulsions.

[h] Sorbitan sesquioleate was dissolved in the paraffin due to its insolubility in water.

D1.2. MORPHOLOGY

The first requirement was to establish that the emulsions had an o/w structure. Dilution and the direction of sedimentation (Sec. A6.1) revealed the o/w nature of the emulsions:

- Light paraffin (0.84 $g.ml^{-1}$) and n-heptane (0.69 $g.ml^{-1}$) were less dense than the aqueous phases (> 1 $g.ml^{-1}$). The clear aqueous phase always separated below the emulsions during creaming.

- The addition of water, followed by gentle stirring, resulted in a homogeneous, diluted emulsion. Added paraffin or heptane separated as clear layers above the emulsions.

D1.3. DECAY MECHANISMS

The observable instability was rapid sedimentation-flocculation followed by (usually slower) coalescence. Microscopic examination indicated that the oil droplets were close-packed in the creamed layer, i.e. the creamed emulsions contained a high internal-phase fraction. Coalescence therefore destabilised this layer. Ostwald ripening was an unlikely decay mechanism since the droplets were much larger than 1 μm in diameter (i.e. the Laplace pressure was small) and paraffin oil is non-polar[29, i]. The methods that were used to quantify the different types of instability were:

1. Creaming rates (sedimentation and flocculation).
2. Droplet distribution increases by laser light scattering and the measurement of planar interface droplet lifetimes (coalescence).
3. Photography (long-term stability in terms of creaming, coalescence and phase separation).

Since increases in droplet distribution parameters are the most fundamental means for determining emulsion decay, this approach was attempted first.

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[i] However, in certain cases surfactant-assisted Ostwald ripening may have occurred (Sec. D4.2.2).

D2. DROPLET SIZE CHANGES

The objective was to plot the stability parameter d_t/d_o against ageing time in order to evaluate coalescence rates (Sec. A6.2). A series of experiments are described below which were necessary to establish:

1. the correct sampling method and sampling time.
2. sampling reproducibility.
3. the sensitivity of the method to the parameters under investigation.
4. whether the ageing process could be accelerated into a more convenient measurement time.

D2.1. SAMPLING METHOD & OPTIMAL STORAGE TIME

A series of creamed emulsions that were prepared from 1 % aqueous sodium dodecyl sulphate and heptane were sampled at the top and bottom of the creamed layer after 5, 30 and 60 minutes had elapsed after emulsification (Table 2).

TABLE 2: EFFECT OF SAMPLING POSITION & TIME ON SIZE DISTRIBUTION

AGEING TIME (minutes)	SAMPLING POSITION IN CREAMED EMULSION LAYER			
	TOP		BOTTOM	
	D[4,3] (μm)	SPAN	D[4,3] (μm)	SPAN
5	51.0 ± 6.12	1.34 ± 0.09	36.1 ± 4.11	1.80 ± 0.50
30	47.1 ± 8.38	1.44 ± 0.15	32.4 ± 4.46	1.71 ± 0.18
60	46.9 ± 6.25	1.25 ± 0.13	22.4 ± 9.39	2.19 ± 0.46

Three conclusions were evident from Table 2:

1. The average droplet sizes were smaller and the spans were larger at the bottom of the creamed layers compared to those at the top. This is consistent with Eq. 2 which

implies a Boltzmann distribution of decreasing droplet sizes from the top to the bottom of the creamed layer. It was therefore neccessary in future experiments to gently invert the sample bottles in order to obtain an aliquot that was representative of the entire creamed emulsion. This was not done originally for fear of inducing artefacts of emulsion coalescence, especially in poorly-stabilised emulsions.

2. There was no observed coalescence of this emulsion within a one-hour ageing period. In order to plot d_t/d_0 as a function of time, longer ageing times would have been necessary.

3. The distribution parameters were inconsistent for estimating decay, at least when the bottles were not inverted. This is so since one would expect only an increase in these parameters on storage. In practice, the reverse sometimes occurred.

D2.2. SAMPLING REPRODUCIBILITY

It is clear from Table 2 and Eq. 2 that sampling reproducibility was highly dependent on the sampling point in the creamed emulsions when the bottles were not inverted. The large deviations in those sizes and spans cannot be used to evaluate the reproducibility of the method, since one may have sampled at slightly different depths (i.e. different sizes) when the bottles were not inverted. It was therefore necessary to establish the reproducibility after the bottles had been inverted.

Accordingly, three samples of 1 % aqueous sodium dodecyl sulphate-paraffin emulsions were used to establish the between-run reproducibility. This was necessary in order to ensure that measured droplet size differences between samples of different composition were real and not an artefact of poor reproducibility, from the aspect of both the droplet sizing and emulsion preparation methods.

The reproducibility was not good (Table 3). The variables under investigation, at their extremes, afforded droplet size differences of a similar magnitude (Sec. D2.3) as these "identical" samples. The interpretation of size and distribution differences therefore had to be treated with caution.

TABLE 3: BETWEEN-SAMPLE REPRODUCIBILITY ("IDENTICAL" EMULSIONS)

EMULSION SAMPLE	D[4,3] (μm)	SPAN
1	106.7	1.17
2	100.5	1.30
3	111.4	1.11
x ± s	106.2 ± 5.51	1.19 ± 0.10
Coefficient of variation (100s/x, %)	5.2	8.4

D2.3. SENSITIVITY AT EXTREMES OF VARIABLES

Prior to multiple-point measurements of the effects of pH, ionic strength, droplet size and surfactant concentration on stability, a preliminary investigation was conducted to establish the sensitivity of the method to extremes of these parameters. For this purpose, bottles of 1% sodium dodecyl sulphate-paraffin emulsions were inverted[j]. From Table 4, an increase in the variable parameters listed below had the following effect.

1. Surfactant concentration

For a constant shear input, increases in concentration resulted in a decreased average droplet diameter and an increased span. The increase in polydispersity conflicts with existing theoretical models[35]. The decrease in droplet size is due to a reduction of the surface tension which facilitated the emulsification process. This trend correlates well with the enhanced stabilisation against creaming and breaking (Sec. D4.2), which was a result of smaller droplet sizes.

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[j] An analogous experiment was performed with heptane. However, the bottles were not inverted. These results appear in the Appendix (Sec. G2).

There was no significant change in distribution parameters when sorbitan sesquioleate was used. This may be rationalised by the unsuitable HLB of sorbitan sesquioleate (Sec. D4.6), i.e. higher concentrations did not reduce the surface tension. However, the virtually indistinguishable droplet sizes conflicts with the marked stabilisation against creaming as the sorbitan sesquioleate concentration was increased (Sec. D4.2.1). This anomaly is discussed in Sec. D4.2.3.

2. Mixing time

An increased mixing time reduced the droplet size but increased the polydispersity. The increase in span conflicts with a literature mathematical prediction[86]. There is good correlation between the reduced droplet size and the enhanced stabilisation against creaming and breaking (Sec. D4.3).

3. pH

With sodium dodecyl sulphate in alkaline media, the droplet size was smaller than at lower pH and the span had increased. This implies a more efficient emulsification upon deprotonation of the sulphate moeiety. However, the creaming and breaking rates were invariant of pH (Sec. D4.4 and Fig. 21). Since the creaming rate was not sensitive to pH, this would imply that the droplet sizes were equal at all pH values, which is not the case. Therefore, interdroplet repulsion (hence flocculation and faster creaming) may have been greater at low pH.

Protonation of the sulphate moeiety of sodium dodecyl sulphate would lower the HLB from 37[1], since the head group would lose its ionic character. Optimally-stable paraffin o/w emulsions require an HLB of 10. One would thus expect that stabilisation would occur at lower pH's because the sodium dodecyl sulphate would have a more suitable HLB. In practice, however, the emulsions were stable at all pH values that were studied.

TABLE 4: EFFECT OF VARIABLE EXTREMES ON DROPLET DISTRIBUTION (PARAFFIN)

VARIABLE	SURFACTANT	NUMERICAL VALUE OF VARIABLE	D[4,3]* (μm)	SPAN*	STORAGE TIME (days)
SURFACTANT CONCENTRATION (% m/v)	sorbitan sesquioleate	1	121.5 ± 10.7	0.99 ± 0.11	9
		5	123.9 ± 1.2	0.93 ± 0.04	
		10	123.4 ± 3.2	0.94 ± 0.03	
	sodium dodecyl sulphate	0.14	121.8 ± 2.5	0.98 ± 0.02	9
		1	103.9 ± 1.2	1.25 ± 0.03	
	sodium laurate	1	104.0 ± 5.38	1.24 ± 0.12	8
		2	95.3 ± 2.56	1.45 ± 0.06	
MIXING TIME (seconds)	sorbitan sesquioleate	30	124.9 ± 1.30	0.95 ± 0.01	9
		300	112.6 ± 1.84	1.09 ± 0.02	
	cetylpyridinium chloride	30	124.9 ± 1.30	0.97 ± 0.03	7
		60	114.4 ± 3.7	1.03 ± 0.05	
		300	103.6 ± 3.8	1.23 ± 0.10	
	sodium laurate	30	105.4 ± 6.00	1.22 ± 0.14	8
		60	104.0 ± 5.4	1.24 ± 0.12	
		300	79.3 ± 2.2	1.61 ± 0.09	
pH	sodium dodecyl sulphate	2.22	108.4 ± 0.70	1.14 ± 0.01	10
		4.27	110.0 ± 4.80	1.13 ± 0.08	
		6.60	103.9 ± 1.20	1.25 ± 0.03	
		12.20	96.2 ± 1.28	1.41 ± 0.04	

★ n = 3 (same sample)

D2.4. ACCELERATED AGEING BY CENTRIFUGATION

After the rapid creaming step, many of the emulsions resisted coalescence and breaking for inconveniently-long periods (see photographs and associated storage times, Sec. D4). Since it was necessary to plot d_t/d_0 as a function of time to evaluate the stability trends, a method for shortening the time scale of decay was investigated. In terms of coalescence, centrifugation for short periods is equivalent to very long shelf storage times[1, 3]. A preliminary experiment was therefore designed in order to force droplet coalescence prior to droplet sizing. The stability parameter d_t/d_0 could then have been plotted as a function of centrifugation time in lieu of real time[3].

An emulsion that was based on sodium dodecyl sulphate and paraffin was used to establish the feasibility of this approach at the extremes of the parameters which are listed below (Table 5). Various centrifugation times were investigated to establish the optimal time that was required to force sufficient coalescence without breaking the creamed emulsions entirely.

TABLE 5: ACCELERATED COALESCENCE BY CENTRIFUGATION

VARIABLE	VALUE	CENTRIFUGATION TIME (minutes)					
		0		5		30	
		D[4,3]★ (µm)	SPAN★	D[4,3] (µm)	SPAN	D[4,3] (µm)	SPAN
IONIC STRENGTH (M)	0	70.8 ± 2.73	1.09 ± 0.07	67.5	1.18	61.1	1.38
	0.5	69.9 ± 2.50	1.10 ± 0.06	74.4	1.00	75.4	0.98
SURFACTANT CONCENTRATION (% m/v)	0.5	71.8 ± 1.94	1.06 ± 0.04	70.4	1.10	67.9	1.15
	5.0	70.3 ± 2.81	1.10 ± 0.07	65.9	1.23	64.0	1.28
SHEAR TIME (seconds)	10	74.1 ± 3.41	1.03 ± 0.06	72.2	1.06	72.6	1.03
	300	59.6 ± 1.77	1.37 ± 0.06	69.6	1.10	60.8	1.39

★ n = 2 (same sample)

Three conclusions are apparent from this experiment:

1. Prior to centrifugation, no difference in average droplet sizes occurred at extremes of the variables, with the exception of shear time. In that case, the droplet size decreased and the span increased as before (Table 4). The method did not detect a smaller droplet size with increased sodium dodecyl sulphate concentration from 0.5 to 5 %. The previously-observed droplet size reduction with sodium dodecyl sulphate (Table 4) and the reduced creaming, which was partially due to smaller droplets (Fig. 11), suggest that the method was inconsistent.

2. With increased centrifugation times, there were inconsistent droplet size changes. If coalescence were being detected, the D[4,3] should increase. In some cases, the distribution parameters decreased, which is improbable.

3. Centrifugation in conjunction with droplet sizing did not reveal the coalescence process. In practice, however, significant breaking was visually apparent in the centrifugated emulsions. It is possible that the sampling of such emulsions could selectively have measured the sizes of smaller, unbroken droplets because large, macroscopic pools of separated paraffin would have eluded measurement by this technique.

D2.5. PROBLEM OF DROPLET SIZING TECHNIQUE

The droplet sizing method was successful in demonstrating the following effects:

1. Boltzmann partitioning of droplet sizes in the creamed emulsions.
2. Decrease in droplet diameter with mixing time and (usually) surfactant concentration.
3. Increase in polydispersity with mixing time and surfactant concentration.

However, it afforded poor reproducibility and inconsistent or non-sensical trends (e.g. decreases in droplet sizes or spans upon centrifugation). Because of the uncertainty in the method, attention was directed at a method for simulating coalescence, viz. planar interface droplet half-lives (Sec. D3).

D3. PLANAR INTERFACE DROPLET COALESCENCE

D3.1. SURFACTANT CONCENTRATION

The planar interface method was used to investigate the effect of sodium dodecyl sulphate concentration on droplet stability. A constant droplet size (2 μl) was used as the surfactant concentration was increased.

The droplet coalescence times were processed by plotting N versus coalescence time t, where N is the number of droplets that have not coalesced within that time[2]. The droplet stability at each surfactant concentration was given by the time required for half of the droplet population to coalesce. This is referred to as the droplet half life. The results are presented in Figs. 3 - 6. The half lives that were obtained from those graphs appear in Table 6.

TABLE 6: HALF LIFE vs SURFACTANT CONCENTRATION

Sodium dodecyl sulphate CONCENTRATION (M)	DROPLET HALF LIFE (s)
5×10^{-4}	14.5
3×10^{-3}	72
10^{-2}	> 24 hours[k]
0.35	430

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[k] Only four drops were used for a surfactant concentration of 0.01 mol.dm^{-3} because, for very long rest times at the interface, the droplets eventually rolled along the convex oil-water interface. Ultimately, droplets with long half lives came to rest at the edge of the interface so that part of the droplet was touching the glass bulb. This artefact of the method was unavoidable, but the effect of the rolling droplet on the half life was unknown. After 24 hours at the edge of the inner bulb, none of the droplets had coalesced.

It is clear that as the sodium dodecyl sulphate concentration was increased, droplet half lives increased, reached a maximum and then decreased. This is consistent with the the trend that is seen for other surfactants[14]. The stability presumably increased below the maximum because of an increase in the viscosity of the aqueous phase and a lengthening of the film thinning stages. At low surfactant concentrations, the amplitude of the surface waves, which caused the film to become thinner, was large. Lower sodium dodecyl sulphate concentrations thus resulted in film rupture at a large critical film thickness. As the sodium dodecyl sulphate concentration was raised, the waves were damped, which caused the films to drain to lower thickness before rupture occurred. The stability maximum at 10^{-2} M was reached near the critical micelle concentration (c.m.c.) for sodium dodecyl sulphate (0.0081 M at 298 K[104]). At the c.m.c., the surface film was completely saturated by sodium dodecyl sulphate[7] and the film elasticity was at a maximum[14].

At 0.35 M sodium dodecyl sulphate, the stability was less than at 10^{-2} M because molecules of the paraffin were probably solubilised and transported by micellar diffusion into the larger droplets[48]. The droplets were therefore less stable at a high sodium dodecyl sulphate concentration due to surfactant-assisted Ostwald ripening. Surfactant micelles can solubilise small amounts of the total volume of a droplet and transport the oil to larger droplets[23]. Surfactant-assisted Ostwald ripening is akin to conventional Ostwald ripening because in both mechanisms, larger droplets of oil grow at the expense of the smaller droplets. However, the surfactant can assist in solubilising large droplets without the requirement for a large Laplace pressure, i.e. a small droplet size. In normal Ostwald ripening, the oil droplets must be in the sub-micron regime in order that their Laplace pressures are sufficiently high to diffuse into the aqueous phase. In the case of dodecyl sulphate-assisted Ostwald ripening, the droplets need not be small in order for the surfactant micelles near the oil-water interface to encapsulate small amounts of the oil molecules near the surface of the droplet. Therefore, surfactant-assisted Ostwald ripening is a viable decay mechanism despite the large droplet sizes. However, the decrease in stability at high concentration was not observed in bulk emulsions that were comprised from sodium dodecyl sulphate, even up to a 10 % aqueous surfactant concentration. This difference between the planar interface method and the observed stabilities of real emulsions is consistent with the conclusion drawn by Davis (next paragraph).

The method was very laborious and is reported to require exceptional care to obtain reproducibility[46, 52, 54]. It is also not necessarily related to bulk emulsion stability, since smaller surfactant concentrations and larger droplets are used. Davis concluded from a detailed study that the method is useful in observing the effect of trends on stability, but does not correlate well with emulsion stability[52]. This difference was observed by the experimenter. For these reasons, the method was not pursued further[1]. Attention was instead focused on more practical methods for obtaining stability trends, viz. creaming rates and photography, which afforded meaningful trends that are discussed below (Sec. D4).

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[1] Literature evidence of these drawbacks became available after the experiment with sodium dodecyl sulphate concentration had been conducted.

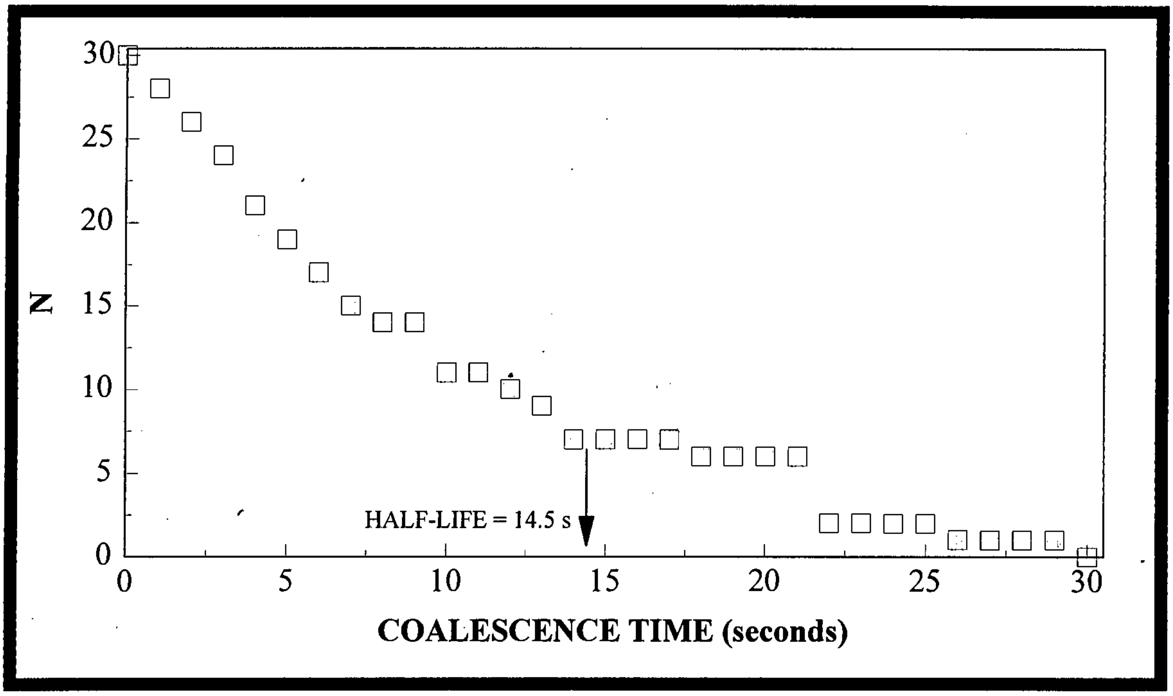

Fig. 3: number of droplets remaining after after time t for 2 μl paraffin oil in 5×10^{-4} M aqueous sodium dodecyl sulphate.

