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Role of Surfactants and Polymers in Disperse Systems *

Th. F. Tadros

Surfactants and polymers are commonly used in the preparation of disperse systems e.g. suspensions, emulsions and microemulsions, and their subsequent stabilisation. This occurs in many industrial applications of which one may mention paints, dyestuffs, cosmetics, agrochemicals, pharmaceuticals, paper coatings, ceramics and polymer colloids. Surfactants and polymers are used in preparation of solid/liquid dispersions either by condensation or comminution methods. In condensation methods surfactants and polymers control the nucleation and growth of particles. This is particularly the case for the preparation of polymer suspensions by emulsion or dispersion polymerisation. With emulsion polymerisation, surfactants and polymers are used for preparation of monomer emulsions which are then polymerised by addition of an initiator. With dispersion polymerisation, the monomer is dissolved in a solvent to which an initiator and a protective agent is added. The protective agents usually consists of a block or graft copolymer that consists of two main chains : an anchoring chain to the particle surface and a stabilising chain that is well solvated by the medium. In dispersion (comminution) methods a surfactant or polymer is added to facilitate wetting of the powder by the liquid ; breaking of aggregates and agglomerates and comminution of the particles. By adsorption at the particle surface and within cracks, the comminution of particles is facilitated.

Surfactants and polymers also are added for emulsification of oil into water or water into oil. The role of the surfactant and/or polymer is several fold. By adsorption at the liquid-liquid interface, the interfacial tension γ is reduced and hence the energy required for creating a new surface is reduced. On the other hand, by creating an interfacial tension gradient (dγ/dA), i.e. Gibbs elasticity, film thinning and rupture is reduced, thus reducing coalescence. Finally, the adsorbed surfactant or polymer will provide an energy barrier that reduces close approach of the particles, thus preventing flocculation and coalescence.

Various types of interaction forces may be envisaged when surfactants and polymers are added to dispersions. With ionic surfactants, a double layer is produced which produces strong repulsion on close approach of the particles or droplets. This double layer repulsion counteracts the Van der Waals attraction, thus ensuring colloid stability. With nonionic surfactants and polymers, repulsion occurs as a result of steric interaction between the adsorbed layer. This steric interaction consists of two main contributions : mixing or osmotic and entropic, elastic or volume restriction interaction. As long as the chains are in good solvent conditions, steric repulsion may produce dispersion that approach thermodynamic stability.

Surfactants are also used for preparation of microemulsions. These are clear isotropic thermodynamically stable systems where specific interactions should occur at the interface resulting in ultra-low interfacial tension. In this case, the positive energy of expanding the interface is compensated by the entropy of dispersion and the net free energy of formation of the microemulsion is zero or negative. Both ionic and nonionic surfactants can be used for preparation of microemulsions and in all cases a system has to be chosen that produces

an ultra-low interfacial tension. The thermodynamic's of formation and stability of microemulsions can be analysed by considering the free energy of the various steps involved in producing the microemulsion. These involve the free energy of mixing the surfactants with both phases, and the free energy required to expand the interface and the free energy of dispersion of the droplets.

Introduction

Surfactants and polymers are commonly used in the preparation of disperse systems, e.g. suspensions, emulsions and microemulsions, and their subsequent application. For that reason surfactants and polymers are used in many industrial preparations of which one may mention paints, dyestuffs, paper coatings, cosmetics, agrochemicals, pharmaceuticals, polymer colloids and ceramics. The role of surfactants and polymers in dispersing solids-in-liquids and liquids-in-liquids is clear from their property of accumulating at the solid/liquid and liquid/liquid interface. A surfactant or polymer usually consists of two portions, one with high affinity to the particle or droplet surface (sometimes referred to as the anchoring chain) and one with a high affinity to the medium (referred to as the stabilising chain).

With surfactants, the molecules may take different orientations depending on the nature of the surface and the medium. In the case of ionic surfactants, the orientation of the molecule at the interface is determined by the balance between electrostatic interaction and other types of interactions such as hydrophobic, hydrogen bonding and polar interactions. For example, for a hydrophobic surface that is also charged, the ionic surfactant may adsorb by hydrophobic bonding or electrostatic interaction (if the surface and head group are oppositely charged). On the other hand, with a nonionic surfactant such as an alkyl ethoxylate, interaction may occur via the alkyl group or poly(ethylene oxide) chain. At relatively high surfactant concentration, same association of the surfactant molecules may occur resulting in the formation of hemimicelles. For a detailed account on surfactant

adsorption, one may refer to some recent review articles on the subject [1, 2].

The adsorption and orientation of polymer is relatively more complicated [3, 4]. Apart from the interaction with the surface and the solvent, one of the major considerations is the conformation of the macromolecule at the interface. This is illustrated in *Fig. 1* which shows the orientation of polymer molecules having different structures. Thus, in describing polymer adsorption one has to consider three main parameters : (a) the total amount of the polymer adsorbed per unit area (Γ) ; (b) the number of segments (or groups) that are in close contact with the surface (fraction of segments p) and their interaction with the surface, and (c) the extension of the polymer layer from the surface, which is described in terms of the segment density distribution $\varrho(z)$ or the adsorbed layer thickness δ. Polymers can interact with the surface with high affinity (*i.e.* irreversibly adsorbed) and they can produce relatively thick layers (compared to surfactants) and hence they are more effective for steric stabilisation.

In this review, which is by no means extensive, I will describe the role of surfactants and polymers in the preparation of solid/liquid dispersions (suspensions) and liquid/liquid dispersions (emulsions). This will be followed by sections on dispersion stabilisation by surfactants and polymers whereby both electrostatic and steric forces will be considered. Finally a section will be devoted to the role of surfactants in the preparation of microemulsions and the origin of their thermodynamic stability.
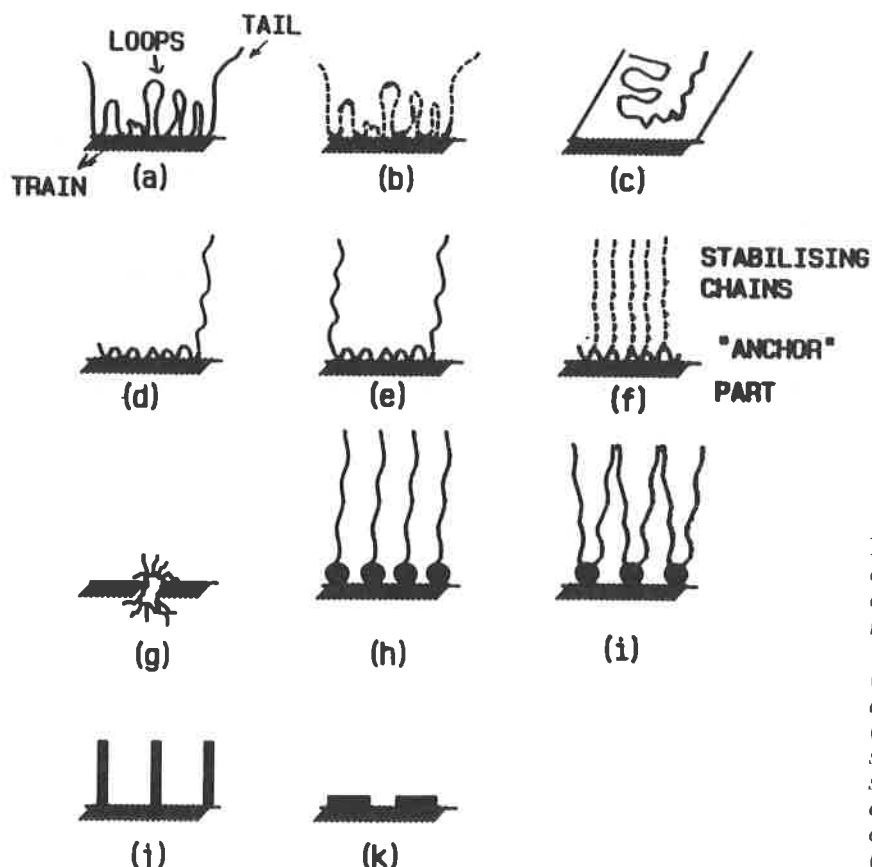

FIGURE 1. - *Various conformations of macromolecules adsorbed on a plane surface. (a) Random conformation of loops-tails-trains (homopolymer) ; (b) preferential adsorption of short "blocks" ; (c) chain lying totally on the surface ; (d) A block with loop-train configuration for B and one long tail for A ; (e) ABA block as with (d) ; (f) BA$_n$ graft with backbone (B) forming small loops leaving tails of A ("teeth") ; (g) "star" shaped molecule ; (h) single point attachment at chain end ; (i) single point attachment at middle of chain ; (j) "rod" shaped molecule lying vertical ; (k) rod shaped molecule lying horizontal.*

Role of surfactants and polymers in the preparation of suspensions and emulsions

Role of surfactants in preparation of suspensions

There are two main procedures for preparation of suspensions. The first depends on the "build up" of particles from molecular units, *i.e.* the so called condensation methods, which involve two main steps, nucleation and growth. In this case, it is necessary to prepare a molecular (ionic, atomic or molecular) distribution of the insoluble substance ; then by changing the conditions precipitation is caused leading to the formation of nuclei that grow to the particles in question. In the second procedure, usually referred to as a dispersion process, larger "lumps" of the insoluble substances are subdivided by mechanical or other means, into smaller units. This method is referred to as comminution when dealing with solid/liquid dispersions and emulsification when dealing with liquid/liquid dispersion. The role of surfactants and polymers in both processes will be considered below.

Role of surfactants and polymers in condensation methods

To understand the role of surfactants in the condensation methods, it is essential to consider the major processes involved, namely nucleation and growth. Nucleation is the spontaneous process of the appearance of a new phase from a metastable (supersaturated) solution of the material in question [5]. The initial stages of nucleation results in the formation of small nuclei, where the surface to volume ratio is very large and hence the role of the specific surface energy is very important. With progressive increase of the size of the nuclei, the ratio becomes small and eventually the free energy of formation of a new phase becomes larger than the surface free energy. This leads to the spontaneous increase of crystal size, with a corresponding reduction in the role played by the specific surface energy. Addition of surfactants and polymer, which can either adsorb on the surface of a nucleus, or act as a centre for inducing nucleation, can be used for controlling such a process of formation of nuclei and the subsequence stabilisation of the particles formed.

According to Gibbs [5] and Volmer [6], the free energy of formation, ΔG, of a spherical nucleus is given by the expression,

$$\Delta G = 4\pi r^2 \gamma - \frac{4\pi r^3 \varrho}{3\,M} RT\,ln\,(S/S_o) \qquad (1)$$

where r is the radius of the nucleus, γ is the specific surface energy, M is the molecular weight, ϱ is the density, (S/S_o) is the relative supersaturation), R is the gas constant and T the absolute temperature.

Since the second term on the right hand side in equation (1) rises faster with increase of r than the first term (r^3 versus r^2 respectively), there is a critical size r^*, above which the free energy of formation falls, after reaching a maximum, and the cluster tends to grow. This is illustrated in *Fig. 2* which shows the variation of ΔG_s (first term on the right hand side of equation), ΔG_v (the second term) and ΔG with nucleus dimension l.

The critical radius r^* can be obtained by differentiation of equation (1) with respect to r and equating to zero. This leads to the following expression,

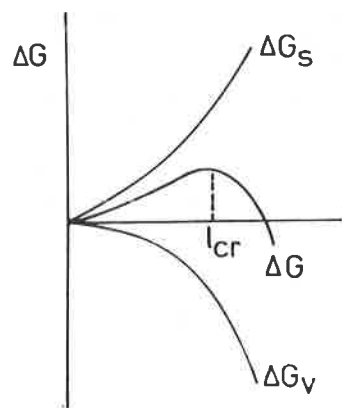$$r^* = \frac{2\,\gamma\,M}{\varrho\,RT\,ln\,(S/S_o)} \qquad (2)$$

FIGURE 2. - *Variation of free energy of formation of a nucleus with radius.*

The free energy ΔG^* at the maximum, *i.e.* at $l = r^*$ is given by

$$\Delta G^* = \frac{16}{3}\,\frac{\pi\,\gamma^3\,M^2}{(\varrho\,RT)^2\,[ln\,(S/S_o)]^2} \qquad (3)$$

It can be seen from equations (1) - (3) that ΔG, r^* and ΔG^* depend on two main parameters γ and (S/S_o) both of which can be affected by surfactants and polymers. Adsorption of surfactants and polymers cause a reduction in γ, whereas any micelles or polymer aggregates may effect (S/S_o) as a result of incorporation of the molecules of the material to be precipitated in these aggregate units. This process, usually referred to as solubilisation, will affect the chemical potential of the species and hence may increase or reduce the rate of nucleation. In addition, if the surfactant and polymer adsorbs preferentially on one of the faces or edges of the resulting particle formed, crystal habit modification may occur.

Surfactants and polymers play a major role in the preparation of suspensions of polymer particles by heterogenous nucleation. This may be illustrated by considering dispersion and suspension polymerisation. In emulsion polymerisation, the monomer is emulsified in a non-solvent (usually water) using a surfactant or polymer, whereas the initiator is dissolved in the continuous phase. Nucleation may occur in the swollen surfactant micelle or the polymer aggregates. Indeed, the number of particles formed and their size depends to a large extent on the nature of surfactant or polymer used and their concentration [7]. In some cases, the number of particles produced is directly proportional to the number of micelles formed [7].

Dispersion polymerisation differs from emulsion polymerisation, in that the reaction mixture consisting of monomer, initiator and solvent (aqueous or non-aqueous) is usually homogeneous, but as polymerisation proceeds, polymer separates out and the reaction continues in a heterogeneous manner [8]. A dispersant, *i.e.* "protective agent", such as a surfactant, block or graft copolymer is added to stabilise the particles once formed. Again, the number of polymer particles found in a given volume of polymer dispersion depends directly on the concentration of surfactant or polymer used. Dispersants are specifically designed to achieve maximum stabilisation. The most effective materials are those of the block and graft type (see *Fig. 1*) which consists of two components, one insoluble in the medium and having a very high affinity to the particles formed (the "anchoring" point) whereas the second component consists of polymer chains that are soluble in the medium and strongly solvated by it [8]. The structure and size of the two components (*i.e.* their molecular weights) depends on the requirements needed such as particle size, stability, etc.

Role of surfactants and polymers in solid/liquid dispersion

Dispersion methods are used and for the preparation of preformed particles. The term dispersion is used to refer to the complete process of incorporating the solid in the liquid such that the final product consists of fine particles uniformly distributed throughout the dispersion medium. The role of surfactants or polymers in the dispersion process can be seen from a consideration of the various stages involved [9] :

(a) weeting of the powder by the liquid ;

(b) breaking of aggregates and agglomerates, and

(c) comminution of the resulting particles by using a wet milling process.

It is obvious that the particles formed should be maintained in the dispersed state during the above mentioned processes.

The wetting of a powder by a liquid is a process in which the solid/air interface is replaced by the solid/liquid interface. For complete wetting, it is essential to replace all the adsorbed air and other contaminants. Moreover, it is also essential to wet the external and internal surfaces and displace any air entrapped between the particles or present in the pore of the agglomerated particles. All these processes require the addition of dispersant (surfactant, polymer or polyelectrolyte) to the continuous medium.