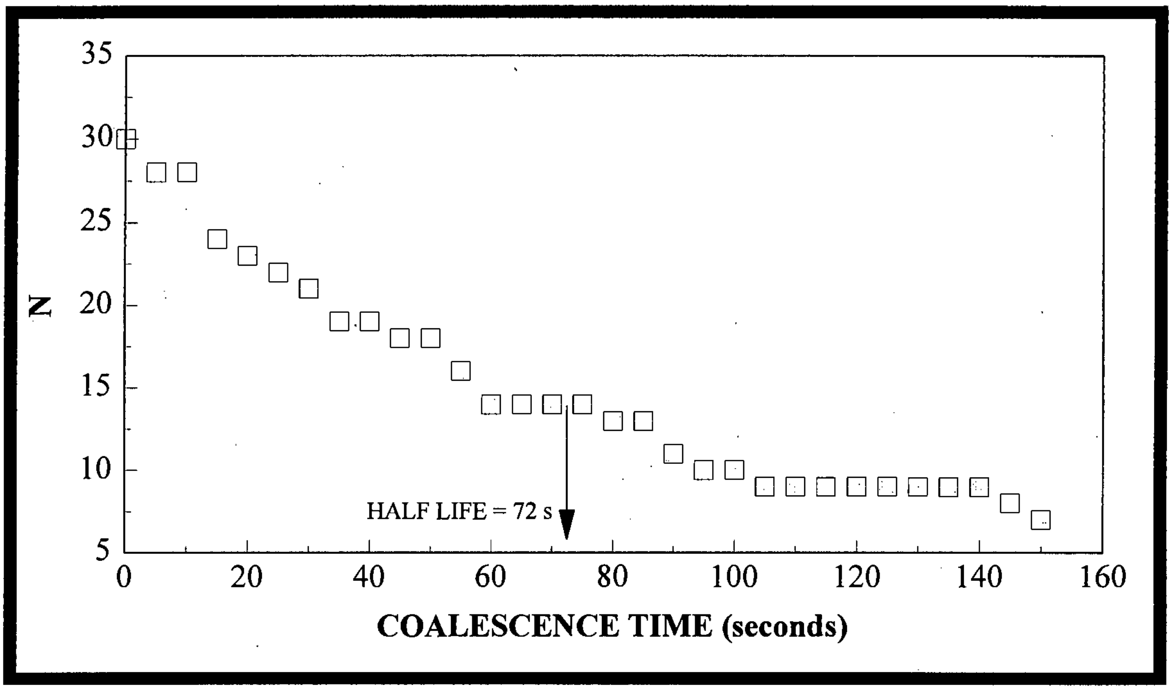

Fig. 4: number of droplets remaining after time t for 2 μl paraffin oil in 3 10^{-3} M aqueous sodium dodecyl sulphate.

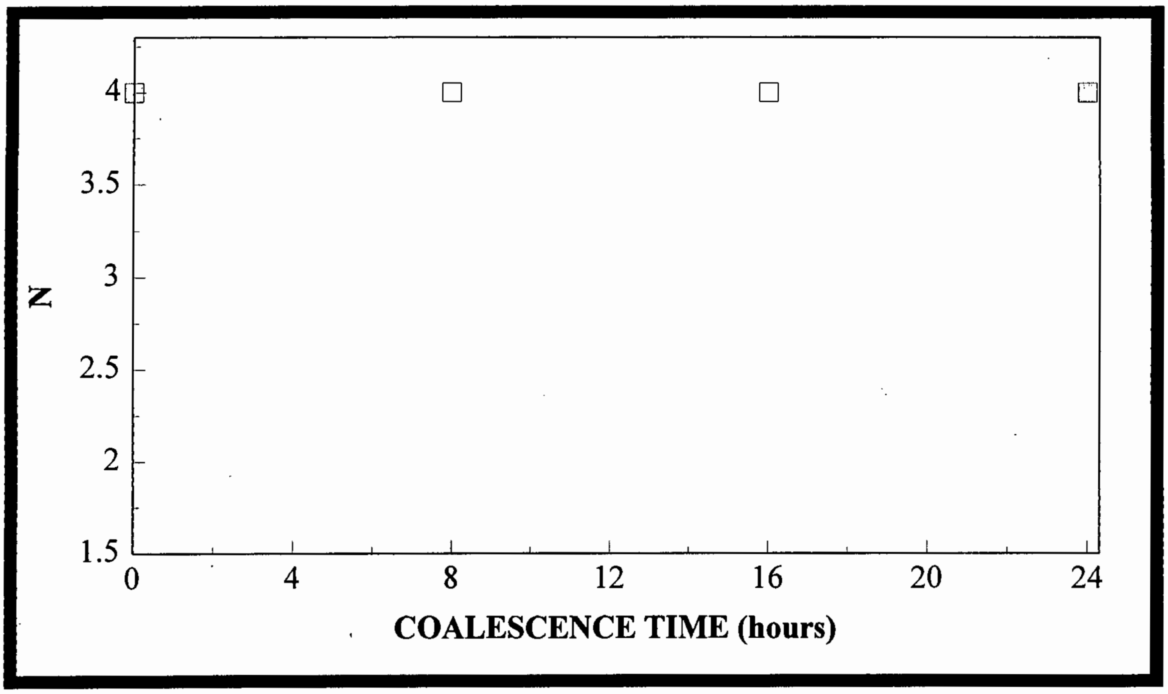

Fig. 5: number of droplets remaining after time t for 2 μl paraffin oil in 10^{-2} M aqueous sodium dodecyl sulphate.

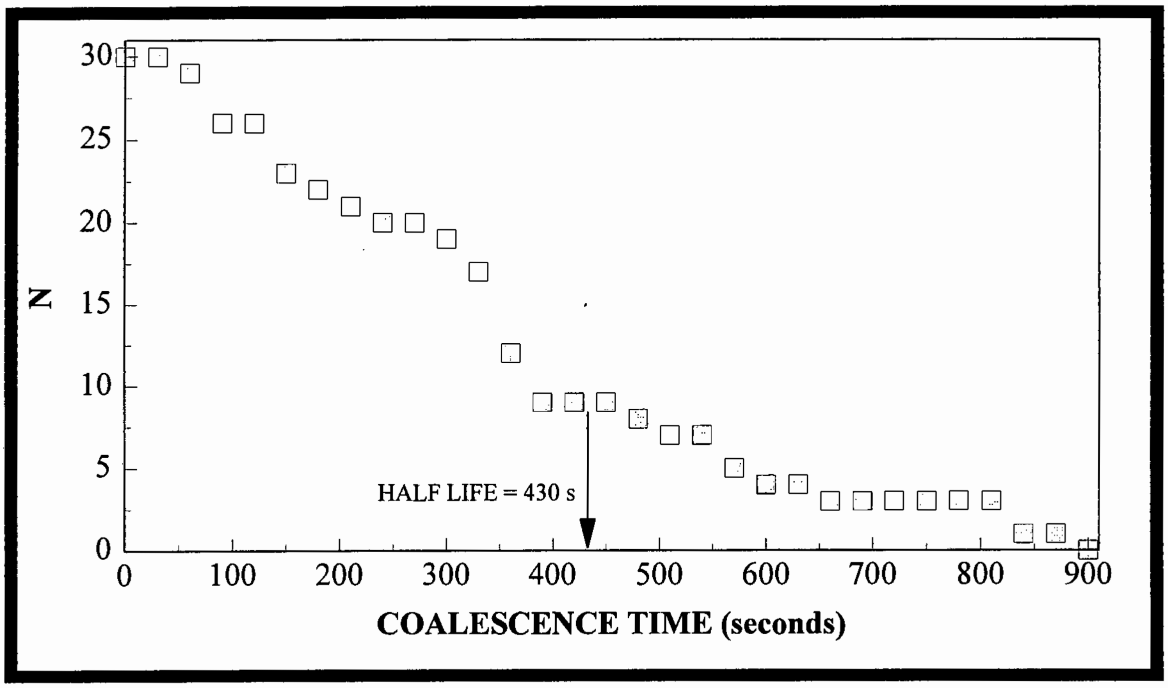

Fig. 6: number of droplets remaining after time t for 2 μl paraffin oil in 0.35 M aqueous sodium dodecyl sulphate.

D4. CREAMING & PHOTOGRAPHY

The creaming rates were expressed as the volume percentage of separated aqueous phase as a function of time. The creaming rates up to 60 minutes of ageing appear in Appendix G3. An example of results in this unprocessed format appears in Fig. 7.

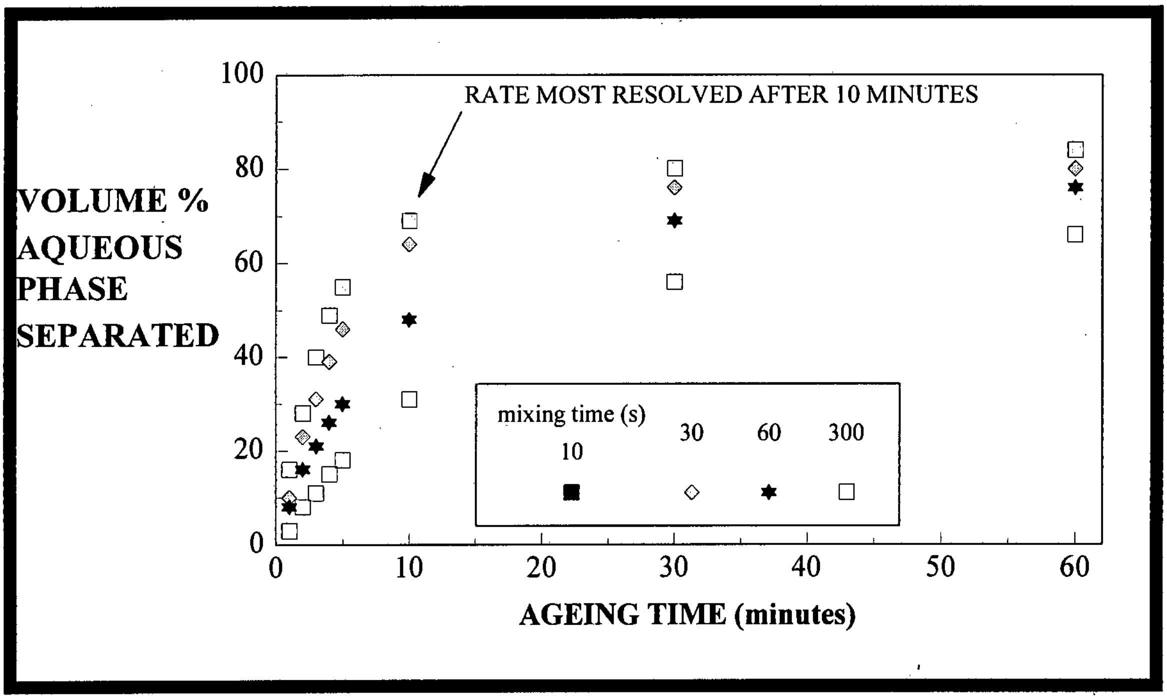

Fig. 7: effect of shear time on creaming rate for o/w emulsions containing 1 % sodium dodecyl sulphate.

The sensitivity towards the parameters which were investigated was at a maximum after ten minutes of creaming had ensued. The data points after ten minutes were therefore used to construct graphs of the extent of separation as a function of each variable. The expression of results in this format is more illustrative for demonstrating the trends and it is these graphs that are discussed in Sec. D4.1 - D4.6.

The creamed, optimally-aged emulsion stability trends are apparent from the photographs. Instability due to coalescence and breaking is evident from the photographs in the form of larger droplets, transparent pools of separated paraffin or a clear upper layer of pure oil above the emulsion. For non-coalesced emulsions, the oil-phase volume was ca. 86 % of the creamed layer once creaming was complete. For homogeneous close-packed spheres, a phase volume of 74 % is required. Microscopy revealed that in the polydisperse emulsions, interstitial spaces between larger droplets were filled by smaller droplets, which resulted in the high packing efficiency.

The trends are discussed below in relation to the parameter which was varied.

D4.1. IONIC STRENGTH

Emulsions could not be formed with sorbitan sesquioleate in aqueous phases with ionic strengths between 0.1 - 0.5 M; the phases separated immediately after shearing was stopped. This is justified by the unsuitably-low HLB of this surfactant (Sec. D4.6). The sparing solubility of sodium laurate, especially in sodium chloride solution, also precluded studies with this surfactant. Attention was therefore focused on the effect of ionic strength on emulsions that were prepared from cetylpyridinium chloride and sodium dodecyl sulphate.

D4.1.1. CREAMING

The interpretation must be treated with caution because changes in ionic strengths also resulted in changes in density between the phases[31]. From Eq. 1, the effect of the increased density difference on creaming rate could be mistaken for the effect of increased ionic strength on the rate. However, the mass creaming rate varies with the fifth power of the effective, number-averaged droplet size and only to the first power on the density difference (Eq. 1). It was therefore assumed that the increase in density with higher ionic strength was small relative to the effect of ionic strength (i.e. effective droplet size) on flocculation and, therefore, creaming[m].

For both surfactants, instability due to creaming was accelerated by increased ionic strengths (Fig. 8). This is in accord with the DLVO theory[1]. The increased ionic strength was

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[m] This assumption is supported by the slower creaming rates with increased surfactant concentrations (i.e. higher densities).

accompanied by a reduction in the Stern radius of the double layers which enveloped the paraffin droplets (Eq. 8). The resultant decreased repulsive force between droplets enabled closer approach as they creamed. When the attractive van der Waals forces over-ruled the repulsive forces, some of the droplets flocculated into a secondary minimum energy well. These aggregates creamed faster than the component droplets since their effective radii were greater than that of their constituent droplets. Since the mass creaming rate is proportional to the number-weighted fifth powers of the average flocculated droplet sizes (Eq. 1), greater instability resulted as the ionic strength was raised.

D4.1.2. PHOTOGRAPHY

Figs. 9 and 10 respectively show the effect of increased ionic strength on the stability of emulsions that contained sodium dodecyl sulphate or cetylpyridinium chloride. It is apparent that cetylpyridinium chloride-type emulsions were increasingly broken by increased ionic strengths and sodium dodecyl sulphate analogues were not. The behaviour of each surfactant is described below.

1. The interfacial film of the cetylpyridinium chloride-based emulsions was apparently too weak to resist film drainage and rupture. Increased coalescence rates result from neutralisation of the surface charge[31]. The increased coalescence at higher ionic strengths may therefore have been due to the closer proximity (reduced repulsion) of the close-packed droplets, with a thinner film to separate them and hence a smaller drainage time.

2. The sodium dodecyl sulphate-stabilised films were suitably robust to prevent continued droplet coalescence. With an increased ionic strength in the aqueous phase, the HLB of sodium dodecyl sulphate decreases[6, 7] and this surfactant becomes more lipophilic. However, the HLB of sodium dodecyl sulphate is very high[1] (37), whereas paraffin-water emulsions require an HLB of 10[105]. It appears that as salt was added, the HLB of this surfactant was lowered, but high ionic strengths could be tolerated before the HLB was lowered to less than the

optimal of 10. However, it is not entirely clear why such high stability was observed for large HLB values.

An explanation for the resistance against coalescence is proposed in terms of the Stochastic model. This model (Sec. A5.3) predicts that many emulsions can restabilise after some coalescence has occurred. The reason for a restabilisation is based on Eq. 9. As the droplets in an emulsion coalesce, the interfacial charge densities on the resultant larger droplets are predicted to increase as the surface area-to-volume ratio decreases[94]. The increasing charge densities on the surface of the coalesced droplets may eventually dominate the attractive van der Waals forces. The result is that the critical aggregation ionic strength increases upon the successive joining of droplets. Ultimately, further coalescence is predicted to cease. In view of this model, the dodecyl sulphate-based emulsions could have restabilised after a certain degree of coalescence had occurred. The restabilisation could be attributed to the increase in electrostatic repulsion that was caused by increasing potentials. These repulsive forces may have progressively over-ruled the increased van der Waals attraction which arose from an increase in droplet volume upon coalescence. The manifestation was that no observable coalescence had occurred.

There is also literature evidence that high salinities do not necessarily lead to coalescence. For example, van den Tempel found that for sodium laurate-stabilised o/w emulsions, high salt concentrations were necessary to obtain rapid coagulation[31].

D4.1.3. CORRELATION OF METHODS

Creaming and photography correlated well for the cetylpyridinium chloride-based emulsions, but not in the case of sodium dodecyl sulphate. In the case of cetylpyridinium chloride, the emulsions were progressively destabilised towards creaming and coalescence as the ionic strength was increased. This effect is apparent, both in the graph and the photographs, from the increase in phase separation with larger ionic strengths. With sodium dodecyl sulphate, higher ionic strengths destabilised the emulsions towards creaming. However, over the 91-day time frame of the experiment, the emulsions were not visibly destabilised by coalescence.

Different types of stability are measured by the creaming and photographic methods. Creaming is a kinetic instability that will increase as the repulsive forces between droplets are reduced. Since an increase in ionic strength will reduce the thickness of the electrical double layer around an oil droplet, the droplets can approach each other more closely as the ionic strength is increased. Creaming will then ensue more rapidly because a flocculated aggregate offers less electroviscous drag than the equivalent ensemble of droplets from which it is comprised. Hence in the case of both surfactants, the creaming rate increased with an increase in ionic strength.

In the case of coalescence, the stability of the emulsion will depend on the interfacial stability conferred by the surfactant that is used. This stability depends on the suitability of a given surfactant for the system and can vary considerably with the selection of surfactant. The difference in stability of the emulsions made from dodecyl sulphate and cetylpyridinium chloride illustrates that some surfactants provide a more robust interfacial film than other surfactants for a given emulsion.