The wetting of a solid by a liquid is described in terms of the equilibrium contact angle θ and the appropriate interfacial tensions, using the classical Young's equation,

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \qquad (4)$$

where γ represents the interfacial tension and S, L and V refer to the solid, liquid and vapour respectively. It is clear from equation (4) that if $\theta < 90^{\circ}$, a reduction in γ_{LV} improves wetting. Hence, the use of surface active agents or polymers which reduce γ_{LV} and γ_{SL} to aid wetting is clear.

The process of wetting of particulate solids involves at least three distinct, types of wetting, namely adhesional wetting w_a, immersional wetting w_i and spreading wetting w_s. This is illustrated in *Fig. 3* by considering the very simple case of wetting of a cube of 1 cm² external surface. In this case, the work of dispersion w_d is given by the equation :

$$w_d = w_a + w_i + w_s = 6\gamma_{SL} - 6\gamma_{SV} = -6\gamma_{LV}\cos\theta \qquad (5)$$

which, put on a unit area basis is the same as equation (4).

Thus the wetting of a solid by a liquid depends on the measurable quantities, γ_{LV} and θ. In practice, since surface active agents are added in sufficient quantities, θ is after very close to zero and spontaneous dispersion of a powder in a surfactant solution is the rule rather than the exception. The addition of the surface active agent also causes a reduction in γ_{LV} and if adsorbed on the surface of the solid also reduces γ_{SL}, both effects result in enhanced wetting.
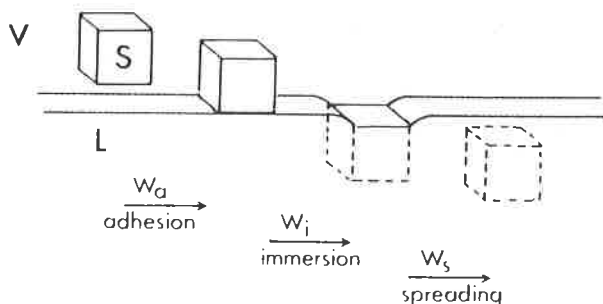

FIGURE 3. - *The three stages involved in the complete wetting of a solid cube by a liquid.*

The next stage to consider is the wetting of the internal surface which implies penetration of the liquid into channels between and inside the agglomerates. This process is analogous to flow of liquids through a capillary, which for a tube of radius r, gives the following equation for the pressure P required for penetration,

$$P = -(2\gamma_{LV}\cos\theta/r) = -2(\gamma_{SV} - \gamma_{SL})/r \qquad (6)$$

where θ is the angle of contact of the liquid with the capillary wall. As long as $\theta < 90^{\circ}$, penetration is spontaneous. To reduce θ, γ_{SL} has to be made as small as possible by sufficient adsorption of the surface active agent. However, when $\theta = 0$, P is proportional to γ_{LV}, *i.e.* a large surface tension is desirable for enhanced penetration. However, an increase in γ_{LV} would lead to an increase in θ and hence a compromise has to be made between the two opposing effects.

Another important factor in the wetting process is the kinetics of penetration of the liquid into the channels between and inside the agglomerates. Assuming the latter to be represented by a bundle of capillaries, the rate of penetration of a liquid into a powder may be treated using the Rideal-Washburn equation [10, 11], *i.e.* :

$$\frac{dl}{dt} = \frac{r\,\gamma_{LV}\cos\theta}{4\,\eta\,l} \qquad (7)$$

where l is the distance the liquid has travelled along the pore at time t, r is the radius of the capillary tube and η is the viscosity of the liquid. Thus, the rate of penetration increases with increase of γ_{LV} and decrease of θ, but is reduced by increase of η. As mentioned above, high γ_{LV} and low θ are normally incompatible and a low η is certainly very important.

Breaking of aggregates (clusters of particles formed at their crystal faces) and agglomerates (clusters formed at corners or edges) is also facilitated by the addition of a dispersant. In some cases, the penetration of the liquid into channels between the particles in agglomerates may provide sufficient pressure to bring about the disintegration of the agglomerate. If this is not sufficient, high speed mixtures may be used. With aggregates having strong bonding forces mechanical methods are needed for their disruption. This mechanical force also results in breakdown of the single crystals into smaller units, a process that is referred to as comminution or milling. This process involves rupturing of chemical bonds to create new surfaces. It has been argued that reduction of surface energy by adsorption of surfactants as polymers may facilitate comminution. Moreover, reduction in surface energy retards the rejoining of the ruptured interfaces and prevents particle aggregation. The role of surface active agents in the process of comminution has been considered by Rehbinder and coworkers [12] who claimed that adsorption of surfaces at structural defects in the surface (which results in a reduction of the interfacial energy at the boundary between the solid and the medium) should aid the process of deformation or destruction of that surface. This effect is usually referred to as the Rehbinder effect [12].

Role of surfactants in emulsification

The formation of droplets from a bulk liquid is the result of deformation of the interface by application of mechanical energy. The emulsifier (surfactant or polymer) plays a number of roles in the formation of the emulsion. The process of emulsification may be envisaged to start by the formation of a film of the future (continuous phase) around the droplets. If no surfactant or polymer is present, this film is very unstable draining rapidly under gravity, until complete drainage occurs. However, in the presence of a surfactant, the film can exist for sometime as a result of the formation of an interfacial tension gradient $d\gamma/dz$. Such a gradient creates a tangential stress on the liquid, or alternatively if the liquid streams along the interface with the surfactant or polymer, an interfacial tension gradient develops. This

interfacial tension gradient supports the film, preventing its rupture by drainage (due to gravitational force) providing $2d\gamma/dz > \varrho_c hg$, where h is the film thickness, ϱ_c is density of the medium and g the acceleration due to gravity.

It should be mentioned, however, that the energy required for emulsification exceeds the thermodynamic energy $\Delta A\gamma$ (where ΔA is the increase in interfacial area) by several orders of magnitude [13]. This is due to the fact that a significant amount of energy is needed to overcome the Laplace pressure, Δp, which results from the production of a highly curved interface (small droplets), i.e. :

$$\Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \qquad (8)$$

where R_1 and R_2 are the principal radii of curvature. For a spherical droplet with radius r, $\Delta p = 2\gamma/r$ and hence deformation leads to a large Δp and energy is required to overcome this high Laplace pressure. This explains why emulsification to produce small droplets requires high energy input, e.g. by the use of ultrasonics, valve homogenisers, static mixers, etc.

Four general main roles may be identified for the emulsifier (surfactant or polymer). The first and most obvious is to lower γ, as mentioned above. This has a direct effect on droplet size. When viscous forces (i.e. in laminar flow) are predominant, the droplet diameter d is directly proportional to γ. Under turbulent conditions, $d_\infty\gamma^{3/5}$.

The second role of the emulsifier is through its effects on the surface free energy for enlarging the drop surface. Both dilational elasticity ε and viscosity η_s have an effect on the free energy for enlarging the drops. ε and η_s are given by the equation,

$$\varepsilon = d\gamma/d\mathit{ln}A \qquad (9)$$

$$\eta_s = (d\gamma/d\mathit{ln}A)/dt \qquad (10)$$

Both ε and η_s depend on the nature of surfactant or polymer. When emulsification occurs, and an equilibrium is set up between the amount adsorbed, and the concentration C in the continuous phase, the effective γ depends on the surface dilational modulus ε. During emulsification, ε decreases as a result of depletion of surfactant and increase of $d\mathit{ln}A/dt$. Hence, the effective γ during break-up will be between the equilibrium value γ and γ_0, the interfacial tension of the bare liquid/liquid interface. The surface free energy for enlarging the drop surface is $\gamma dA + Ad\gamma$, which implies that more energy is needed, although this energy is lower than $\gamma_0 dA$. Moreover, if the surface dilational viscosity is larger, viscous resistance to surface enlargement may cost entropy.

The third role of the surfactant is to create a tangential stress $d\gamma/dz$, which can build up a high pressure (of the order of 10^4 Pa for $\gamma \sim 10$ Nm^{-1} and droplet diameter of 1 µm). This tangential stress impedes or prevents internal circulation, thus facilitating droplet formation and break-up.

The fourth role of the emulsifier is to reduce coalescence during emulsification. The stabilising mechanism of a surfactant or polymer is usually ascribed to the Gibbs Marangoni effect [14, 15]. During emulsification, adsorption of surfactant is usually incomplete, so that the interfacial tension γ decrease with time and the film becomes rapidly depleted of surfactant as a result of its adsorption. The Gibbs elasticity, E_f, is given by the equation [14, 15].

$$E_f = \frac{2\gamma \, (d\mathit{ln}\Gamma)}{(1 + (1/2) \, h \, (dC/d\Gamma)} \qquad (11)$$

where Γ is the surface excess (number of moles of surfactant adsorbed per unit area of the interface). As shown in equation (11), the Gibbs elasticity is highest in the thinnest part of the film. As a result the surfactant will move in the direction of the thinnest part and this motion will drag liquid along with it. The latter effect is the Maragoni effect. The final result is to reduce thinning and hence coalescence is reduced.

The fifth role of the surfactant is to initiate instability. Disruption of a plane interface may take place by turbulence, Rayleigh instability and Kelvin-Helmholtz instability. Turbulence eddies tend to disrupt the interface [16] since they create local pressures of the order $(\varrho_1 - \varrho_2) \, u_c^2$ (where u_c is the shear stress velocity of the eddy) which may exceed the Laplace pressure $(2 \gamma/r)$. The interface may be disrupted if the eddy length is about $2r$. However, disruption turbulent eddies do not take place unless γ is very low. The Kelvin-Helmholtz instability arises when two phases moves with different velocities u_1 and u_2 parallel to the interface [17]. Interfacial instabilities may also occur for cylindrical thread of oil that forms during emulsification or when a liquid is injected into another from small orifices. Such cylinders undergo deformation [18, 19] and become unstable when the weve length λ of the perturbation of a sinusoidal disruption of the radius of the cylinder exceeds the circumference of the undisturbed cylinder. Under these conditions, the waves are amplified until the thread breaks up into droplets [20]. The presence of surfactant or polymer will accelerate this process of break up due to interfacial tension gradients, since the curved part will have a higher γ as it receives the smallest amount of surfactant per unit area.

Suspension and emulsion stabilization by surfactants and polymers

Several processes need to be controlled for stabilisation of suspensions and emulsions. The first and most important is the control of particle or droplet aggregation, which determines the final properties of the suspension or emulsion, such as its flow characteristics, its behaviour on application and its state on standing. Particle or droplet aggregation is determined by the interaction forces that exist between them which may be classified into electrostatic, Van der Waals and steric forces. Depending on the magnitude of these forces, various states may be reached varying from totally deflocculated (where the repulsive forces exceed the attractive forces by orders of magnitude) to weakly flocculated and strongly flocculated (coagulated) systems. With emulsions one needs to prevent coalescence of the droplets, a process that is determined by the thinning and disruption of the liquid film between the droplets. The second process that needs to be controlled with suspensions and emulsions is that of sedimentation and creaming. When the density of the particles or droplets is higher than that of the medium and their size is outside the colloid range, the weak Brownian motion produced by the particles is insufficient to overcome the gravitational force. As a result the particles or droplets settle to the bottom of the container, forming a compact layer (which in technical terms is referred to as "cake" or "clay"). If the density of the particles or droplets is lower than that of the medium, the compact layer will form at the top of the container. This process is usually referred to as creaming.

Another breakdown process that may occur with polydisperse systems is that of Ostwald ripening. As a result of the larger solubility of the smaller particles or droplets, these tend to dissolve and become deposited on the larger ones. Again such a process is affected by the presence of surfactants or polymers. Below a brief description of the role of surfactants and polymers in three of the above process, namely flocculation, coalescence and Ostwald ripening will be given.

Role of surfactants and polymers in prevention of flocculation

Aggregation (usually referred to as flocculation) results from the

Van der Waals attraction between the particles or droplets which is long-range in nature and increases significantly at short distances of separation. The Van der Waals, interaction energy for two spherical particles and droplets with radius of the same material with Hamaker constant A_{11}, in a medium with a Hamaker constant A_{22}, is given at short distances of separation (h << a) [20, 21] :

$$G_A = - \frac{A_{12} a}{12\,h} \qquad (12)$$

where A_{22} is the effective Hamaker constant that is given by the expression,

$$A_{12} = \left(A_{11}^{1/2} - A_{22}^{1/2}\right)^2 \qquad (13)$$

The Hamaker constant of any material is determined by the number of atoms or molecules per unit volume and the London dispersion constant that is related to the polarizability of the atoms or molecules.

The role of surfactants a polymer is to create a repulsive force that counteracts the Van der Waals attraction, *i.e.* to create a barrier against aggregation. With ionic surfactants (anionic, cationic or zwitterionic) and polyelectrolytes, the repulsive force arises from the presence of an electrical double layer, which extends from the surface of the particle or droplet to an extent that is determined by electrolyte concentration. When two particles or droplets, each carrying diffuse layer of counter ions, approach each other, *e.g.* in a Brownian encounter, repulsion occurs as a result of overlap of the diffuse layers. For spherical particles, that repulsion energy is given by the approximate expression due to Deryaguin [22], when the range of interaction is small compared to the particle radius,

$$G_E = 2\,\pi\,a\,\varepsilon_r\,\varepsilon_o\,\psi_o^2\,ln\,[1 + \exp - (\varkappa h)] \qquad (14)$$

where ε_r is the relative permittively (dielectric constant) of the medium, ε_o is the permittivity of free space, ψ_o the surface potential and $\varkappa$ is the reciprocal of the thickness of the double layer that is given by,

$$\varkappa = \left(\frac{2\,Z^2\,e^2\,C}{\varepsilon_r\,\varepsilon_o\,kT}\right)^{1/2} \qquad (15)$$

where Z is the valency of counter ions, C the electrolyte concentration in bulk solution, k is the Boltzmann constant and T the absolute temperature.

It is clear from equation (14) that G_E depends on ψ_o, a and $\varkappa$. The surface potential is determined by the number of surfactant was adsorbed per unit area ; usually one replaces ψ_o by the measured ζ-potential and the assumption is made that the higher the ζ-potential, the higher the repulsion. On the other hand, G_E is reduced in magnitude by an increase in $\varkappa$, *i.e.* increase in electrolyte concentration.