These observations are good examples of the fact that overall emulsion stabilities are best evaluated by a batch of different tests. Generally, there is no universally-applicable method that can produce a number which serves as an index of stability[1, 7]. In the event of the dodecyl sulphate-based emulsions the determination of the creaming rate alone does not provide an accurate assessment of the long-term shelf life of the emulsion. This is clear from the difference between the creaming rate graph and the photographs.

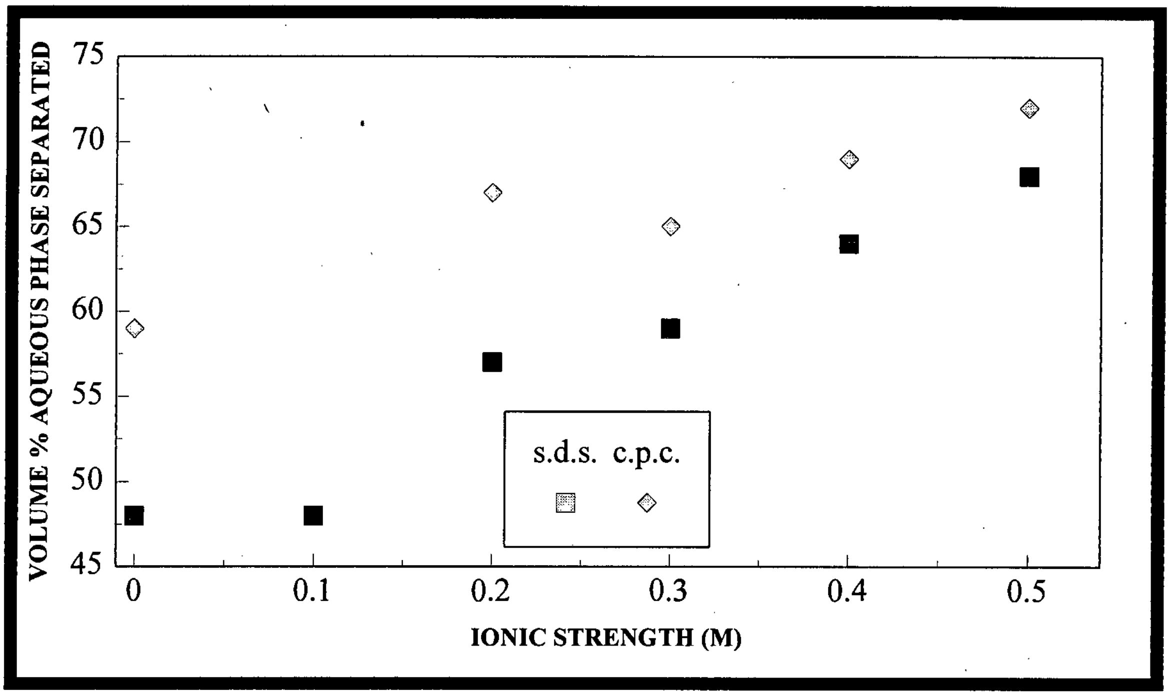

Fig. 8: effect of ionic strength on creaming 10 minutes after emulsion preparation.

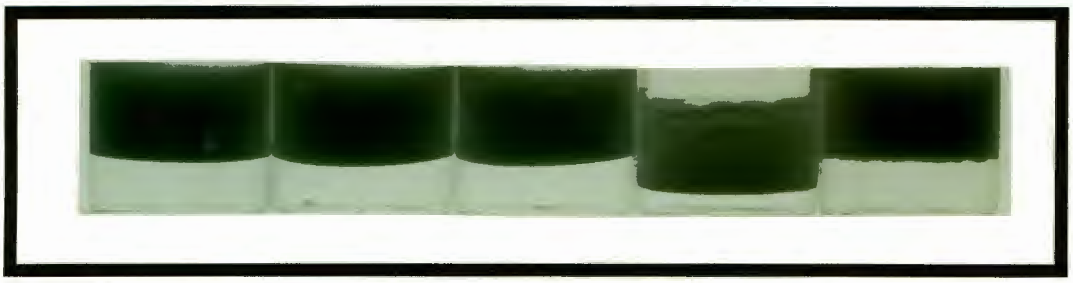

Fig. 9: effect of ionic strength on stability: 1% sodium dodecyl sulphate, 91 days storage. Ionic strength (M) L to R: 0.1; 0.2; 0.3; 0.4; 0.5.

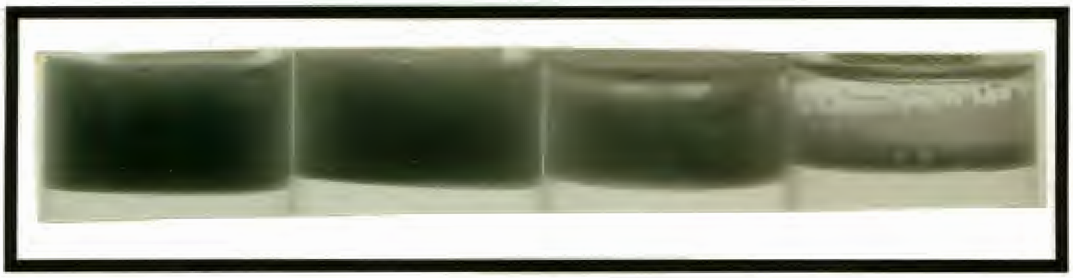

Fig. 10: effect of ionic strength on stability: 1 % cetylpyridinium chloride, 16 days storage. Ionic strength (M) L to R: 0.1; 0.2; 0.4; 0.5.

D4.2. SURFACTANT CONCENTRATION[n]

D4.2.1. CREAMING

Fig. 11 shows that for all four surfactants, creaming was inhibited by an increase in surfactant concentration. This effect may be rationalised by two stabilisation processes.

1. As the surfactant concentration was increased, the interfacial tension was progressively lowered. For the same amount of shear, emulsions with more surfactant thus attained a greater refinement, or smaller average droplet size[23, 35, 40, 43, 86] (cf. Table 4). This was a kinetically-controlled process, i.e. less shear energy was required to attain the same droplet size compared to an equivalent emulsion that contained less surfactant. The smaller droplets that resulted from surfactant-rich emulsions would have had an increased electroviscous drag and hence a slower mass creaming rate (Eq. 1).

2. Bulk emulsion- and surfactant-soluble phase viscosities increase with increased surfactant concentration[37, 43, 47]. In the case of sodium dodecyl sulphate, cetylpyridinium chloride and sodium laurate, the surfactant-soluble phase was the external phase. An increased external phase viscosity retards creaming (Eq. 1). Stabilisation was therefore also enhanced with these surfactants by an increased viscosity of the aqueous phase due to the formation of micelles or gel networks. The stabilising effect of an increased aqueous phase viscosity was particularly prevalent in the case of emulsions that were made using sodium laurate. In those emulsions, the aqueous phase was very viscous. The increased viscosities of aqueous solutions that contained increasing amounts of

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[n] Comparisons were made on a mass percentage basis and not on molarities. One reason for this is that sorbitan sesquioleate is a mixed ester (Fig. 2; Sec. C1) and, as such, it has no defined molar mass. In retrospect, it may have been better to use sorbitan mono-, di- or tri-oleate. However, these were only available as mixed esters with different fatty ester moeities. Another reason that molarities were not used is that comparisons based on concentrations are then invalid, i.e. the choice is arbitrary.

these surfactants were apparent from the syrup-like rheologies of the more concentrated solutions. Although the viscosities were not measured, the increased resistance to flow was apparent when bottles, in which the surfactants were stored, were slowly inverted. For the sorbitan sesquioleate-based emulsions, the enhanced stability against creaming with increased sorbitan sesquioleate concentration was only a result of decreased droplet sizes, since this surfactant was dissolved in the external phase[o]. This was done due to its low HLB (i.e. low solubility in water) and selective partitioning into the paraffin.

D4.2.2. PHOTOGRAPHY

Figs. 12 - 15 show the complex stability trends that depended both on the surfactants and their concentration. Over the concentration ranges and time frames that were studied, dodecyl sulphate- and laurate-based emulsions remained indefinitely stable, regardless of the surfactant concentration. Cetylpyridinium chloride-based emulsions displayed an optimal stability at a concentration of 2 %. Below and above this concentration, breaking was observed in the form of larger droplets and pools of paraffin in the creamed emulsion. Sorbitan sesquioleate-based formulations were progressively destabilised by an increase in the sorbitan sesquioleate concentration. These seemingly-random trends may be reconciled as follows.

1. In the dodecyl sulphate-based emulsions, great interfacial stability seems likely except when calcium(II) was present. It appears that sodium dodecyl sulphate was an especially suitable emulsifier for this system. Although its HLB is very large, it conferred stability at all concentrations. An upper concentration-stability decline was not apparent in the concentration range that was studied.

2. For sodium laurate-based emulsions, the continuous aqueous phase was very viscous and eventually set into a semi-rigid, opaque gel which effectively froze the drainage of the thin film (Sec. A2.4). Therefore, over the time span of

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[o] Table 4 suggested that there was no reduction in droplet size with sorbitan sesquioleate concentration. However, refer to the discussion in Sec. D4.2.3 for a likely explanation.

storage, no difference in stability was observed regardless of the laurate concentration. The limited solubility of sodium laurate precluded the observation of any decreased stability at higher laurate concentrations. If the stability trends were assessed by subjecting the emulsions to high-temperature storage, a lower relative stability may have occurred due to the observed absence of the gel at higher temperatures. The gel structure was rapidly destroyed within seconds when sample vials containing the gelatinous emulsions were placed in hot water (between 60 to 70 degrees C) in order to dispose of the contents at the end of the experiments. Photographs of the occurrence were not obtained because the lower aqueous phases of these emulsions merely lost their opaque, white appearance and gelatinous rheology and became colourless, mobile liquids. However, the event was recorded and interpreted as above.

3. For cetylpyridinium chloride-type emulsions, there was optimal stability at a concentration of 2 % of this surfactant. With 0.5 % cetylpyridinium chloride, the thin film drainage rate was faster because the film had insufficient elasticity or rigidity to dampen surface waves, which caused film rupture. Additionally, the initial droplet distribution would have occured at a larger average droplet size below 2 % cetylpyridinium chloride, since the interfacial tension during emulsification would have been larger (cf. Table 4). A larger initial droplet size implies that less coalescence was required before breaking became apparent. At 5 % cetylpyridinium chloride, the stability was also reduced. This may have been due to solubilisation and transport of the paraffin through the aqueous phase, via encapsulation in surfactant micelles, from smaller droplets into larger droplets. This was probably a type of surfactant-assisted Ostwald ripening[48].

4. For sorbitan sesquioleate-type emulsions, the stability towards coalescence was low relative to the other surfactants and it decreased as the sorbitan sesquioleate concentration was increased. Fig. 15 illustrates the increased degree of coalescence in the clear, uppermost layers of separated paraffin oil as the sorbitan sesquioleate concentration was increased. This layer is particularly prevalent at

a surfactant concentration of five percent, less extreme in the two percent regime and least manifest between one to two percent. It is noteworthy that even in the latter two samples, the emulsions have begun to coalesce more than for the other surfactants (Fig. 12 to 14).

The low stability is understood in terms of the unsuitably-low HLB of sorbitan sesquioleate and Bancroft's rule[14, 18, 49] (i.e. emulsions in which the surfactant is soluble in the droplet phase are less stable than those in which the surfactant partitions mainly in the film phase). Since paraffin-water emulsions require an HLB of 10[105], sorbitan sesquioleate (HLB 3.7[1]) typifies w/o-type emulsifiers. Surfactants with low HLB's will break o/w emulsions. The extent to which sorbitan sesquioleate does so increased as its concentration was raised[1]. Thus, although this surfactant (surprisingly) formed o/w emulsions, the stability was especially poor when the sorbitan sesquioleate concentration was raised. Sorbitan sesquioleate was dissolved in, and selectively partitioned in, the paraffin because of its insolubility in the aqueous phase. Hence the aqueous thin film contained little surfactant and coalescence was rapid. This was reflected in the relatively small time which was required for instabilities to appear, relative to emulsions that were prepared from surfactants with more suitable HLB's (16 and 91 days respectively).

It is also possible that the upper concentration limit for optimal stability had been exceeded in the concentration range that was studied, so that greater instability occurred as more sorbitan sesquioleate was used[45]. If this were so, the oil-like but more-polar sorbitan sesquioleate may have destabilised the non-polar paraffin oil droplets by transporting the alkane molecules in micelles through the aqueous phase to larger droplets. That is, surfactant-assisted Ostwald ripening may have occurred.

The sorbitan sesquioleate may also have been poorly adsorbed onto the interface, so that film thinning was rapid[14].

D4.2.3 CORRELATION OF METHODS

There was little correlation between the creaming and breaking trends. This is not unexpected. Sec. A2.1 impressed that the ease of formation and subsequent stability of an emulsion may differ[2, 3]. The reduction in initial droplet size upon emulsification, and its effect on the rapid creaming step, is a kinetic process which has little bearing on the subsequent thermodynamic stability of the thin films that are formed by the surfactant. Therefore, an increase in surfactant concentration always resulted in greater stability towards initial creaming, but its effect on long-term breaking varied, depending on the type of surfactant.

The droplet sizing results for sorbitan sesquioleate-based emulsions suggested that, after nine days of storage, all of these emulsions had virtually the same droplet sizes. However, creaming measurements indicated that the only reason for enhanced stabilities with higher sorbitan sesquioleate concentrations must have been due to smaller droplet sizes. On the basis of the time frames of the experiments, these results can be reconciled. This is explained in the next paragraphs.

Stability trends are best resolved at some optimal time, before or after which the differences in stability can become more marginal or apparently non-existent. If an optimal time frame is not chosen to resolve real differences in stability, a series of emulsions may ultimately restabilise to a metastable state in which no significant difference in stability is discernible. The time-dependent resolution of stability trends, even within a chosen method, is evident from creaming rate measurements in Fig. 7. It was evident from preliminary experiments that the differences in stability due to creaming had virtually equalised over a 24-hour period. Over a 24-hour time frame, all of the creamed emulsions were close-packed and there was little difference in stability if the percentage of separated aqueous phase was the measure of stability. That is, the emulsions had restabilised once creaming was complete.

The next phase in the decay was the coagulation of the close-packed droplets by drainage of the interfacial film. The restabilisation of emulsions towards coalescence, after an initial increase in droplet size, is predicted by the Stochastic model (Sec. A5.3). The same argument that was presented for the time dependence of creaming trends is therefore also true of coalescence trends. If the emulsions are not photographed within the most discriminatory time frame, they may all appear to be equally stable because a restabilisation has occurred.

The time frame for the creaming measurements (one hour) was small in comparison to the period over which the sorbitan sesquioleate-based emulsions were stored to evidence the coalescence trends (16 days). The creaming measurements were therefore performed in less than 0.3% of the time that was required to manifest the coalescence trends.

In view of the above statements, it is proposed that during the small time frame of the creaming measurements, stability trends could be resolved. However, in the case of coalescence, a restabilisation could have occurred such that all the emulsions had average droplet sizes of ca. 120 μm. Therefore no apparent difference in stability, as determined by droplet sizes, was seen after nine days of storage. If the droplet sizes were measured within a more discriminatory time period (e.g. within the time frame of the creaming rate measurements), higher sorbitan sesquioleate concentrations could have yielded lower droplet sizes.

The above argument may explain why there is an apparent conflict between stabilities of sorbitan sesquioleate-based emulsions as established by droplet sizing, creaming and photography.

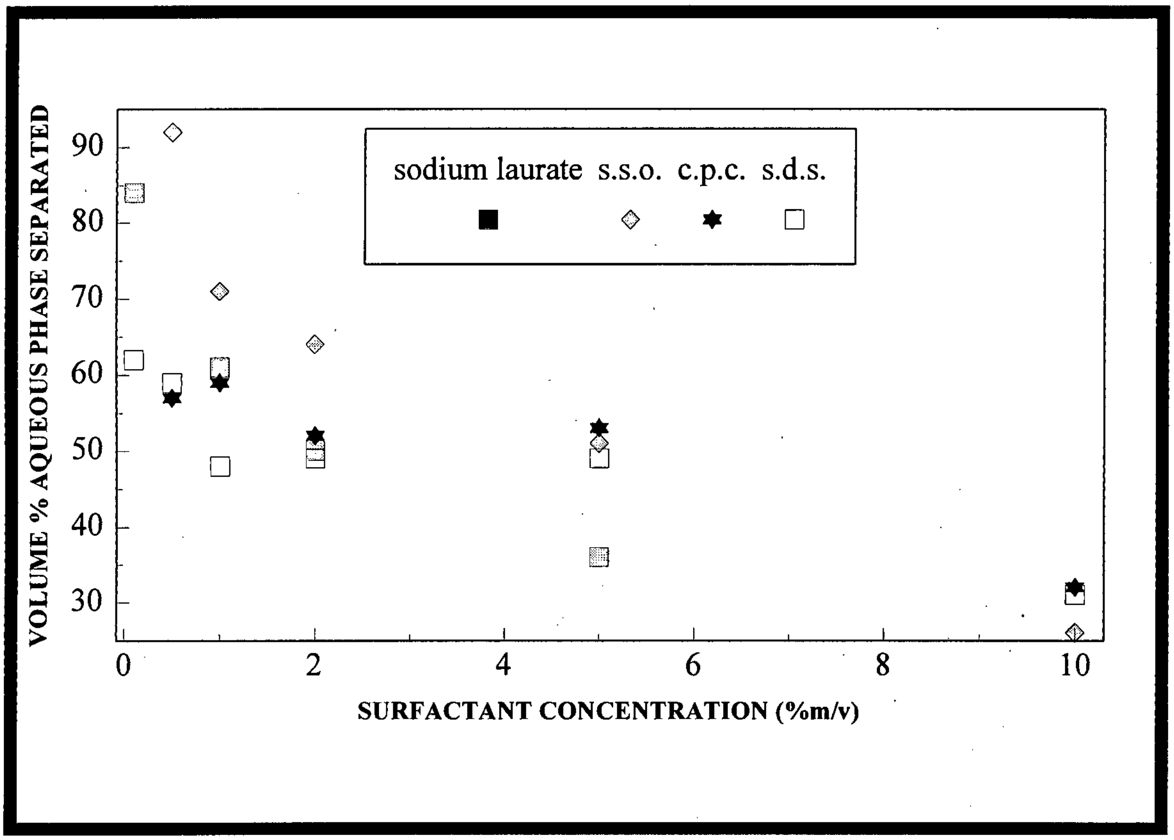

Fig. 11: effect of surfactant concentration on creaming 10 minutes after emulsion preparation.

Fig. 12: effect of surfactant concentration on stability: 91 days storage, L to R: 0.5; 2; 5 % sodium dodecyl sulphate.