When G_E is combined with G_A, this results in the familiar energy-distance curve due to Deryaguin, Landau, Verwey and Overbeek [23] (the DLVO theory) which is schematically shown in *Fig. 4*. The energy-distance curve is characterised by three main parameters : G_{min}, $(G_{min})_{primary}$ and $(G_{min})_{sec}$, the magnitudes of, which are determined by the surface potential (or the measured ζ-potential), electrolyte concentration, particle size and Hamaker constant. If G_{max} is high (>> kT *e.g.* greater than 25 kT) and $(G_{min})_{sec}$ is shallow, a deflocculated suspension or emulsion is produced. This is usually the case when C is low, say < 10^{-3} mol dm^{-3} 1 : 1 electrolyte. On the other hand, if G_{max} is small (< 5-10 kT) or absent, the suspension or emulsion becomes coagulated (since the particles are able to surmount the small energy barrier and enter the deep primary minimum). This is the case when there are only a few adsorbed surfactant molecules (at low concentration) or when these molecules are weakly adsorbed or when the electrolyte concentration is high (*e.g.* > 10^{-1} mol dm^{-3} 1 : 1 electrolyte). Therefore, to stabilise a sus-
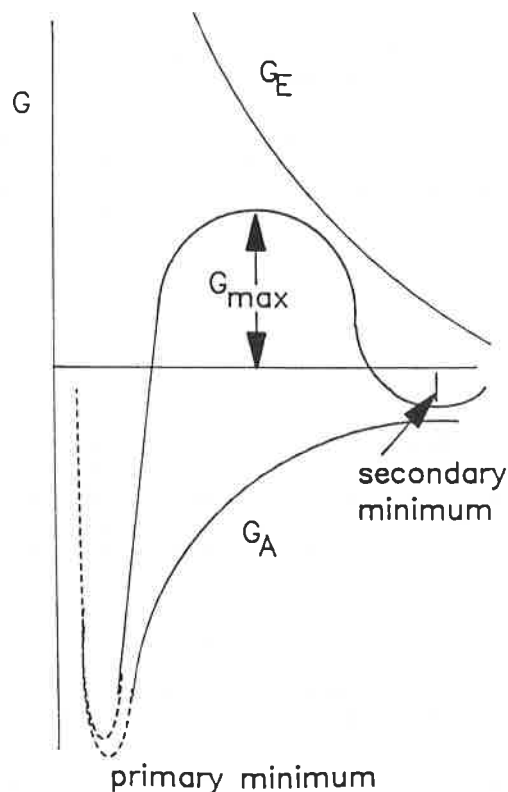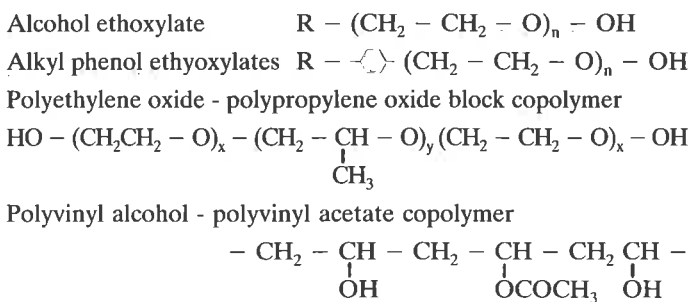

FIGURE 4. - *Total interaction energy distance curve according to the DLVO theory.*

pension or emulsion against aggregation one should choose a surfactant that is strongly adsorbed, add sufficient amount to saturate the surface with surfactant and reduce the electrolyte concentration to a minimum.

An interesting case arises when G_{max} is reasonably large (> 10 kT) and $(G_{min})_{sec}$ is fairly deep (1-5 kT). This results in a state of weak flocculation, whereby the particles or droplets are now held by a relatively weak attraction at separation distances around the location of $(G_{min})_{sec}$. The weak flocculation is reversible and by shaking the dispersion, the particles become redispersed. This phenomenon of weak flocculation could be applied for prevention of formation of compact sediments or creams.

Another way of producing repulsion is to create a steric barrier between the particles or droplets [24]. This is obtained by the use of nonionic surfactants or macromolecules. Examples for such dispersants in aqueous medium are given below.

Alcohol ethoxylate $\qquad R - (CH_2 - CH_2 - O)_n - OH$

Alkyl phenol ethyoxylates $\quad R - \text{⟨◯⟩} - (CH_2 - CH_2 - O)_n - OH$

Polyethylene oxide - polypropylene oxide block copolymer

$HO - (CH_2CH_2 - O)_x - (CH_2 - \underset{\underset{CH_3}{|}}{CH} - O)_y (CH_2 - CH_2 - O)_x - OH$

Polyvinyl alcohol - polyvinyl acetate copolymer

$- CH_2 - \underset{\underset{OH}{|}}{CH} - CH_2 - \underset{\underset{OCOCH_3}{|}}{CH} - CH_2 \underset{\underset{OH}{|}}{CH} -$

Graft copolymers of the "comb" type *e.g.* polystyrene or polymethyl methacrylate backbone with polyethylene oxide side chains.

When the above dispersants are used to stabilise hydrophobic solid particles or emulsion droplets, the hydrophobic portion, *i.e.* alkyl, alkyl phenol, poly(propylene oxide), poly(vinyl acetate), polystyrene (or polymethyl methacrylate) become adsorbed on the particle surface or dissolved in the oil phase leaving the hydrophilic poly(ethylene oxide) (PEO) or polyvinyl alcohol (PVA) dangling in solution. Thus hydrophilic portion which is strongly solvated by the medium (when the latter is a good solvent for the chains) provides a strong repulsion force as a result of two main effects. The first contribution (mixing effect) results from the unfavourable mixing of the chains on overlap when the separation distance between the particles or droplets becomes smaller than twice the adsorbed layer thickness. If such overlap is forced, the segment concentration in the overlap region becomes larger than that in the rest of the layer. This means that the chemical potential of the solvent in this region will be smaller than in the rest of the layer (*i.e.* a higher osmotic pressure in the overlap region). As a result, solvent will diffuse from bulk solution to this zone, thus forcing the particles or droplets apart. The free energy of mixing, ΔG_{mix}, is given for two spherical particles with layers of thickness δ, by the simple expression [25] :

$$\frac{\Delta G_{mix}}{kT} = \frac{4 \pi \phi_2^2}{3 V} \left(\frac{1}{2} - \chi \right) \left(\delta - \frac{h}{2} \right)^2 \left(3a + 2\delta + \frac{h}{2} \right) \quad (16)$$

where χ is the chain-solvent (Flory-Huggins) interaction parameter. It is clear from equation (16) that when $\chi < 0.5$ (*i.e.* the chains are in good solvent conditions), ΔG_{mix} is positive *i.e.* repulsion occurs and this increases rapidly in magnitude as $\delta < (h/2)$. When $\chi = 0.5$, *i.e.* under θ-conditions for the chains, $\Delta G_{mix} = 0$, whereas if $\chi > 0.5$ (worse than θ-conditions), ΔG_{mix} is negative and the mixing interaction is attractive.

The second contribution to steric interaction arises from the loss of configurational entropy of the chains on significant overlap. This effect is usually referred to as volume restriction or entropic or elastic interaction. The term volume restriction arises from the fact that on significant overlap, the volume available for the chains becomes much smaller. Elastic interaction arises from the compression of the chains and is given by the equation [26, 27],

$$\Delta G_{el} = N_s kT \theta_\infty [1 - (h/\delta)] \quad (17)$$

where N_s is the number of adsorbed chains per unit area, θ_∞ is the fraction of surface coverage by an adsorbed layer at $h = \infty$.

The above theories for steric interaction have to be modified for nonionic polymers to take into account the non-uniform segment distribution of the chain in the adsorbed layer. This distribution depends on the structure of the polymer and the conformation at the interface. Several theories exist to deal with this problem and the resulting equation for ΔG_{mix} and ΔG_{el} are rather complex but they can be solved analytically [24]. However, the general trend for change of G_{mix} and G_{el} with distance of separation is still the same as with simple nonionic surfactants. This is illustrated in *Fig. 5* which shows the variation of G_{VR} ($\equiv G_{el}$) and G_M ($\equiv G_{mix}$) and G_T ($\equiv G_M + G_{VR}$) with separation distance h. Unlike the DLVO theory, the energy-distance curve shows only one minimum, G_{min}, whose depth depends on δ, a and A. Provided that G_{min} is shallow (when thick adsorbed layers are present) a highly deflocculated suspension or emulsion results since G_T shows a very steep rise with reduction of h below 2δ. Thus, provided the dispersant is strongly adsorbed (*i.e.* it contains good "anchor" group), steric stabilisation offers a powerful means of producing stable systems. Since "anchoring" of the chains is important, the merit of using A-B, A-B-A block copolymers or BA_n graft copolymers, is now obvious. By choosing the B chain with very low solubility in the medium and having a high affinity to the surface, it is possible to "anchor" the chain to the surface, leaving the A chains (which are chosen to be highly solvated by the medium) dangling in solution to provide the steric barrier.
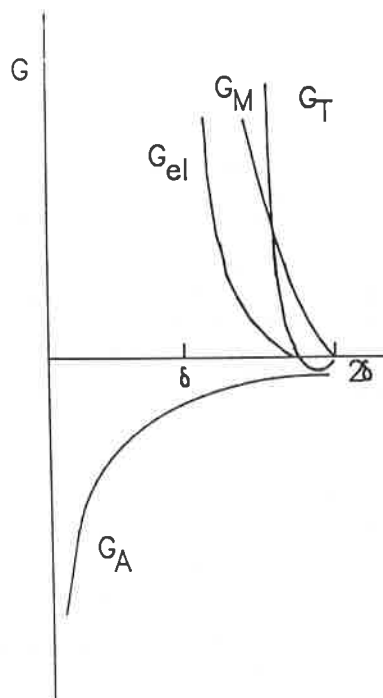

FIGURE 5. - *Variation of* G_M, G_{el} *and* G_T *with* h *for a sterically stabilised system.*

Role of polymers and surfactants in preventing coalescence

When two emulsion droplets come in close contact in a sedimented or creamed layer in a floc or during Brownian collision, thinning and disruption of the liquid film may occur, resdulting in its eventual rupture and hence the droplets join each other, *i.e.* they coalesce. The process of thinning and rupture of liquid lamellae between emulsion droplets is complex. For example, during a Brownian encounter, in a cream or sediment or in a floc, emulsion droplets may produce surface or film thickness fluctuations in the region of closest approach. The surface fluctuations produce waves which may grow in amplitude and during close approach, the apexes of these fluctuations may join causing coalescence (region of high Van der Waals attraction). Alternatively, any film thickness fluctuations may result in regions of thin films where the Van der Waals attraction is very strong, causing even more thinning with the ultimate disruption of the whole film. Unfortunately, the process of coalescence if far from being well understood, although some guidelines may be obtained by considering the balance of surface forces in the liquid lamellae between the droplets. A useful picture was given by Deryaguin and coworkers [28] who introduced the concept of the disjoining pressure π (h) for thin films adhering to substrates. π (h) balances the excess normal pressure P (h) $- P_o$, where P (h) is the normal pressure of a film for thickness h and P_o is that of a sufficiently thick film such that the interaction free energy is zero. It should be noted that π (h) is the net force per unit area acting across the film, *i.e.* normal to the interfaces. Thus, π (h) is simply equal to $-$ d V_T/dT, where V_T is the net force resulting from three main contributions, Van der Waals, electrostatic and steric forces, *i.e.* :

$$\pi (h) = \pi_A + \pi_E + \pi_S \quad (18)$$

π_A is usually negative, whereas π_E and π_S are positive. For π (h) to be positive, $\pi_E + \pi_S$ should be greater than π_A. Therefore, to reduce coalescence one needs to enhance the repulsion between the surfactant or polymer layers, *i.e.* using double layer and/or steric repulsion.

For reduction of coalescence, one also needs to dampen the fluctuation in surface waves or film thickness. This, as discussed before, is produced by enhancement of the Gibbs-Maragoni effect. As a result of surface or film fluctuations, regions of high interfacial tension (which are depleted of surfactant or polymer) are produced in the thinnest part of the film. Surfactants or polymers tend to diffuse to these regions drawing with them solvent molecules. This will dampen the fluctuations and produce thicker films. Several methods may be used to enhance the Gibbs-Marangoni effect and hence reduce coalescence. One of the earliest methods is to use mixed surfactant films which will have the effect of enhancing the Gibbs elasticity and/or surface viscosity. In addition, mixed surfactant films are usually more condensed and hence diffusion of the surfactant molecules from the interface is greatly hindered. An alternative explanation for enhanced stability using surfactant mixtures was introduced by Friberg and coworkers [29] who considered the formation of a three dimensional association structures (liquid crystals) at the oil/water interface. The presence of these structures prevent coalescence since one has to remove several surfactant layers before droplet-droplet content may occur.

Another method of reducing coalescence is to use macromolecular surfactants such as gums, proteins and synthetic polymers of the A-B, A-B-A block copolymers or BA_n graft copolymers. As discussed above, these molecules are strongly adsorbed since the B chain is chosen to be soluble at the oil phase, where as the A chain that is strongly solvated by the medium produces a "thick" steric film that prevents coalescence.

Ostwald ripening

As mentioned before, the driving force for Ostwald ripening is the difference in solubility between the small and large droplets. This difference is given by the Ostwald equation,

$$\frac{RT}{M} ln \frac{S_1}{S_2} = \frac{2\gamma}{\varrho}\left(\frac{1}{R_1} - \frac{1}{R_2}\right) \qquad (19)$$

where S_1 is the solubility of a droplet of radius R_1 and S_2 that of a droplet of radius R_2 (note that $S_1 > S_2$ when $R_1 < R_2$), M is the molecular weight and ϱ the density of the oil.

The above process of Ostwald ripening is reduced by surfactants or polymers which play two main roles. Firstly, by adsorption at the o/w interface, γ is reduced, thus reducing the driving force for Ostwald ripening. Secondly, surfactants and polymers produce an interfacial tension gradient (Gibbs elasticity) which will also reduce Ostwald ripening. This can be understood from the following argument [30]. A droplet is mechanical equilibrium if $dp/dR > 0$, i.e. when $d\gamma/dln\, R > \gamma$. Since $A = 4\pi R^2$, then $2d\gamma/dlnA > \gamma$ or $2\varepsilon > \gamma$. Thus when twice the interfacial elasticity exceeds the interfacial tension, Ostwald ripening is greatly reduced.

Another method of reducing Ostwald ripening, introduced by Davies and Smith [31] is to incorporate a small proportion of a highly insoluble oil within the emulsion droplets. This reduces the molecular diffusion of the more soluble oil molecules, which is assumed to be the driving force for Ostwald ripening.

Role of surfactants in microemulsion formation and stability

Microemulsion are isotropic thermodynamically stable systems consisting of water, oil and surfactants [32]. The origin of thermodynamic stability (i.e. zero or negative free energy of formation) stems from the low interfacial energy of the system which is

outweighed by the negative entropy of dispersion. Several theories exist to account for such stability and these may be classified into three main categories : interfacial or mixed film theories, solubilisation theories and thermodynamic theories. A brief summary of the basic concepts of such theories is given below.

The interfacial or mixed film theories were originally introduced by Schulman and coworkers [33, 34] and later extended by Prince [35]. The essential feature of these theories is the consideration of the film as a liquid two dimensional third phase in equilibrium with both oil and water, implying that such a monolayer could be a duplex film, i.e. giving different properties on the water side and on the oil side. According to these theories, the net interfacial tension, γ_T is given by the expression,

$$\gamma_T = (\gamma_{o/w})_a - \pi' \qquad (20)$$

where $(\gamma_{o/w})_a$ is the oil-water interfacial tension ; the subscript a is introduced to take into account any reduction produced by the cosurfactant (alcohol), π is the two dimensional spreading pressure of the mixed films. Contributions to π were considered to be crowding of the surfactant and cosurfactant molecules and penetration of the oil phase into the hydrocarbon part of the interface. According to equation (20), if $\pi > (\gamma_{o/w})_a$, γ_T becomes negative leading to the expansion of the interface until γ_T reaches zero or a small positive value. Since $(\gamma_{o/w})_a$ is of the order of 15-20 mNm^{-1}, surface pressures of that order are required for γ_T to approach a value of zero.