Fig. 13: effect of surfactant concentration on stability: 91 days storage, L to R: 0.5; 2; 5 % sodium laurate.

Fig. 14: effect of surfactant concentration on stability: 91 days storage, L to R: 0.5; 2; 5 % cetylpyridinium chloride.

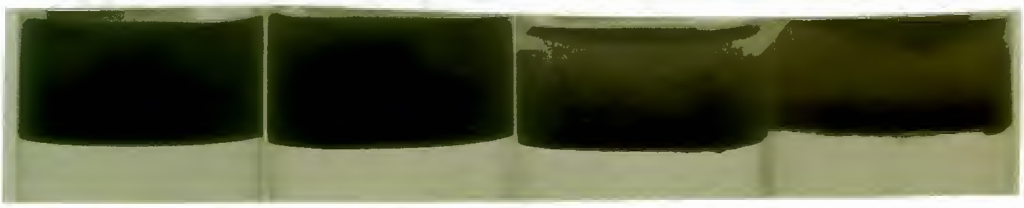

Fig. 15: effect of surfactant concentration on stability: 16 days storage, L to R: 0.5; 1; 2; 5 % sorbitan sesquioleate.

D4.3. SHEAR TIME

An increase in shear time, which was correlated to a reduction in droplet sizes but an increase in polydispersity (Table 4), always stabilised the emulsions against creaming and breaking (Figs. 16 - 20).

D4.3.1. CREAMING

The rate of separation of continuous phase decreased with an increase in agitation time, in accord with the literature[43]. Since an increase in shear time is proportional to a decrease in droplet size (Sec. A4.12 and Table 4) and the mass creaming rate varies as the fifth power on the weighted average droplet size (Eq. 1), the degree of separation became smaller as the shear time was increased. The enhanced stability that was conferred by longer emulsification periods reached a limiting value. The trend is shown by the shallow shape of the functions after extended shear was applied (Fig. 16). This is consistent with mathematical models which show that the droplet size is reduced by mixing up to a limiting value, beyond which more shear does not refine the emulsion any further[35, 86]. The stabilisation towards creaming with increased shear time obeyed a law of diminishing returns for protracted shear periods. However, it appears that the sodium laurate-based emulsions could have been further stabilised by additional shear beyond 300 seconds, since the curve for that surfactant had not acquired a limiting value.

D4.3.2. PHOTOGRAPHY

Sorbitan sesquioleate- and cetylpyridinium chloride-based emulsions broke less as the shear time was increased[p]. This implies that a decreased droplet size stabilised the emulsions towards breaking. The dodecyl sulphate- and laurate-based emulsions were stable even with little shear input; no breaking was evident for any of the mixing times that were studied. It

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[p] For sorbitan sesquioleate, an explanation that was based on the time frames of the the two methods, was suggested in Sec. D4.2.

appears that both the ease of formation[q], as well as the thermodynamic stability, of emulsions that are made from these surfactants, is large. In the case of laurate-based emulsions, the high viscosity of the aqueous phase also retarded coalescence, whose rate is partially determined by the thin film viscosity. It is presumed that the adsorption kinetics for dodecyl sulphate-based emulsions are such that this surfactant was rapidly adsorbed onto the interface, so that small droplets and robust interfacial film were formed even for small emulsification times (Sec. A2.4).

D4.3.3. CORRELATION OF METHODS

The two methods correlated well since in both cases the increased stability was due to smaller droplets (Eq. 1 and Sec. A4.3).

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[q] After 60 seconds of shear, both surfactants afforded mean droplet diameters of 104 μm and spans of ca. 1.25. By contrast, cetylpyridinium chloride and sorbitan sesquioleate afforded larger diameters (114 μm and 123 μm respectively) with smaller degrees of polydispersity (Table 4).

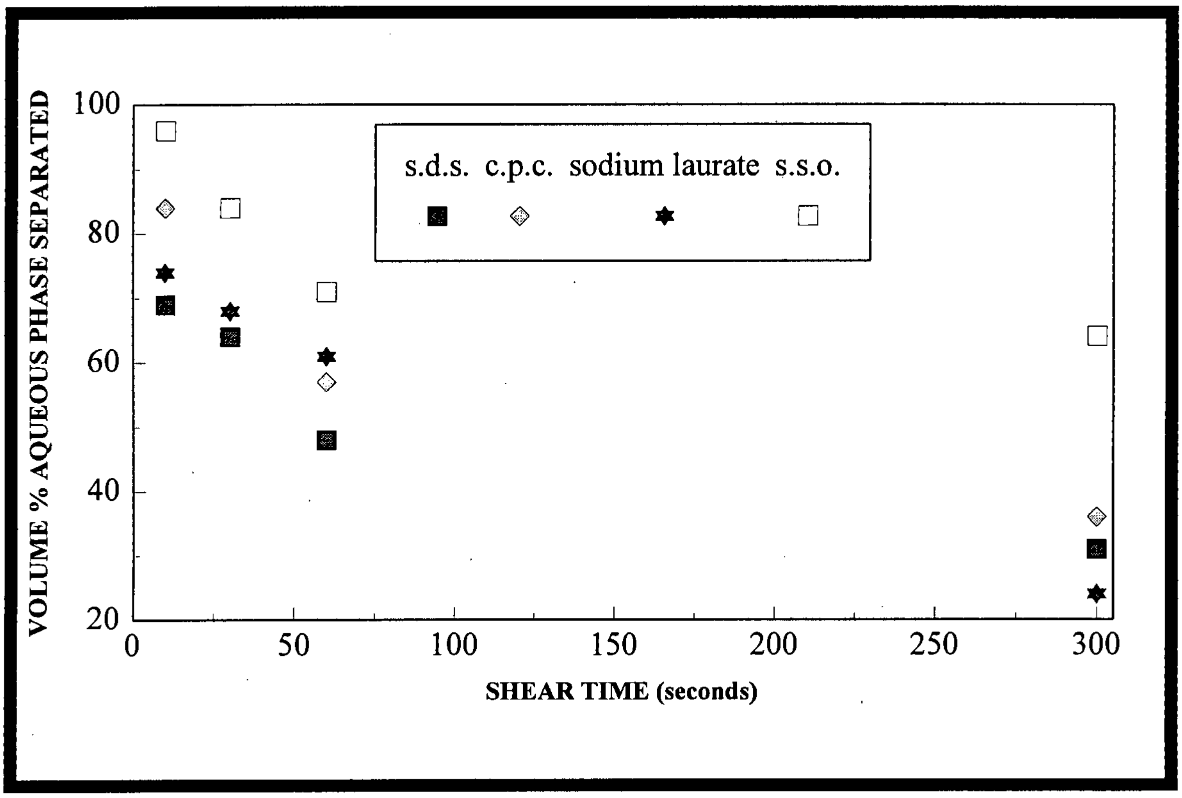

Fig. 16: effect of shear time on creaming 10 minutes after emulsion preparation.

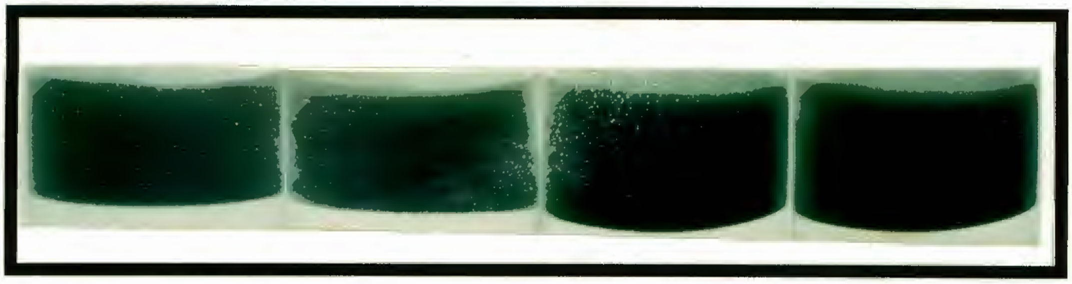

Fig. 17: effect of shear time on stability: 1% sodium dodecyl sulphate, 91 days storage. L to R: 10; 30; 60; 300 seconds.

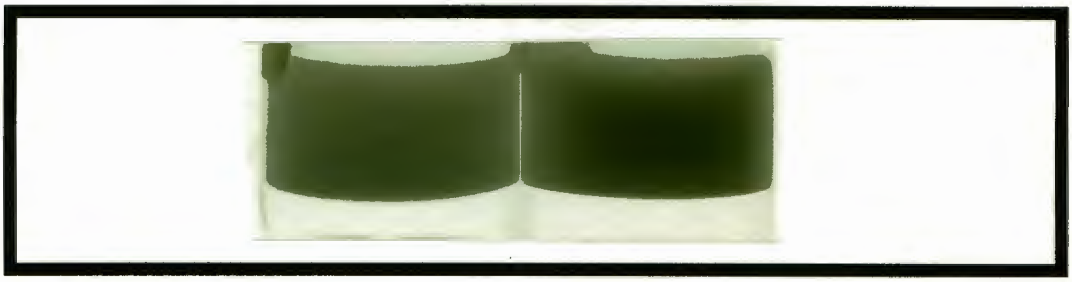

Fig. 18: effect of shear time on stability: 1 % sodium laurate, 91 days storage. L to R: 10; 300 seconds.

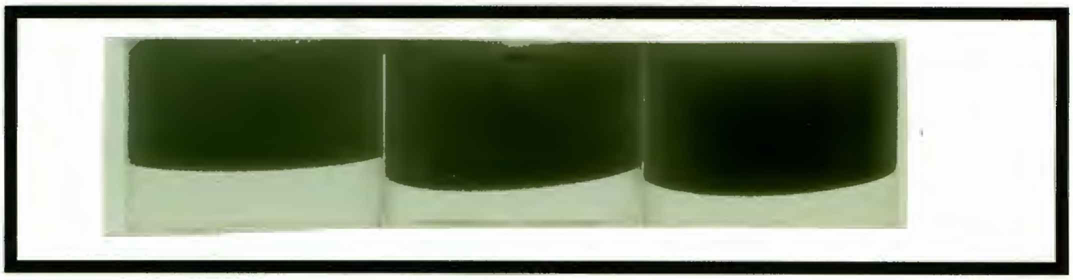

Fig. 19: effect of shear time on stability: 1 % cetylpyridinium chloride, 91 days storage. L to R: 10; 30; 300 seconds.

Fig. 20: effect of shear time on stability: 1 % sorbitan sesquioleate, 16 days storage. L to R: 10; 30; 300 seconds.

D4.4. pH

Sodium laurate could not be studied over a suitably-large pH range since lauric acid precipitated from solution at pH values below ca. 9. The effect of pH on dodecyl sulphate-, cetylpyridinium chloride- and sorbitan sesquioleate-based emulsions depended on the stability of the surfactant towards pH.

D4.4.1. CREAMING

The results appear in Fig. 21. The trends are discussed below in relation to the surfactant that was used.

1. There was no change in the degree of separation as a function of pH for dodecyl sulphate-based emulsions. Their stability was therefore pH-independent. The sulphate moeiety has a pK_a that is too low for protonation, even at low pH's. If protonation could have occurred, the hydrophilicity of the head group would have been lowered and the HLB would have decreased. However, the HLB would have to have been lowered from 37 to less than 10 before instability would become apparent[1]. Over the pH scale that was studied, this did not occur. It is odd that the droplet sizing measurements indicated smaller droplet sizes at high pH (Table 4). Those results implied a stabilisation towards creaming in the basic regime, presumably to the presence of deprotonated dodecyl sulphate, since the droplets were smaller. However, this was not seen in practice (Fig. 21).

2. Cetylpyridinium chloride-based emulsions were destabilised at high pH's. This is evidenced by the positive slope of the degree of separation from low to high pH. Cetylpyridinium chloride appeared to be labile in basic media, since at high pH, a solution of this surfactant changed colour rapidly from colourless to yellow. Since there is no protonizable moeiety in cetylpyridinium chloride (Fig. 2), this colour must have been due to a chromophore in a hydrolytic product(s). The lability of the surfactant at high pH implies a less efficient reduction of the

droplet sizes during emulsification, since there would have been less unhydrolysed cetylpyridinium chloride to lower the surface tension. Since larger droplets cream more rapidly (Eq. 1), greater instability was seen at high pH.

3. Sorbitan sesquioleate-type emulsions were much less stable than either of the other surfactants, especially at pH extremes. The lower stability appears in Fig. 21 as a more rapid creaming rate, especially outside the pH range between 4 to 7. The greater degree of separation, relative to that of dodecyl sulphate- and cetylpyridinium chloride-stabilised emulsions, is justified by the low HLB of sorbitan sesquioleate (Sec. D6). There are two possibilities which can justify the rapid creaming at pH extremes:

1. Hydrolysis of the ester moeiety, which would have generated oleic acid and sorbitol, implies an alteration of the surfactant from sorbitan sesquioleate to oleic acid (at low pH) or oleate (at high pH). Oleic acid has a very low HLB (ca. 1[1]), which would afford less stable emulsions than sorbitan sesquioleate. The larger droplets that would have resulted from a higher surface tension at low pH would have creamed more rapidly. However, oleate has a relatively high HLB (~ 18)[1]. This would be expected to stabilise an o/w emulsion[1]. The destabilisation at high pH is therefore difficult to understand by this mechanism.

   Complete hydrolysis as described above is a less probable explanation because the sorbitan sesquioleate was dissolved in the oil phase. Only the ester groups at the o/w interface would be subject to hydrolysis. Within the short time scale of emulsification (droplet size reduction) and creaming, it is unlikely that significant hydrolysis would have occurred. For example, a pH of 9.5, where a high instability was observed, is mildly basic.

2. Alteration of the ability of sorbitan sesquioleate to lower the surface tension adequately. This is probable since after emulsification was stopped, the

majority of the paraffin separated immediately as a non-emulsified layer. This implies that the process of emulsion formation was impeded beyond pH 4 - 7. However, in a stored sample at high pH, emulsification proceeded (Fig. 24). The pyranosidic structures of the sorbitan oleates (Fig. 2) may have equilibrated in favour of open-chain sorbitol residues under acidic or basic conditions. The acyclic sorbitol head groups may not have had the correct conformation to partition themselves correctly at the o/w interface. In that case, the surface tension would not have been lowered adequately and emulsion formation would have been impeded.

D4.4.2. PHOTOGRAPHY

Figs. 22 - 24 show the dependence of stability on pH for dodecyl sulphate-, cetylpyridinium chloride- and sorbitan sesquioleate-based emulsions respectively.

1. The dodecyl sulphate-stabilised emulsions were equally robust regardless of pH. Presumably, dodecyl sulphate was not degraded by pH extremes and therefore the integrity of the interfacial film was not compromised.

2. The cetylpyridinium chloride-based emulsion at a pH of 11.9 had a yellow aqueous phase. This was indicative of surfactant decomposition because that emulsion displayed significant breaking. At neutral and acidic pH values, cetylpyridinium chloride afforded more stable emulsions.

3. The sorbitan sesquioleate-based emulsions were progressively destabilised as the pH was lowered from 11.45 to 1.27. This conflict with the creaming rate trend may be rationalised in terms of the hydrolysis of sorbitan sesquioleate over the longer three-day storage period to yield oleic acid (at low pH) or oleate (at high pH). The order of HLB's is: oleic acid (1) < sorbitan sesquioleate (3.7) < oleate (18)[1]. Since o/w emulsions are destabilised by w/o emulsifiers such as sorbitan sesquioleate and (more so due to its lower HLB) oleic acid, the greatest stability

was seen with the o/w emulsifier, viz. oleate at high pH. The stability decreased as the pH was lowered due to a reduction of the HLB of the surfactant from oleate (at high pH) to sorbitan sesquioleate (at neutrality) to oleic acid (at low pH). However, it is difficult to rationalise this trend with the observation during the creaming rate experiments that emulsification was impeded at high pH.

D4.4.3. CORRELATION OF METHODS

The methods correlated well for sodium dodecyl sulphate and cetylpyridinium chloride, but differed for sorbitan sesquioleate This may be due to the time frame of the two methods. For creaming at pH extremes in the sorbitan sesquioleate-based emulsions, the destabilisation was probably due to alteration of the structure and ability of this surfactant to lower the surface tension adequately. Hydrolysis of sorbitan sesquioleate in the time frame of the creaming experiment was unlikely. During breaking of the sorbitan sesquioleate-based emulsions over three days, hydrolysis of the ester to yield surfactants with different HLB values was probable.

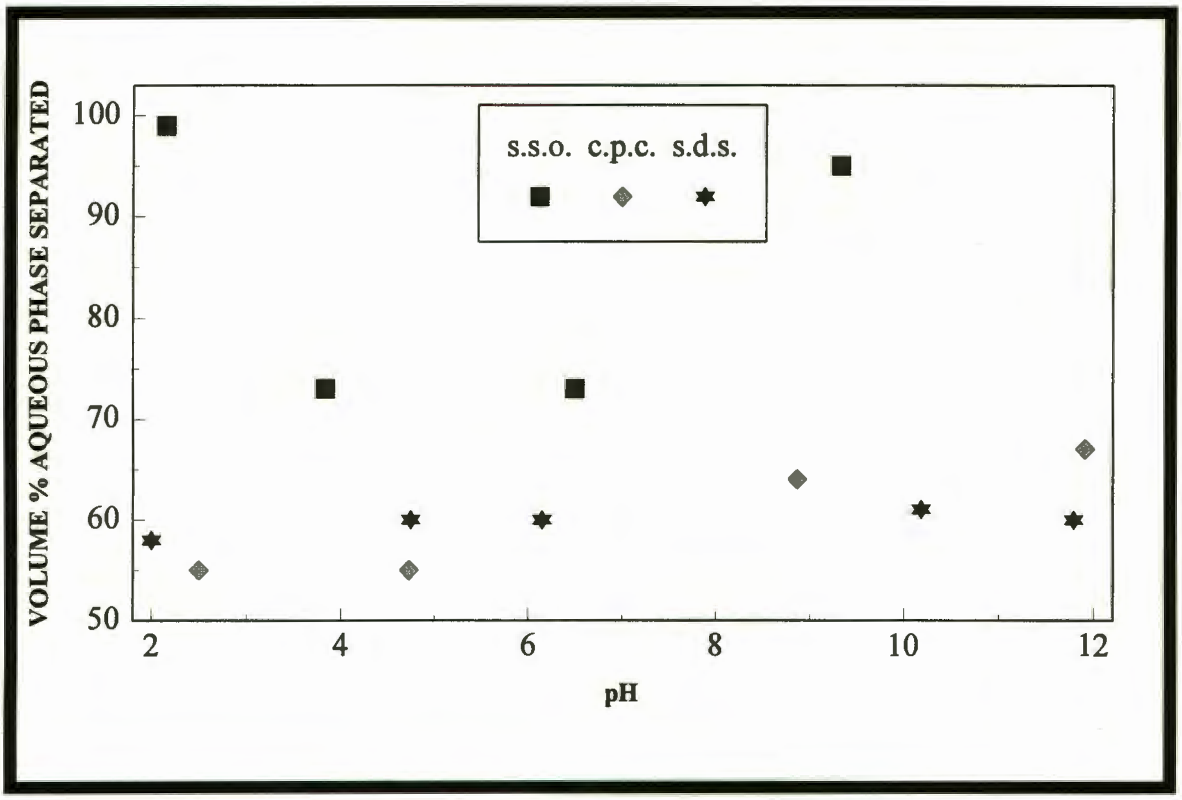

Fig. 21: effect of aqueous phase pH on creaming 10 minutes after emulsion preparation.

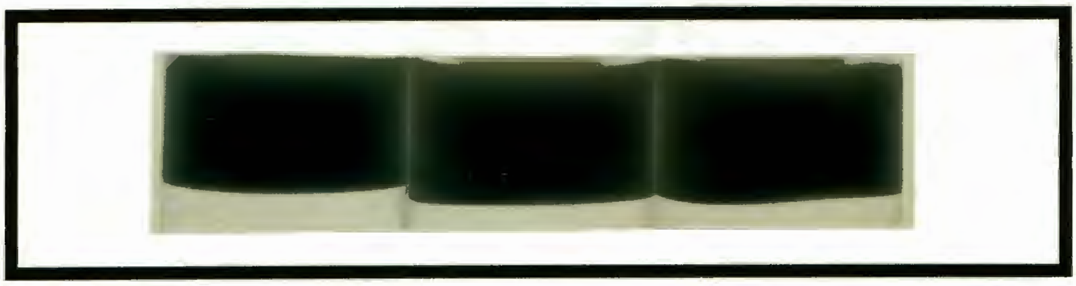

Fig. 22: effect of pH on stability: 1 % sodium dodecyl sulphate, 16 days storage. L to R: 1.93; 6.13; 11.50.

Fig. 23: effect of pH on stability: 1 % cetylpyridinium chloride, 16 days storage. L to R: 1.99; 6.00; 11.90.

Fig. 24: effect of pH on stability: 1 % sorbitan sesquioleate, 3 days storage. L to R: 1.27; 6.50; 11.45.

D4.5. CALCIUM:SURFACTANT RATIO

Sorbitan sesquioleate did not form emulsions in the presence of calcium(II), which is a reflection of its unsuitable HLB (Sec. D4.6). Figs. 25 - 28 demonstrate the adverse effect of calcium(II) on the stability of emulsions that were stabilised by anionic surfactants and the impunity with a cationic surfactant. Molar ratios of Ca^{+2}:surfactant were used at a 1% surfactant concentration.

D4.5.1. CREAMING

Calcium(II) rapidly destabilised emulsions that were prepared from dodecyl sulphate and laurate. The instability was marked even at a Ca^{+2}:surfactant ratio of 0.4, especially for sodium laurate. Cetylpyridinium chloride-stabilised emulsions, however, were relatively unaffected by Ca^{+2} even at a Ca^{+2}:cetylpyridinium chloride ratio of 3, above which slight destabilisation occurred.

- The sensitivity towards Ca^{+2} of anionic surfactant-stabilised emulsions was severe since calcium(II) forms water-insoluble salts with these anions. The formation of water-insoluble salts rendered these surfactants inactive (even counteractive[71]) to the formation of o/w emulsions, in proportion to the Ca^{+2}:surfactant ratio. Since there would have been proportionally less active surfactant present during the emulsification process, larger droplets would have been formed compared to when less calcium(II) was present. The larger droplets would have creamed faster (Eq. 1). It is tempting to propose that the slight increase in stability between 0.3 - 0.5 mole equivalents of Ca^{+2}:laurate was due to steric stabilisation by the solid particles of calcium laurate. However, the fact that such particles stabilise w/o emulsions cannot be reconciled with this explanation. It is known that calcium alkanoates favour the formation of w/o emulsions, whereas Group I alkanoates favour o/w emulsions[71]. This implies that calcium favoured the inversion of o/w emulsions that were stabilised by laurate.

- Cetylpyridinium chloride-stabilised emulsions were insensitive to the presence of Ca^{+2} since the cetylpyridinium cation was not co-ordinated by the like-charged calcium cation. The surfactant was therefore not altered or inactivated by the presence of calcium(II). Consequently, cetylpyridinium chloride-type emulsions were tolerant of larger mole ratios of Ca^{+2}. At a ratio of 4:1, slight instability had ensued. This is in line with the Schulze-Hardy rule and the DLVO theory. Calcium(II) is bivalent and increased the total ionic strength of the aqueous phase ($I = \frac{1}{2}\Sigma c_i z_i^2$). The inverse Debye length (κ) of the electrical double layer would have been reduced (Eq. 8) and the repulsive component of the total droplet interaction would have been less (Eq. 7). Flocculation therefore ensued. Since the flocculated aggregates would have creamed more rapidly than the constituent droplets (Sec A2.2), the mass creaming rate was accelerated at 4 mole equivalents of Ca^{+2}.

D4.5.2. PHOTOGRAPHY

1. The destabilisation of dodecyl sulphate- and laurate-stabilised emulsions was evident by the degree of destabilisation at Ca^{+2}:surfactant ratios of 0.1 - 0.2. The precipitated surfactant is seen as a scum at the paraffin-water interface. At ratios of 0.4 and 1.0, however, the emulsions were not entirely broken. It is tempting to ascribe this to steric stabilisation by the precipitated calcium salts of the surfactants, but it is unlikely since, for example, calcium laurate favours the formation of w/o emulsions[71]. Therefore, the reason for the stabilisation at higher calcium concentrations is unclear.

2. Cetylpyridinium chloride-stabilised emulsions remained relatively unbroken up to a Ca^{+2}:cetylpyridinium chloride ratio of 4:1. Some breaking had occurred, in the form of clear paraffin globules that were dispersed in the creamed emulsion, at a ratio of 4:1 because of the increased ionic strength. The reasons for the stability, except at high calcium concentrations, was explained in Sec. D4.5.1.

D4.5.3. CORRELATION OF METHODS

The creaming rates and photographs demonstrated that a cationic-based surfactant will resist the effects of calcium (II) in comparison with anionic surfactants. With cetylpyridinium chloride, both the creaming rate and degree of droplet coalescence is relatively invariant of the calcium (II) concentration until the concentration of this ion contributes to a high ionic strength.

However, there is a difference between the stability trends of the anionic surfactant-stabilised emulsions when the creaming and coalescence studies are compared. Sec. D4.1.3 emphasised that different trends can be expected for methods which measure different types of instability. The reason for this difference is based on the time period of decay that had elapsed between the two methods. All of the creaming rate measurements were performed within a one-hour period after emulsification was completed. Furthermore, the graphs that were constructed from these measurements had used the data after only ten minutes of creaming had occurred (e.g. Fig. 7). Within this time period, the droplets in the emulsion had flocculated and creamed significantly as indicated by the extent of phase separation in the creaming rate graphs. However, the creaming emulsion droplets had not coalesced as much after ten minutes when compared to the three-day period after which photographs were taken to illustrate the coalescence trends. After three days in the closely-packed creamed emulsions, the thin liquid films that separated the droplets had drained to the extent that many of the emulsions had coalesced very significantly. The degree of drainage (and thus the trend that is observed) is a time-dependent factor. It is clear that the time period of measurement for the two types of experiments can play a role in determining the degree of separation that is observed. Therefore, the photographs display the condition of the emulsions closer to thermodynamic equilibrium, whilst the creaming rates are indicative of the kinetic decay of the emulsion. However, the stability against relatively long storage times for anionic surfactant-stabilised emulsions with higher calcium concentrations is anomolous.

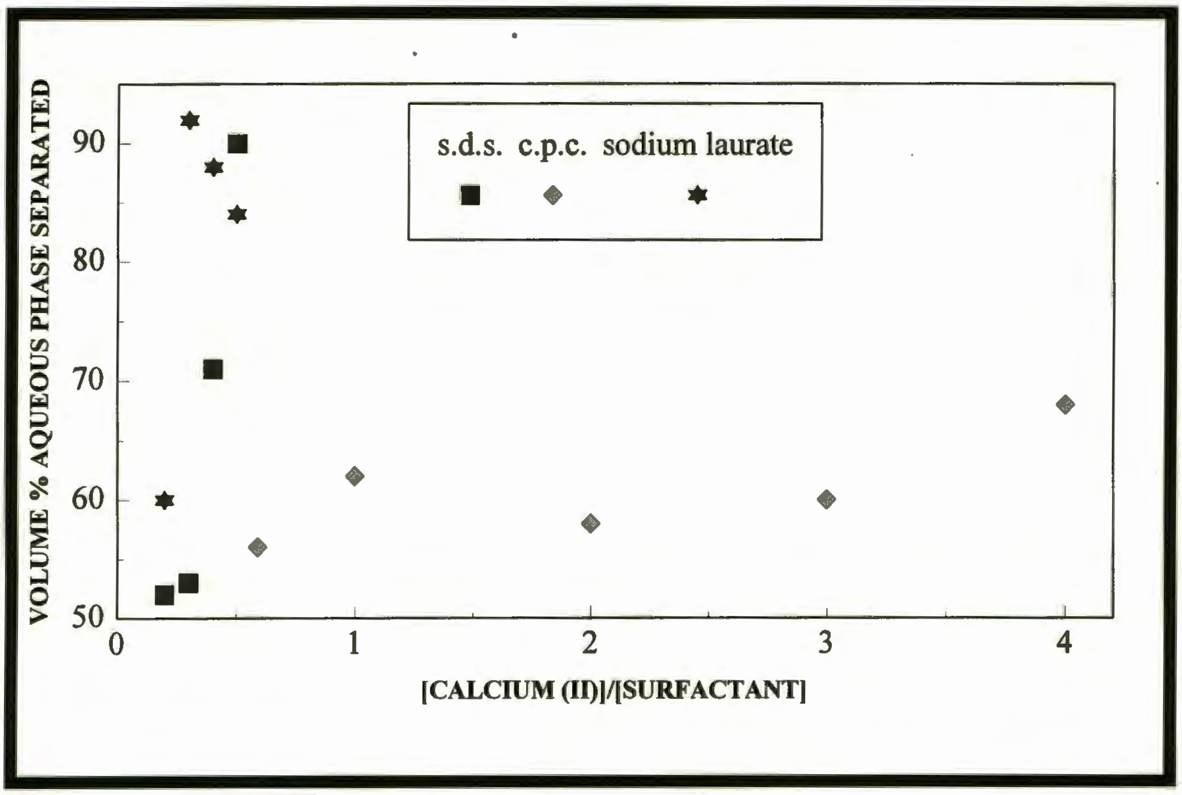

Fig. 25: effect of Ca^{+2}:surfactant ratio on creaming 10 minutes after emulsion preparation.

Fig. 26: effect of Ca^{+2}:surfactant ratio on stability: 1 % sodium dodecyl sulphate, 3 days storage. L to R: 0.1; 0.2; 0.4; 1.0.

Fig. 27: effect of Ca^{+2}:surfactant ratio on stability: 1 % sodium laurate, 3 days storage. L to R: 0.1; 0.2; 0.4; 1.0.

Fig. 28: effect of Ca^{+2}:surfactant ratio on stability: 1 % cetylpyridinium chloride, 3 days storage. L to R: 0.5; 1.0; 2.0; 3.0.

D4.6. HYDROPHILE-LIPOPHILE BALANCE (HLB)

O/w emulsions that are made from paraffinic mineral oil require surfactants with an HLB of ca. 10 for optimal stability[1, 105]. Surfactants with HLB's less than 6 favour the formation of w/o emulsions, whereas higher HLB's favour o/w emulsions. This is a direct consequence of Bancroft's rule, since low HLB values imply a low affinity for an aqueous phase and vice versa.

The HLB's of the four surfactants (Table 7) and the relative stability trends, that were inferred from the creaming rate and photography studies (Table 8), are indicated below:

TABLE 7: HYDROPHILE-LIPOPHILE BALANCES

SURFACTANT	HLB
sorbitan sesquioleate	3.7[r]
cetylpyridinium chloride	>13[s]
sodium laurate	20.9[t]
sodium dodecyl sulphate	ca. 40[r]

The trends are discussed below in relation to each surfactant, in order of increasing o/w emulsion stability.

1. Sorbitan sesquioleate formed the least stable emulsions. Sorbitan sesquioleate prefers to form a w/o emulsion, since its HLB is less than 6. It is odd that this surfactant formed o/w emulsions at all (Sec. D1.2). Bancroft's rule is closely related to the surfactant's HLB because the HLB is reflective of the solubility of

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[r] experimental value; calculated $HLB_{\text{sorbitan sesquioleate}} = 5.7^1$; calculated $HLB_{\text{sodium dodecyl sulphate}} = 37^1$

[s] freely soluble in water[1]

[t] calculated from[1]: HLB = 7 + Σ (hydrophilic group numbers) - Σ (lipophilic group numbers); -COONa = 19.1, CH_3 = -0.475, CH_2 = -0.475

the surfactant in oil and water. Sorbitan sesquioleate selectively partitioned into the paraffin and, according to the rule, gave less stable o/w emulsions since the film contained little surfactant. The inferior stability of sorbitan sesquioleate-based emulsions is evidenced by the following:

- emulsification could not be induced when sodium- or calcium chloride were present, regardless of shear rate or shear time. The addition of electrolytes increased the ionic nature of the aqueous phase. This would have lowered the HLB of the sorbitan sesquioleate to below the threshold that was required to form an emulsion.

TABLE 8: STABILITY TRENDS RELATIVE TO SURFACTANT TYPE

PARAMETER	STABILITY TREND[*]	
	CREAMING	BREAKING
IONIC STRENGTH	sodium dodecyl sulphate > cetylpyridinium chloride » sorbitan sesquioleate[u]	sodium dodecyl sulphate > cetylpyridinium chloride » sorbitan sesquioleate[u]
SURFACTANT CONCENTRATION	sodium dodecyl sulphate > sodium laurate, cetylpyridinium chloride > sorbitan sesquioleate	sodium dodecyl sulphate, sodium laurate> cetylpyridinium chloride » sorbitan sesquioleate
SHEAR TIME	sodium dodecyl sulphate > sodium laurate, cetylpyridinium chloride > sorbitan sesquioleate (general trend)	sodium dodecyl sulphate, sodium laurate > cetylpyridinium chloride > sorbitan sesquioleate
pH	sodium dodecyl sulphate > cetylpyridinium chloride » sorbitan sesquioleate	sodium dodecyl sulphate > cetylpyridinium chloride > sorbitan sesquioleate
CALCIUM CONCENTRATION	cetylpyridinium chloride > sodium dodecyl sulphate, sodium laurate » sorbitan sesquioleate[u]	cetylpyridinium chloride > sodium dodecyl sulphate, sodium laurate » sorbitan sesquioleate[u]

★ In order of decreasing o/w emulsion stability

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[u] No emulsion was formed.

creaming and breaking rates were faster when the variable was pH, shear time or surfactant concentration. With pH as the variable, breaking was apparent after 3 days compared to 16 days for sodium dodecyl sulphate and cetylpyridinium chloride. When surfactant concentration was varied, the breaking trend was manifest after 16 days compared to 91 days for the other surfactants.

2. The stabilising influence of cetylpyridinium chloride was superior only to sorbitan sesquioleate, except when calcium(II) was present. In the presence of calcium, cetylpyridinium chloride afforded the most stable emulsions because it did not complex with the Ca^{+2} (lose its surface-active properties) and did not form a solid precipitate which was oil-wettable.

   It is difficult to interpret the stabilities in terms of the HLB, since an exact figure was not available for cetylpyridinium chloride.

3. Laurate-based emulsions were very stable. It is difficult to correlate the stability of laurate-based emulsions with HLB, since such emulsions were also stabilised by the gelatinous aqueous phase as a result of the entropically-stabilised gel network. In the presence of calcium(II), it formed calcium laurate, which is an oil-wettable steric stabiliser for the inverse system. Consequently, it was a poor surfactant in the presence of this ion.

4. Sodium dodecyl sulphate generally afforded the most stable emulsions, both in terms of ease of emulsification (Table 4) and subsequent stability. It is not clear why a surfactant with an HLB much greater than the optimum should form such stable emulsions.

SECTION E

CONCLUSIONS & FUTURE STUDIES

E1. CONCLUSIONS

E1.1. DROPLET SIZE CHANGES

1. As predicted by the theory of creaming, a Boltzmann distribution of droplet sizes occurred in the creamed layer. The largest droplets appeared at the top of the layer and the polydispersity increased towards the bottom of the layer.

2. An increase in surfactant concentration or mixing time generally decreased the average droplet size but increased the polydispersity.

E1.2. STABILITY TRENDS

Stability trends were established by the development of suitable creaming rate and photographic methods and are discussed in terms of stability against creaming, flocculation and coalescence.

E1.2.1. IONIC STRENGTH

1. Sodium dodecyl sulphate- and cetylpyridinium chloride-based emulsions were destabilised towards flocculation by an increase in ionic strength. This was rationalised by the decreased electrical repulsive forces in the Stern layer. This was manifested in faster creaming rates due to larger aggregates.

2. Coalescence rates with increased ionic strength were faster in the case of cetylpyridinium chloride, but not with sodium dodecyl sulphate. The latter situation was reflective of the restabilisation that is caused by an eventual over-riding of attractive forces by repulsive forces as the average droplet size was increased upon coalescence.

E1.2.2. SURFACTANT CONCENTRATION

1. Creaming was reduced as all surfactant concentrations were increased. This was

attributed to an increase in the aqueous-phase viscosity (when the surfactants were water-soluble) and a smaller average droplet size (due to a reduction in the surface tension) during emulsification.

2. Coalescence rates with increased surfactant concentrations varied depending on the surfactant. For sodium dodecyl sulphate and sodium laurate, the emulsions were equally stable, regardless of surfactant concentration, over the concentration range and time that was studied. With cetylpyridinium chloride, an upper stability limit occurred, above which surfactant-assisted Ostwald ripening destabilised the emulsion. As the sorbitan sesquioleate concentration was increased, the stability steadily decreased for the same reason, as well as the propensity of this surfactant to form w/o emulsions.

E1.2.3. SURFACTANT TYPE & HLB

The stability trend against flocculation and coalescence was (in order of decreased stability): sodium dodecyl sulphate, laurate ⟩ cetylpyridinium chloride » sorbitan sesquioleate. Low stability with sorbitan sesquioleate was attributed to the low HLB (preference to form w/o emulsions). As the ionic nature of the aqueous phase was increased by the addition of electrolyte, sorbitan sesquioleate did not form o/w emulsions. This was due to a further lowering of its HLB. The stability of laurate-based emulsions was partially due to gel formation in the aqueous phase.