The above concept of duplex films can be used to explain both the stability of microemulsions and the bending of the interface to produce o/w and w/o microemulsion. Considering that the initially flat duplex have different tension, i.e. different π values on either side of it, then the driving force for film curvature is the stress or the tension gradient which tends to make the pressure or tension on both sides of the curved film the same. This is schematically shown in Fig. 6. For example, if $\pi'_w > \pi'_o$ on the flat film, then the film has to be expanded more at this water side than at the oil side (which indeed contracts as a result of the curvature effect) until the pressure becomes equal on both sides of the duplex film, i.e. $\pi_w = \pi_o = 1/2 (\pi_{o/w})_a$. In this case an o/w microemulsion is produced. On the other hand, if $\pi'_o > \pi'_w$, then the film expands at the oil side and contracts at the water side of the film resulting in the formation of a w/o microemulsion.

The above simple theory can be used to predict the nature of the surfactant that is required to produce an o/w or w/o microemulsion. In a duplex film, the surface pressure at the oil and water sides of the interface depend on the interactions of the hydrophobic and hydrophilic portions of the surfactant in both sides respectively. For example, if the hydrophobic portions are bulky in nature relative to the hydrophilic groups, the former tend to crowd, forming a high surface pressure at the oil side of this film. In this cas, bending occurs to expand the oil side forming a w/o microemulsion. On the other hand, with surfactant molecules with relatively bulky hydrophilic groups, crowding occurs at the water side of the interface, tending to form an o/w microemulsion.

The solubilisation concept was introduced by Shinoda and coworkers [36-38] who preferred to treat microemulsions as swollen micellar systems, thus relating them directly to the phase diagram of their components. For example, the phase diagram of
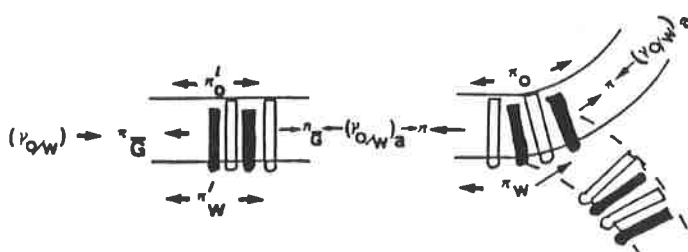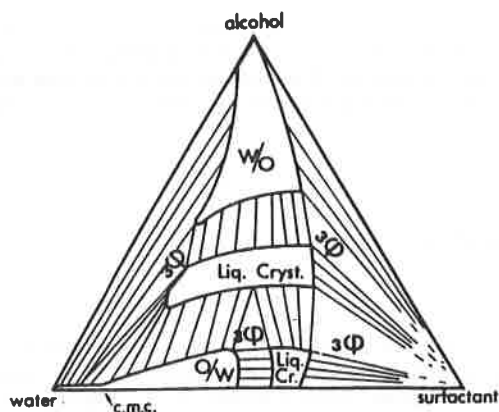

FIGURE 6. - *Schematic representation of film bending.*

FIGURE 7. - *Schematic three component phase diagram for a water surfactant and cosurfactant combination.*

a three component system of water, ionic surfactant and alcohol, usually displays one isotropic aqueous liquid region L_1, from the water corner (normal micelles) and one isotropic liquid region L_2 from the alcohol corner (reverse micelles). This is illustrated in *Fig. 7* which gives a schematic representation of a three component phase diagram of water, surfactant and alcohol (cosurfactant) combination [39]. The phase diagram contains four one-phase (1 φ) regions : L_1 (o/w normal), L_2 (w/o inverse micelles) and two liquid crystalline regions. The o/w and w/o isotropic regions may be considered as microemulsions. Between the various one-phase regions, two-phase regions occur where the phases in equilibrium are connected by tie lines, or triangular 3 φ regions having zero degree of freedom at constant p and T in a three-component system [39].

Addition of a small amount of oil, miscible with the cosurfactant, changes the phase diagram only slightly, but in the presence of substantial amounts of oil, the phase diagram changes significantly. This is illustrated in *Fig. 8* which shows the phase diagram for the four component systems : water/oil/surfactant/cosurfactant, displayed in a two dimensional triangle with the water corner now replaced by a 50 : 50 water : oil [39]. The w/o microemulsion region (1 φ) at the cosurfactant corner becomes expanded. The o/w microemulsion near the water/surfactant axis is not in equilibrium with the lamellar phase, but with a non colloidal oil plus cosurfactant phase. If cosurfactant is added to such a two-phase equilibrium at high surfactant all the oil is taken up and a one-phase microemulsion appears. However, addition of cosurfactant at low surfactant concentration may lead to separation of
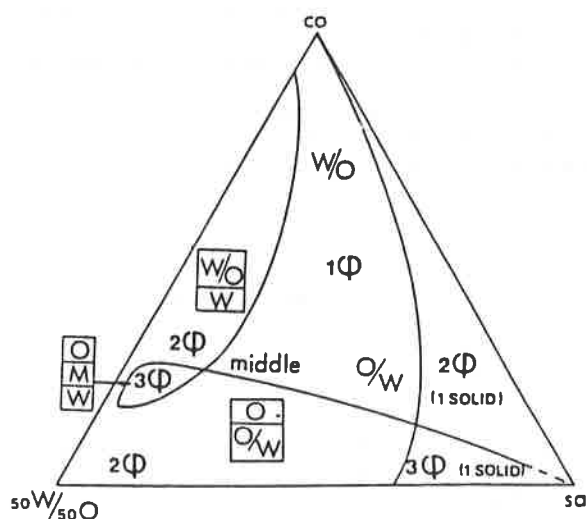

FIGURE 8. - *Schematic four component phase diagram of water/oil/surfactant and cosurfactant.*

an excess aqueous phase before all the oil is taken up in the microemulsion. A three-phase system (3 φ) is formed containing a microemulsion in equilibrium with water and oil. This micro-emulsion, that is sometimes referred to as middle phase (Winsor III) cannot be clearly identified as w/o or o/w and is usually referred to as bicontinuous. This middle microemulsion phase has a very low interfacial tension with oil and water $(10^{-4} - 10^{-1}$ $mNm^{-1})$.

Solubilisation as a concept for microemulsion formation can be illustrated by considering the phase diagram of nonionic surfactants containing poly(ethylene oxide) head group. Such surfactants do not generally need a cosurfactant for microemulsion formation. At low temperatures, the ethoxylated surfactants is soluble in water and at a given concentration is capable of solubilising a given amount of oil. The oil solubilisation increases with increase of temperature near the cloud point of the surfactant. This is illustrated in *Fig. 9a* which shows the solubilisation and cloud point curves of the surfactant. Between these two curves, an isotropic o/w solubilised system exists. At any given temperature, any increase in the oil weight fraction above the solubilisation limit results in oil separation, *i.e.* oil solubilised plus oil,
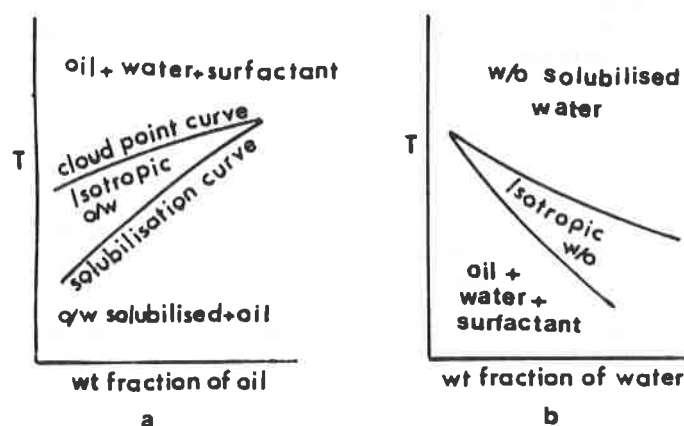

FIGURE 9. - *Schematic representation of solubilisation : (a) oil solubilised in a nonionic surfactant solution ; (b) water solubilised in an oil solution of nonionic surfactant.*

whereas at any given surfactant concentration, any increase in temperature above the cloud point of the surfactant results in separation into oil, water and surfactant. On the other hand, if one starts from the oil phase with dissolved surfactant and adds water, solubilisation of the latter takes place and this increases rapidly with reduction of temperature near the haze point of the surfactant. This is illustrated in *Fig. 9b*, which shows both the haze point and solubilisation curves. Between these two curves, an isotropic region of w/o solubilised system exists. At any given temperature, any increase in water weight fractions above the solubilisation limit results in water separation, *i.e.* w/o solubilised plus water, whereas at a given surfactant concentration, any decrease in temperature below the haze point results in separation into water, oil and surfactant.