E1.2.4. SHEAR TIME

An increase in shear period always stabilised the emulsions against creaming and coalescence. This was attributed to the increased time required for smaller droplets to break entirely and their increased drag against creaming. The greater polydispersity with increased shear time was over-ruled by the smaller droplet sizes.

E1.2.5. pH

1. Sodium dodecyl sulphate-based emulsions were equally stable at all pH's towards

creaming. Cetylpyridinium chloride decomposed at higher pH's, which resulted in larger droplet sizes and faster creaming. Sorbitan sesquioleate-based emulsions were destabilised towards creaming at pH extremes. This was probably due to alteration of the ability of this surfactant to lower the surface tension sufficiently for emulsification to occur.

2. For sodium dodecyl sulphate and cetylpyridinium chloride, the coalescence trends were the same as those of the creaming rates. For sorbitan sesquioleate, progressive destabilisation was observed as the pH was lowered. This was attirbuted to the different HLB's of the hydrolysates (oleic acid and oleate) compared to that of sorbitan sesquioleate at neutral pH.

E1.2.6. CALCIUM:SURFACTANT CONCENTRATION

Cetylpyridinium chloride-based emulsions were stable against creaming and coalescence up to high Ca^{+2} concentrations because cetylpyridinium chloride is not co-ordinated by calcium(II). Sodium dodecyl sulphate- and sodium laurate-based emulsions were progressively destabilised as the Ca^{+2} concentration was raised owing to the precipitation of solid calcium salts of these surfactnats which stabilise w/o emulsions.

E1.3. CORRELATION BETWEEN METHODS

1. The correlation between droplet sizing, creaming rates and photography depended on the origins of the instability. In situations where the cause of the instability was the same for each method, correlation was excellent. An example of this situation is larger droplet sizes due to less shear. The time scales and energetic considerations of the methods differed. The initial, rapid, kinetic creaming instability sometimes yielded different results compared to the protracted, thermodynamic instabilities that were revealed by the photographic method. This occurred when the origins of the instability for the two methods differed. For example, the effect of pH on sorbitan sesquioleate showed high nstability towards creaming at both pH extremes. This was probably due to

alteration of the surface tension due to a change in the structure of the sorbitol moeiety. By contrast, the effect on storage was different because in this case, hydrolysis per se of the sorbitan sesquioleate yielded surfactants with different HLB values.

The importance of using synergic methods to ascertain overall emulsion stability (Sec. A6) is therefore highlighted by this study.

2. Rapid estimates of stability are often the most practical. In this context, droplet sizing, planar interface coalescence and photography were too time-consuming or were unrepresentative of bulk emulsion stability. The former method was also not very reproducible. The measurement of creaming rates was the most rapid quantitative method. However, because it is a kinetic parameter, it does not always correlate with long-term thermodynamic instabilities.

E1.4. OPTIMAL FORMULATION

The most stable o/w emulsions may be formulated by using low ionic strengths, long shear times, an optimal surfactant type and concentration and an optimal pH. The selection of the correct type and concentration of surfactant and the best pH may be ascertained by using photography and creaming rate measurements.

E2. FUTURE STUDIES

The study should be extended to cover the following:

1. Modelling of the instabilities using the Stochastic model and correlating these results to the empirically-determined stabilities. The experimental validation of this model would also require the measurement of zeta potentials and droplet distributions before and after coalescence.

2. Re-investigation of the droplet sizing technique. It may be best to use a

surfactant which yields less-stable emulsions than the initially-used dodecyl sulphate emulsion did. Additionally, one should measure the droplet sizes immediately after emulsification as well as in weekly intervals for a period of three months.

3. Greater focus on the HLB that is required to stabilise the emulsions. This could include using an emulsifier with the optimal HLB (e.g. polyoxyethylene sorbitan monooleate with five polyoxyethylene moeities has an HLB of 10.0[106]) and combinations of the surfactants (co-emulsifiers). As part of this study, one should establish the reason that sorbitan sesquioleate did not form a w/o emulsion and the kinetics of sorbitan sesquioleate hydrolysis.

4. The use of high-temperature storage to accelerate the coalescence process, thereby combining photography as a rapid adjunct to creaming rates for the assessment of overall stability.

5. Correlation of the aqueous phase viscosities with the observed emulsion stabilities by measurement of those viscosities.

SECTION F

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SECTION G

APPENDIX

G1. RELATIVE REFRACTIVE INDICES

TABLE 9: RELATIVE REFRACTIVE INDICES OF AQUEOUS AND OIL PHASES

PHASE COMPOSITION	REFRACTIVE INDEX $({}^{D}{}_{20}n)$	REFRACTIVE INDEX RELATIVE TO HEPTANE	REFRACTIVE INDEX RELATIVE TO PARAFFIN
sodium dodecyl sulphate (aq., 0.005 M) in NaCl (mol.dm^{-3}):		1.04	1.10
0	1.3341		
0.05	1.3333		
0.1	1.3357		
0.2	1.3362		
0.3	1.3371		
0.5	1.3375		
1.0	1.3421		
sodium dodecyl sulphate (aq., % m/v):			
0.25	1.3333		
1	1.3341		
2.5	1.3358		
5	1.3389		
sodium laurate (aq., %m/v):			
1	1.3351		
2	1.3362		
cetylpyridinium chloride (aq., % m/v):			
0.5	1.3343		
1	1.3352		
sorbitan sesquioleate in paraffin oil (% m/v):		-	1.11★
1	1.4766		
5	1.4766		
10	1.4769		
Heptane	1.3878	-	-
Paraffin oil	1.4739		
Water	1.3333		

★ Relative to water

G2. DROPLET SIZING: VARIABLE EXTREMES

TABLE 10: EFFECT OF VARIABLE EXTREMES ON DROPLET DISTRIBUTION (HEPTANE)

VARIABLE	VALUE	SAMPLING POSITION IN CREAMED LAYER*			
		TOP		BOTTOM	
		D[4,3] (µm)	SPAN	D[4,3] (µm)	SPAN
IONIC STRENGTH (M)	0	38.9 ± 7.60	1.53 ± 0.14	30.3 ± 7.57	1.48 ± 0.06
	0.3	42.3 ± 0.03	1.34 ± 0.04	40.2 ± 5.78	1.40 ± 0.11
SURFACTANT CONCENTRATION (% m/v)	0.25	26.7 ± 5.34	2.18 ± 0.54	24.3 ± 6.71	1.93 ± 0.27
	2.5	41.7 ± 2.54	1.46 ± 0.10	25.0 ± 6.66	1.97 ± 0.76
pH	2	36.9 ± 3.43	1.31 ± 0.11	33.6 ± 2.55	1.54 ± 0.23
	11	33.1 ± 3.11	1.38 ± 0.07	41.3 ± 5.64	1.50 ± 0.18

★ n=3 (same sample)

G3. CREAMING RATES

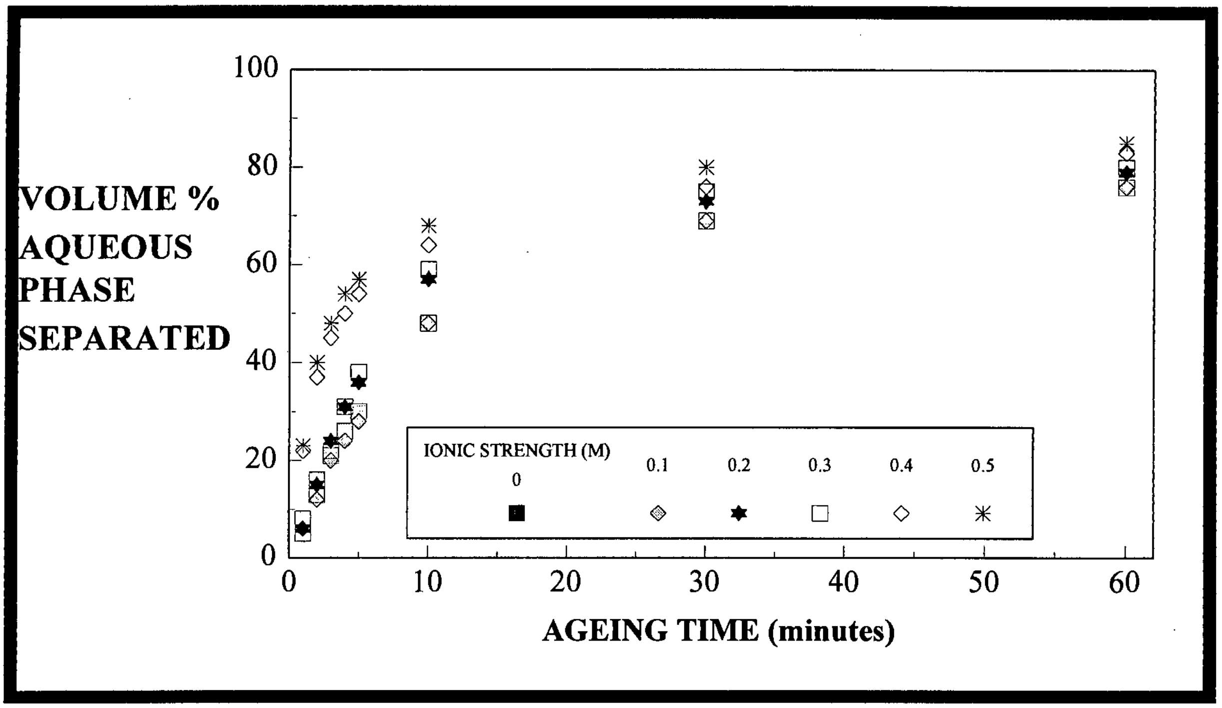

Fig. 29: effect of ionic strength on creaming rate of o/w emulsions containing 1 % sodium dodecyl sulphate.

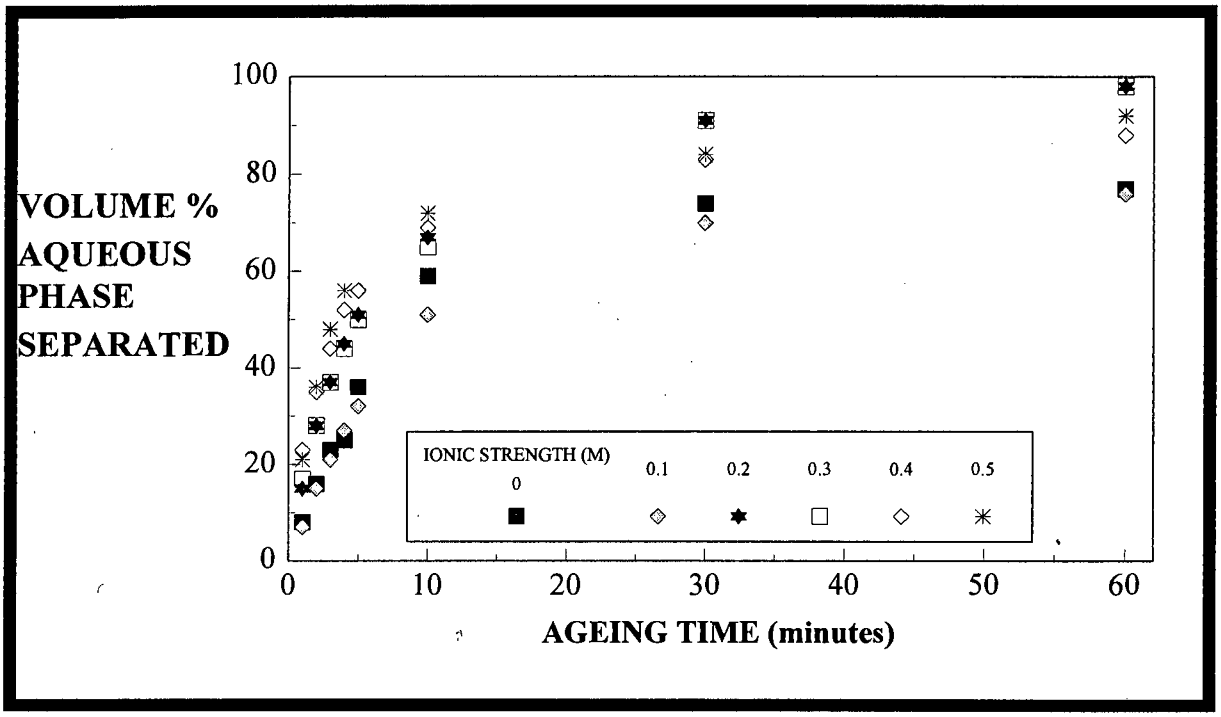

Fig. 30: effect of ionic strength on creaming rate of o/w emulsions containing 1 % cetylpyridinium chloride.

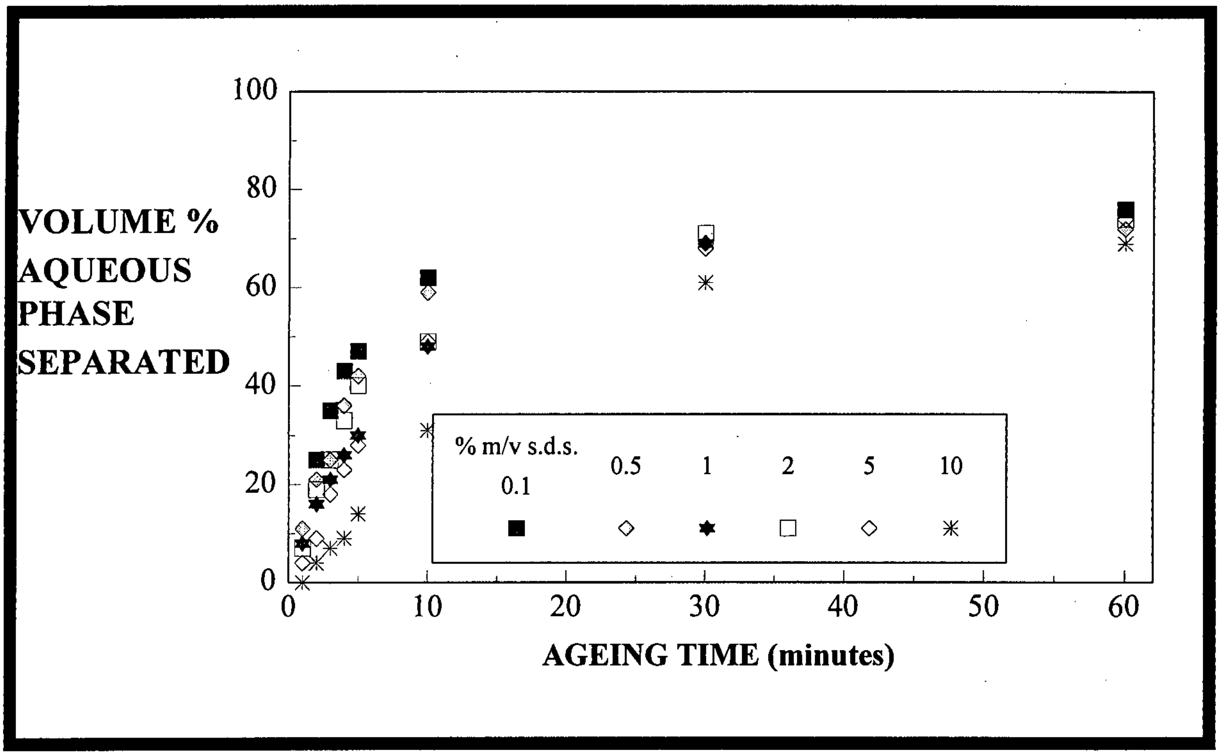

Fig. 31: effect of surfactant concentration on creaming rate for o/w emulsions containing sodium dodecyl sulphate.

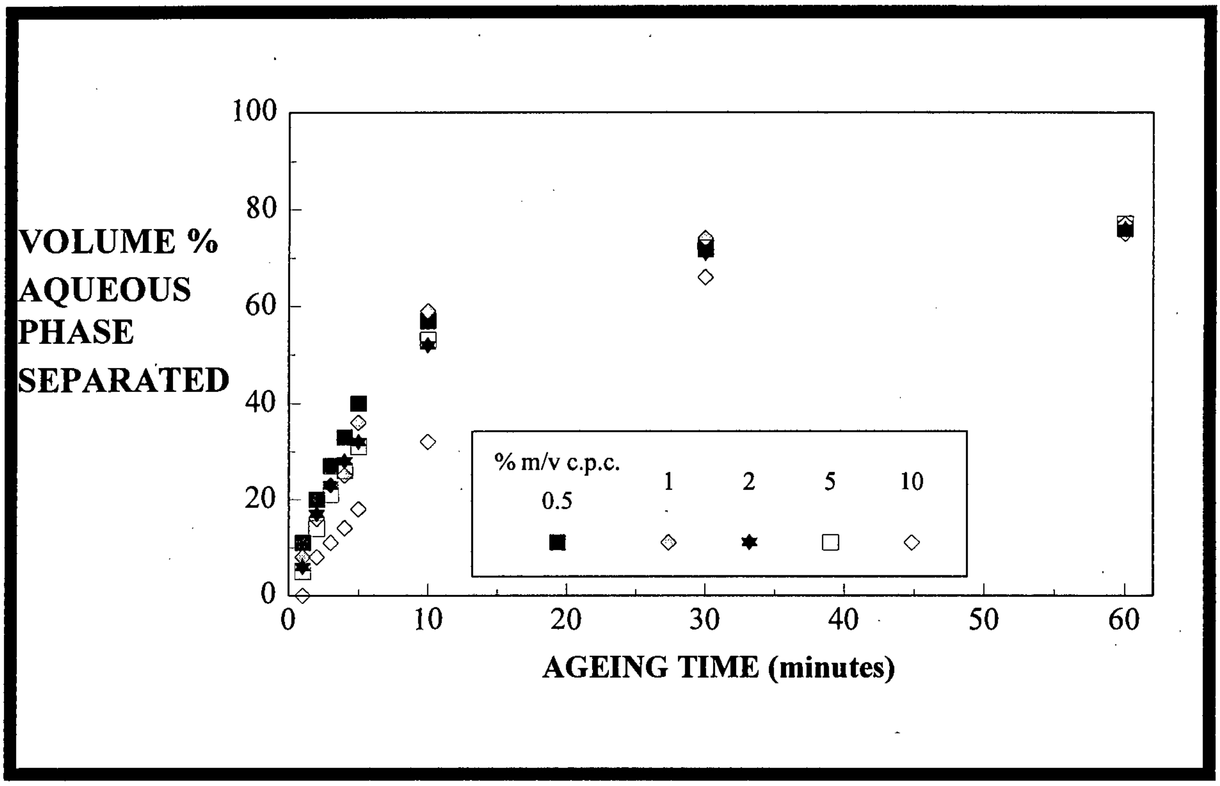

Fig. 32: effect of surfactant concentration on creaming rate for o/w emulsions containing cetylpyridinium chloride.

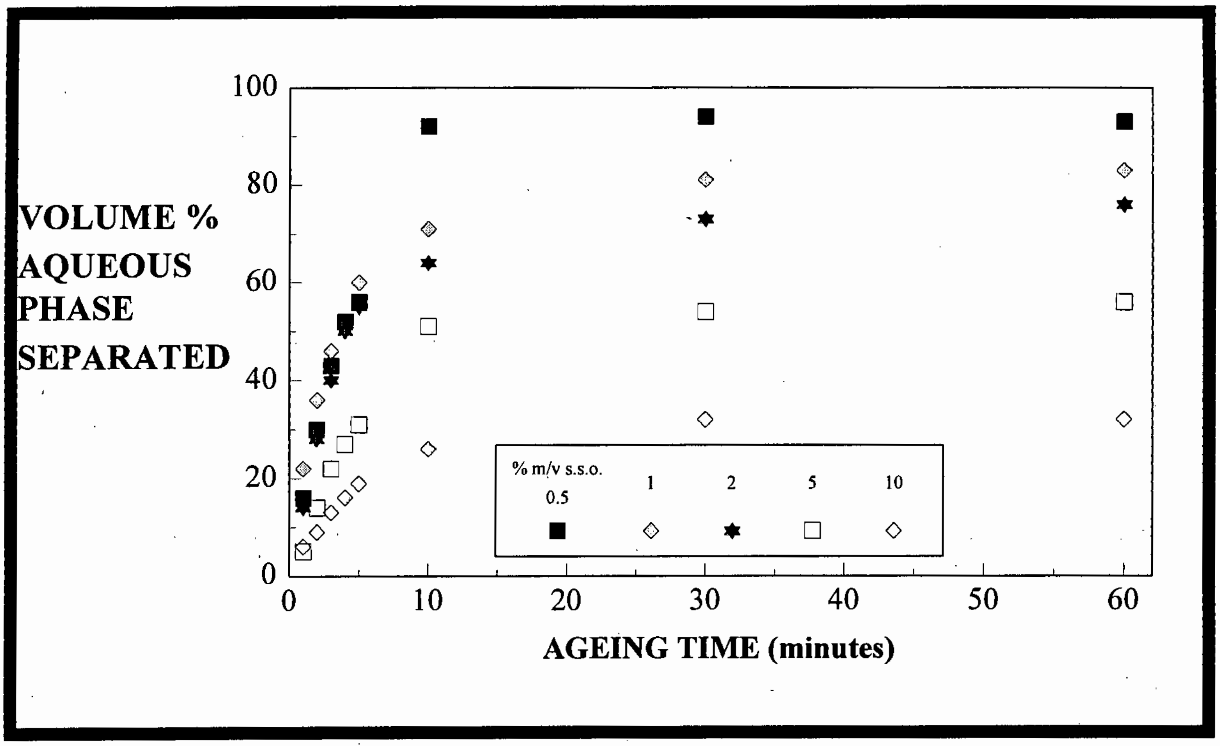

Fig. 33: effect of surfactant concentration on creaming rate for o/w emulsions containing sorbitan sesquioleate.

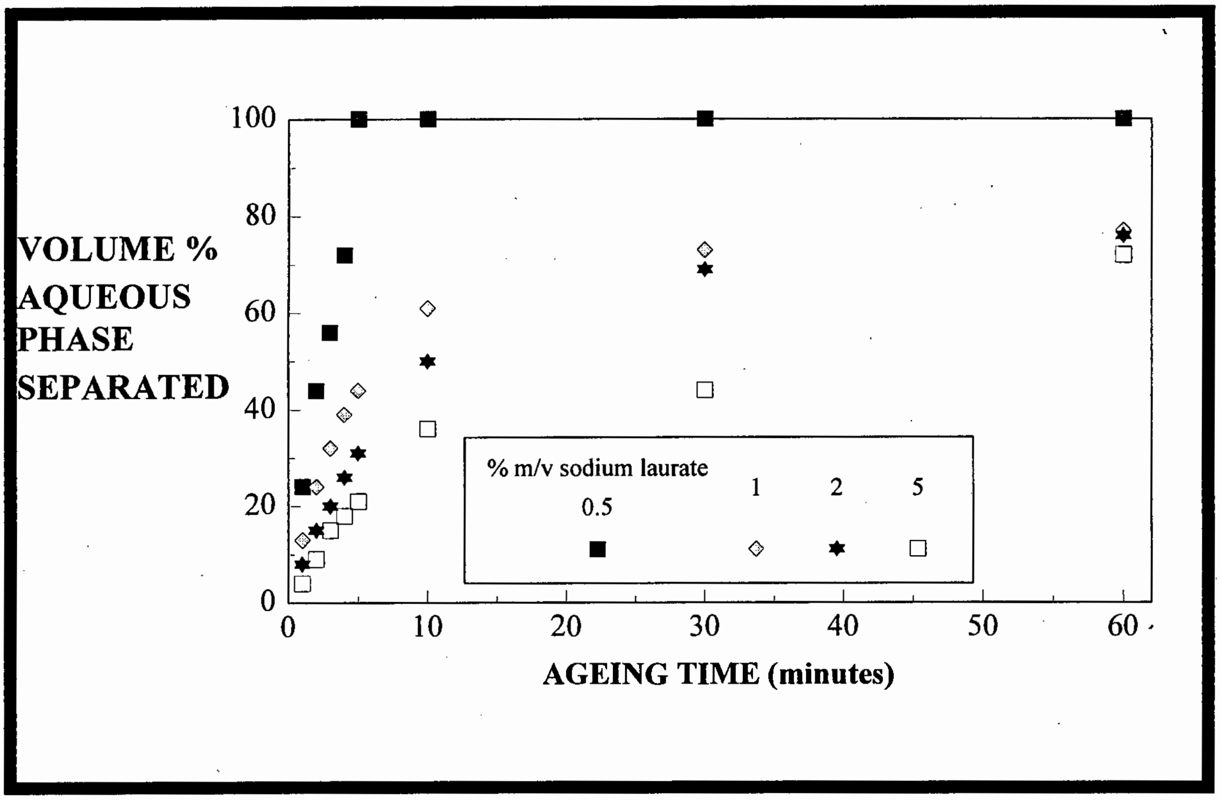

Fig. 34: effect of surfactant concentration on creaming rate for o/w emulsions containing sodium laurate.

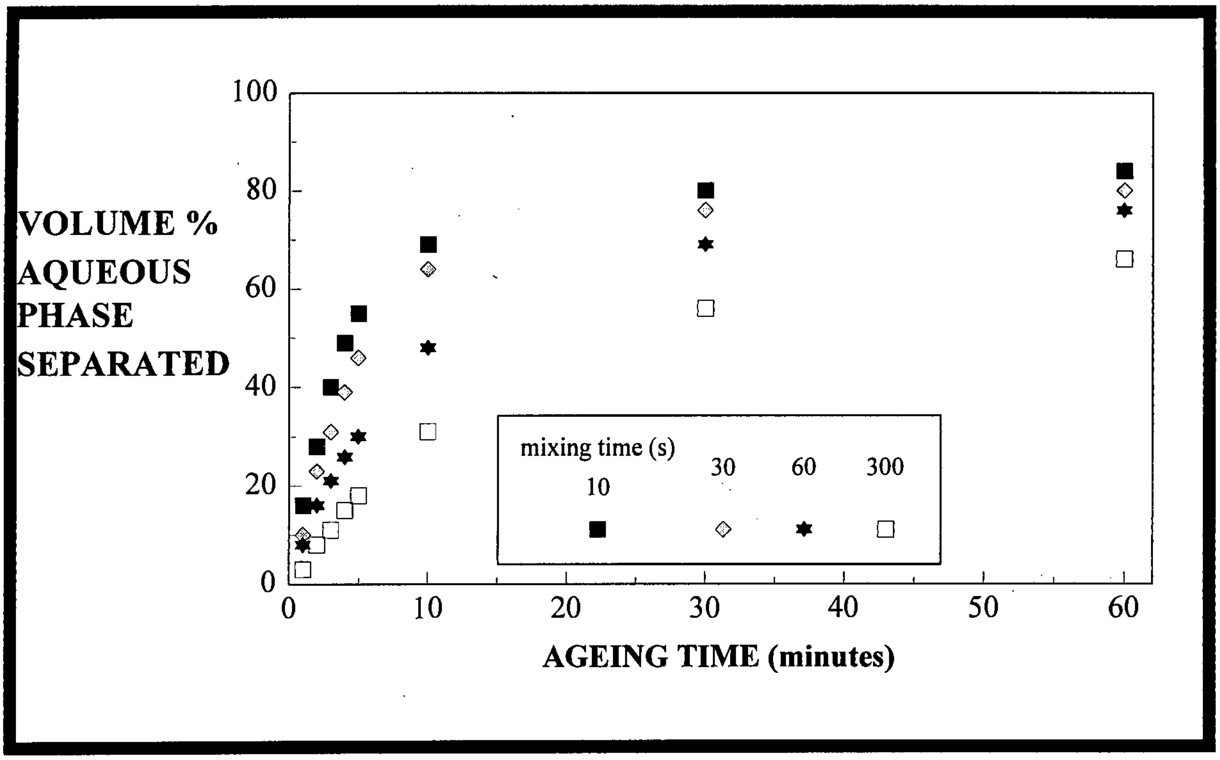

Fig. 35: effect of shear time on creaming rate for o/w emulsions containing 1 % sodium dodecyl sulphate.

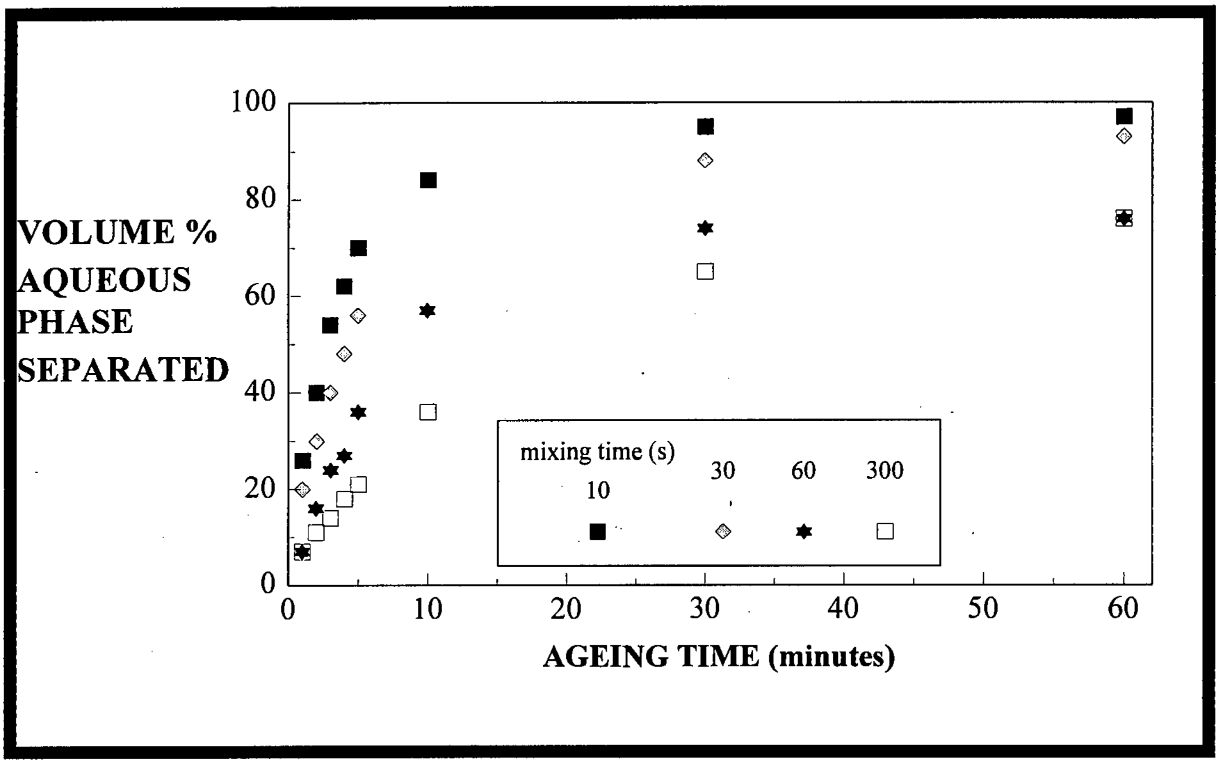

Fig. 36: effect of shear time on creaming rate for o/w emulsions containing 1 % cetylpyridinium chloride.

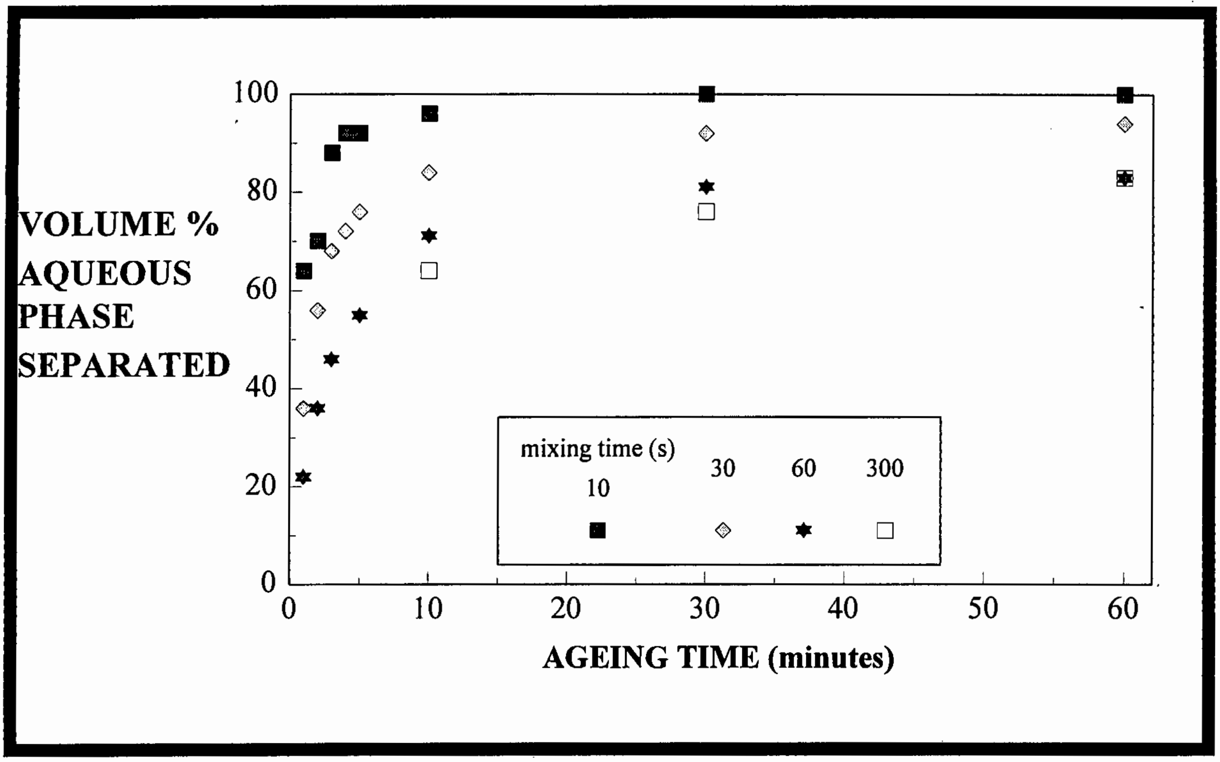

Fig. 37: effect of shear time on creaming rate for o/w emulsions containing 1 % sorbitan sesquioleate.

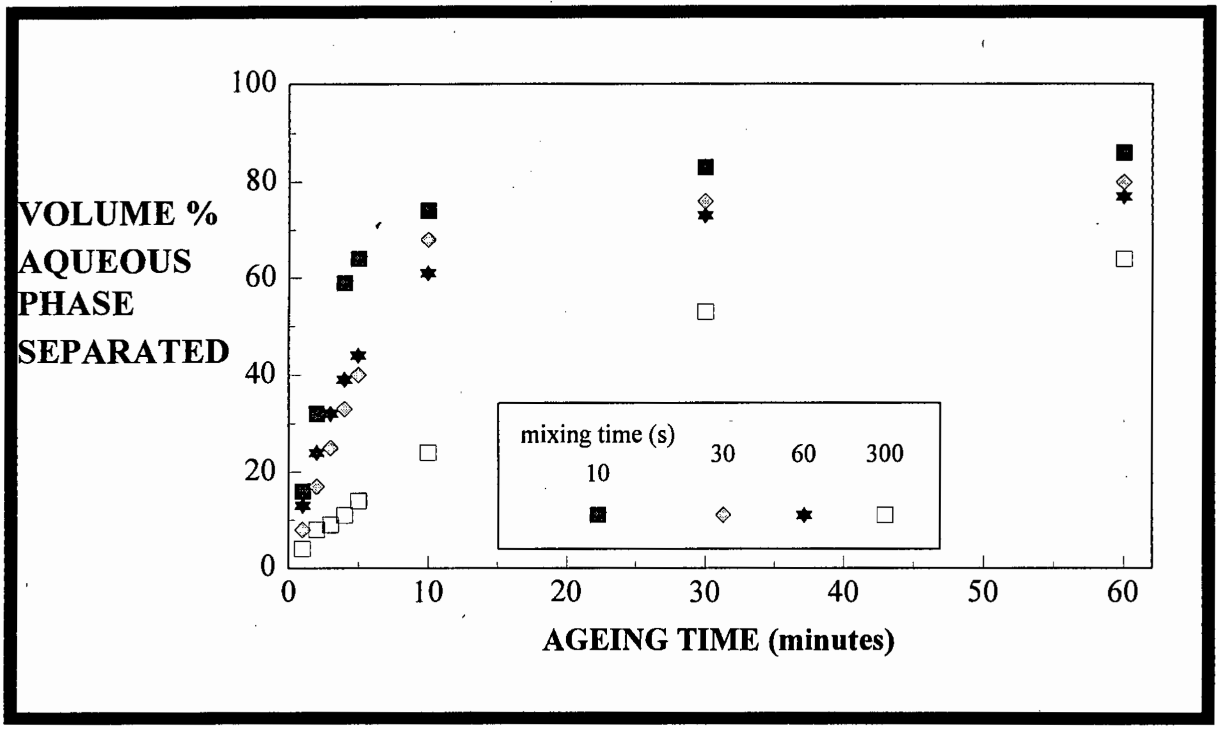

Fig. 38: effect of shear time on creaming rate for o/w emulsions containing 1 % sodium laurate.