Two main thermodynamic treatments for microemulsion formation and stability were considered by Ruckenstein and Chi [40] and Overbeek *et al* [41, 42]. The treatments follow roughly the same argument but vary somewhat in detail [43]. A brief summary of Overbeek *et al* [41, 42] treatment is given. These authors first considered the reason for combination of two surfactants to reduce γ to values that are sufficiently low such that the free energy of the interface can be overcompensated for by the entropy of dispersion of the droplets in the medium. Simple surfactants do lower γ, but in most cases, the c.m.c. is reached before γ is close to zero. Addition of a second surfactant of a completely different nature *i.e.* predominantly oil soluble, *e.g.* an alcohol, to be referred to as cosurfactant, then lowers γ further and very small, even transiently negative values may be rea-
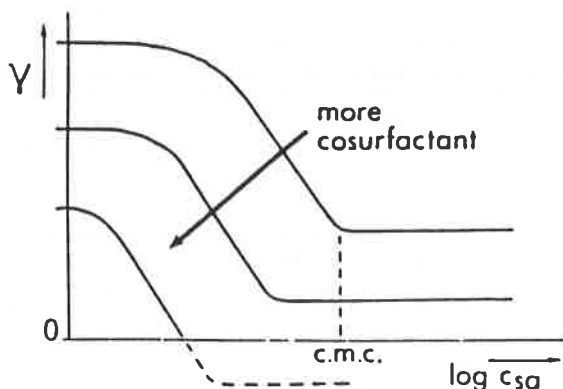
FIGURE 10. - γ — log C curves for surfactant + cosurfactant mixtures.

ched. This is illustrated in *Fig. 10* which shows that increasing the cosurfactant concentration, shifts the whole curve to lower γ value and the c.m.c. is shifted to low values. The reduction in γ as a result of the presence of two surfactants can be understood from a consideration of the Gibbs equation that may be extended to multicomponent systems, *i.e.* :

$$d\gamma = -\Sigma_i \Gamma_i \, d\,\mu_i = - \Sigma_i \Gamma_i \, RT \, d\,l\,n \, C_i \qquad (21)$$

where Γ_i is the surface excess of component i with chemical potential μ_i and concentration C_i. Thus, where two components are present, γ is lowered twice, provided the two surfactant molecules are adsorbed simultaneously and they do not interact with each other (otherwise they lower their respective activities). To reduce interaction, the two molecules are chosen to vary in nature, *i.e.* one being predominantly water soluble and one predominantly oil soluble.

The second consideration by Overbeek *et al* [41, 42] is the minimization of free energy with respect to change in interfacial area A, which could account for the thermodynamic stability of the system. For that purpose, Overbeek *et al* [41, 42] considered a model w/o system whereby the droplets were assumed to be of equal size. The Helmholtz free energy is calculated by considering a number of steps in the formation of the microemulsion. The Helmholtz free energy was chosen because the pressure inside the drops is higher by the Laplace pressure 2 γ/a. The first step was to prepare the oil phase in its final concentration (*i.e.*, with the cosurfactant). The second step is to prepare the aqueous phase in its final concentration. The third step is to form the water phase into droplets, close packed in the oil, and add all the adsorbed material. The fourth step is to allow the close packed structure to expand to its final volume fraction ϕ, *i.e.* the Helmholtz energy of mixing. The total Helmholtz free energy F is given by the sum of the above mentioned four contributions and this is minimized with respect to a change in interfacial area A. This involves transfert of adsorbed compounds to or from the interface, thereby changing the bulk concentration and thus γ. The result is then that;

$$\gamma = - \text{const.} \frac{1}{a_2} g \, (\phi) \qquad (22)$$

where $g(\phi)$ is a function of ϕ. a is the droplet radius which is equal to $3V/A$, where V the total value of the droplets and A is their area. Since a has to fit equation (22), the correct value of γ is obtained by adaptation of the concentration of surfactant. According to equation (22), any value of a is allowed in the accessible range of γ. In particular, if γ can be close to zero very large radii, *i.e.* very large water/surfactant ratios are allowed,

but in the phase diagram such high ratio leads to demixing. It is, therefore, necessary to add an explicit influence of the radius of curvature on the interfacial tension to the model thus giving the interfacial layer a limited range of curvatures that are acceptable.

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Formulating Microemulsions that Decontaminate a Toxic Substance *

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I have before me a pencil. It may be regarded as a "system" in that several components work in concert to produce a useful object. There is a wood shaft with a graphite core ; a metal band attached to a rubber eraser ; and yellow paint covers the wood. Some components are more useful than others. For example, the graphite is necessary for the pencil to function, but the paint is of secondary importance. The point is that multiple components operate cooperatively to produce something better than available from a single component alone. And so it is with systems on a molecular scale. Chemists have discovered that groups of molecules can perform useful tasks that are unachieveable from "single molecule" chemistry (Nature, with its incredibly complex system, the cell, has of course discovered this long ago).

It is my purpose to describe here a multi-component system that is remarkable in its ability to destroy mustard, a highly dangerous compound being produced worldwide. Operation of the system depends on water, hydrocarbon, surfactant, cosurfactant, oxidant, and mustard working in concert within an array of self-organizing molecules [1]. Destruction of mustard is rapid, cheap, selective, and mild.

Our research group has over the years examined a variety of organic systems including micelles, films, water pools, vesicles, laminates, polyaphrons, polymeric systems, and microemulsions. This work is reviewed in a recent *Angewandte Chemie* [2]. In the present article, I will focus on only one type of system, the microemulsion. Since there may be many readers who are unfamiliar with microemulsions, I will begin by briefly describing what they are and why they attracted our attention.

A microemulsion is an isotropic and optically clear dispersion of oil-in-water (O/W) or water-in-oil (W/O) where "oil" is a hydrocarbon [3, 4]. The name "microemulsion" derives from the fact that oil droplets in O/W systems, and water droplets in W/O systems, are small (50-500 Å). Microemulsions are thermodynamically stable, and they remain clear indefinitely. They form spontaneously when the following four components are mixed in specific proportions : water, oil, surfactant, and cosurfactant (generally a low molecular weight alcohol). *Figure 1* shows the structure of an O/W microemulsion. The presence of cosurfactant is critical to reducing the interfacial tension between droplets and continuous phase to near zero. In the absence of cosurfactant at the droplet interface, the emulsions become unstable and milky owing to the creation of much larger droplets.

How does one know what proportion of the four components to use ? It is possible, of course, to take microemulsion recipes from the abundant literature on the subject. We found it just as simple to develop our own by "titration". Thus, microemulsions were prepared on a 100 gram scale by weighing a mixture of alcohol, surfactant, and hydrocarbon into a 250 mL Erlenmeyer flask. This white slurry was swirled into a smooth paste. Water was then added with mild agitation to achieve clarity. A few minutes sonication was used occasionally to hasten the process. *Table I* gives the percentage composition by weight of nine