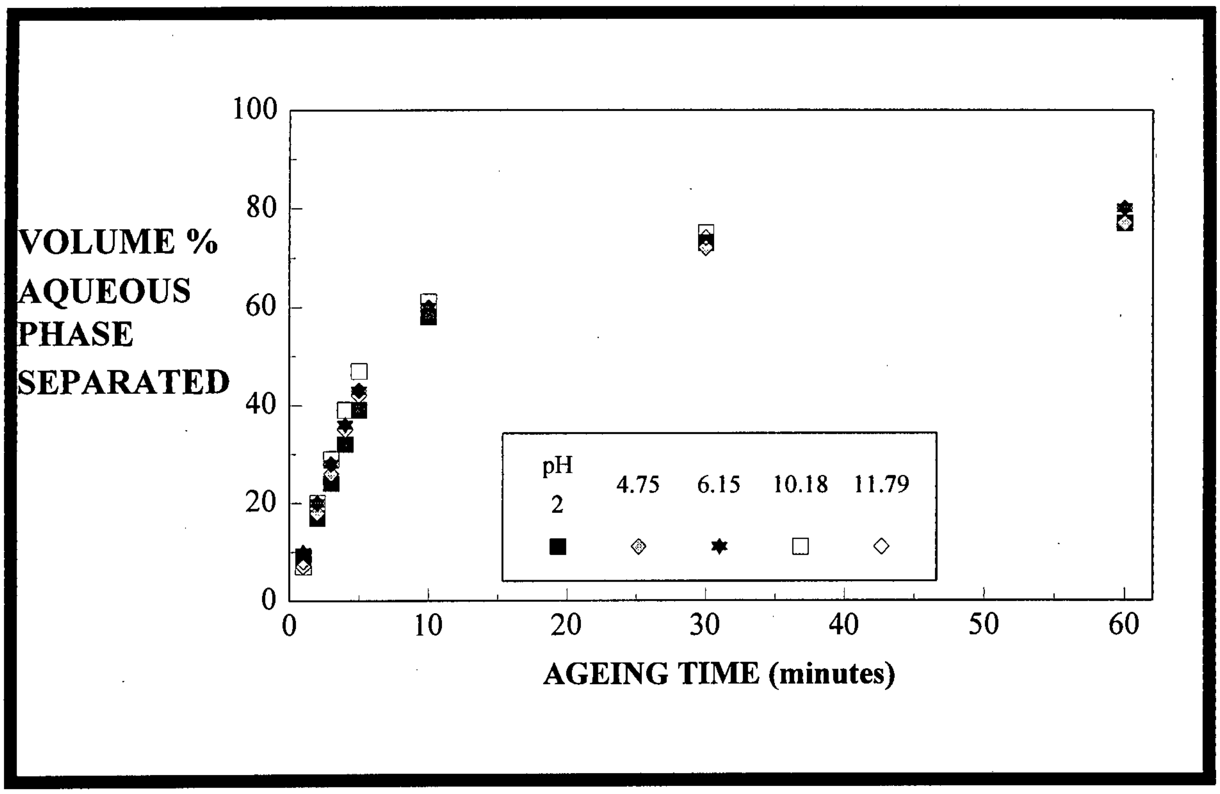

Fig. 39: effect of aqueous phase pH on creaming rate of o/w emulsions containing 1 % sodium dodecyl sulphate.

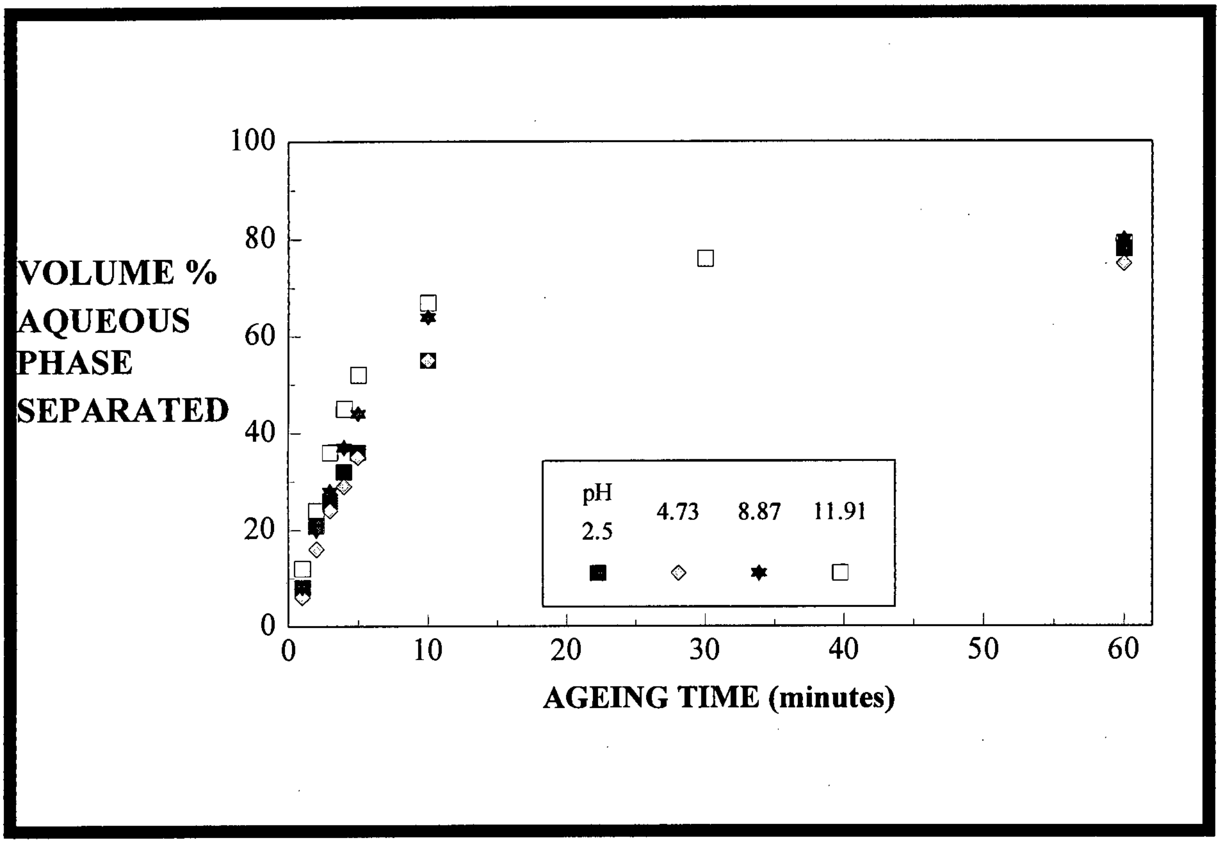

Fig. 40: effect of aqueous phase pH on creaming rate of o/w emulsions containing 1 % cetylpyridinium chloride.

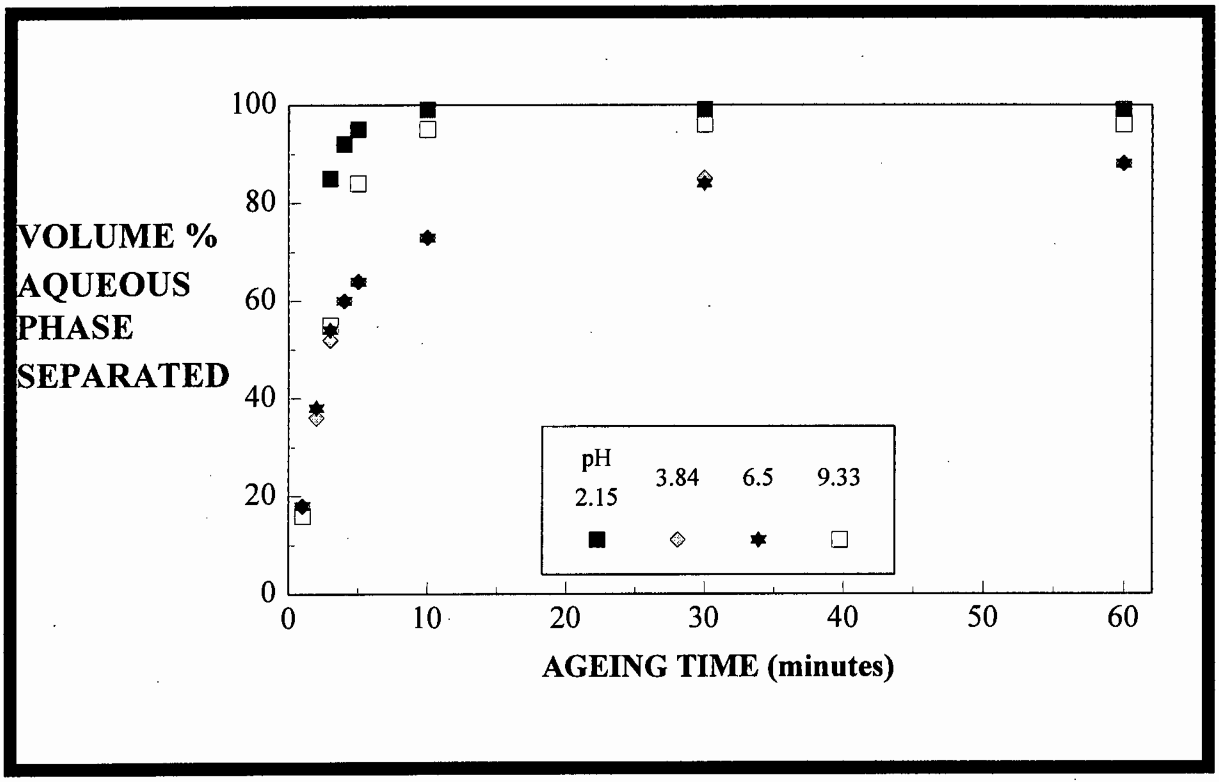

Fig. 41: effect of aqueous phase pH on creaming rate of o/w emulsions containing 1 % sorbitan sesquioleate.

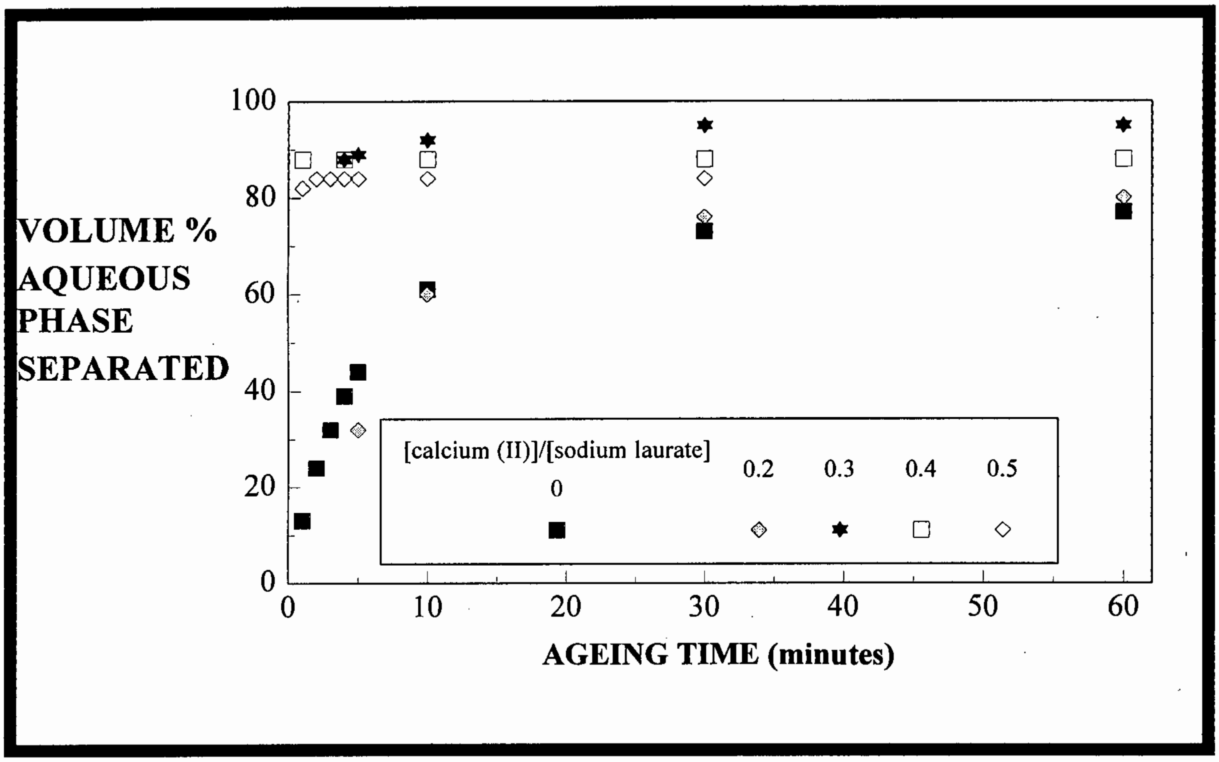

Fig. 42: effect of Ca^{+2}:sodium laurate concentration on creaming rate of o/w emulsions containing 1 % sodium laurate.

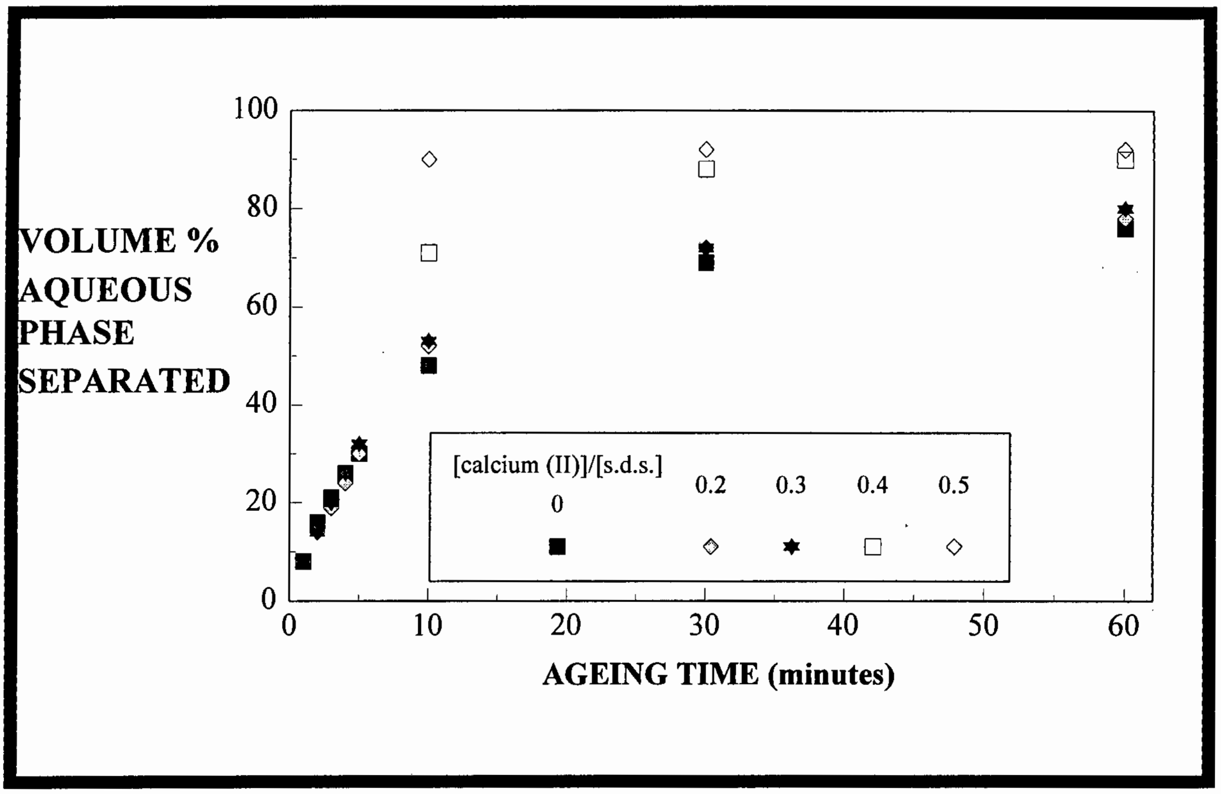

Fig. 43: effect of Ca^{+2}:sodium dodecyl sulphate ratio on creaming rate of o/w emulsions containing 1 % sodium dodecyl sulphate.

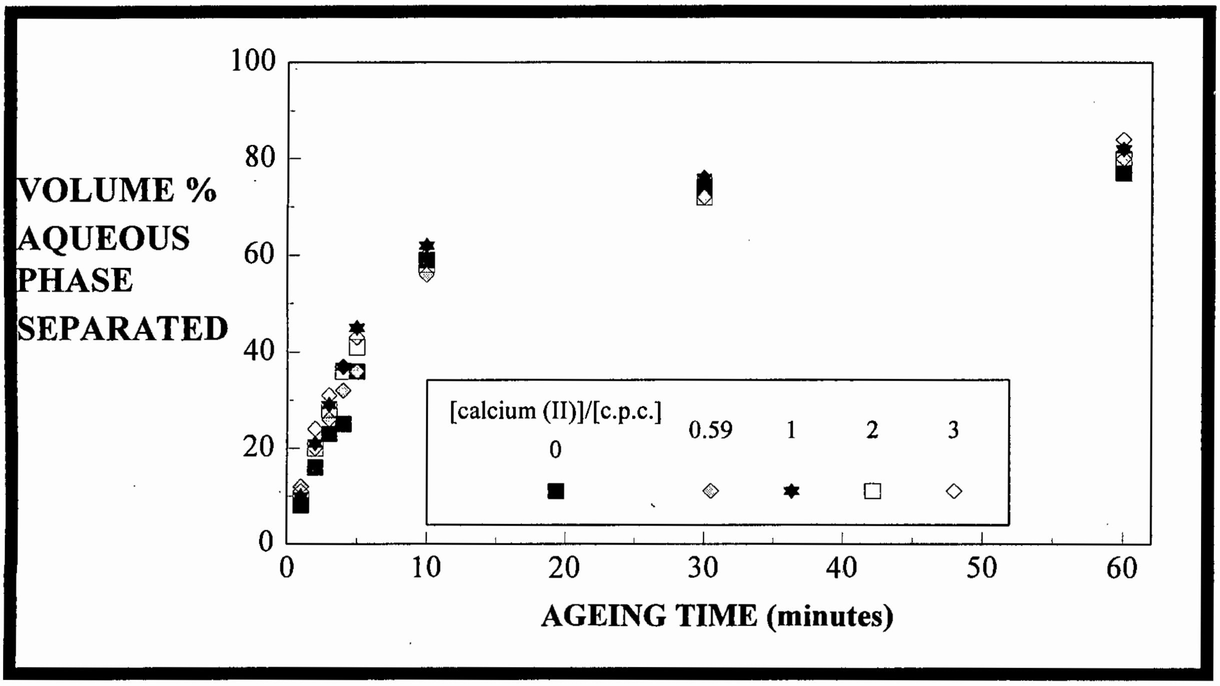

Fig. 44: effect of Ca^{+2}:cetylpyridinium chloride ratio on creaming rate of o/w emulsions containing 1 % cetylpyridinium chloride.