THE FIRST RIDEAL LECTURE

Microemulsions, A Field at the Border Between Lyophobic and Lyophilic Colloids

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Microemulsions can be regarded as thermodynamically stable dispersions of droplets of one phase in another phase. There are continuous transitions to swollen micelles, when the droplets become extremely small, and to coarse emulsions when the droplets are large. The mechanism leading to the formation of microemulsions is the tendency to extend the interfacial area until the concentrations of surfactants are sufficiently low that non-negative interfacial tension is achieved. The role of the combination of a surfactant and a cosurfactant is seen in their leading to a decrease in the interfacial tension to potentially negative values. An expression is given for the Gibbs energy of the whole system, for the special case of an ionized surfactant and a non-ionized cosurfactant. The minimization of this Gibbs energy leads to the stability conditions for the microemulsion. The factors which promote O/W and W/O emulsions, respectively, are briefly discussed. The electrical contribution to the interfacial tension depends on the particle size. This leads to a narrow size distribution. It is finally pointed out that, in principle, fine dispersions of solids in a liquid may be thermodynamically stable in the presence of large amounts of easily adsorbed compounds.

1. INTRODUCTION

This lecture is given to honour the memory of Sir Eric K. Rideal. I felt that it would not be adequate for me to give a review on some older subject, but that I would be expected to offer something completely new or at least to offer a new look at some older problem. I have chosen this last approach.

I shall talk to you about systems lying on the borderline (one might say: forming the interface) between lyophobic and lyophilic colloids and more specifically about microemulsions.

Microemulsions are mixtures of water and " oil " (*e.g.*, toluene or cyclohexane) made transparent and apparently homogeneous by the presence of a fairly large amount of surfactant, or more usually of a surfactant and a cosurfactant. Their spontaneous formation and long lasting stability indicate that they are thermodynamically stable and not only stable in the kinetic sense. They have found several practical applications and have attracted a great deal of attention in recent years on account of their use in tertiary oil recovery and as examples of (nearly) isodisperse suspensions of spherical particles. Vrij's presentation[1] on " Application of modern concepts in liquid state theory to concentrated particle dispersions " in the present meeting is an

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example of the use of the last named property. Much literature on microemulsions is available, including a recent book, edited by L. M. Prince,[2] but notwithstanding all the work done on these systems since their introduction by Hoar and Schulman[3] in the early forties, our understanding of their properties still has many gaps. In this lecture I will not be able to fill these gaps, but I will try to analyse why these dispersed systems are stable, whether and how extensively they differ from ordinary emulsions and from micellar solutions and how we might understand their isodispersity.

Finally I want to discuss briefly the possibility that other, especially solid in liquid, dispersions may be thermodynamically stable.

2. MICROEMULSIONS

Microemulsions may be described as small droplets (diameter 5–50 nm) of a liquid (I) dispersed in another liquid (II) by virtue of the presence of a fairly large concentration (*e.g.*, 20%) of a suitable combination of surfactants. It is then obvious, as shown schematically in fig. 1, that, at least in principle, there are continuous transitions to micellar systems having some liquid (I), solubilized in the micelles and to coarse emulsions (diameter 500 nm and above) on the other hand.

In this discussion I shall direct my attention primarily to systems in which the droplets are large enough (*i.e.*, diameter > 5 nm) to bring their centre and its immediate surroundings out of the range of short range interactions with the surfactants in the interface. Without denying the importance of microemulsions stabilized by non-

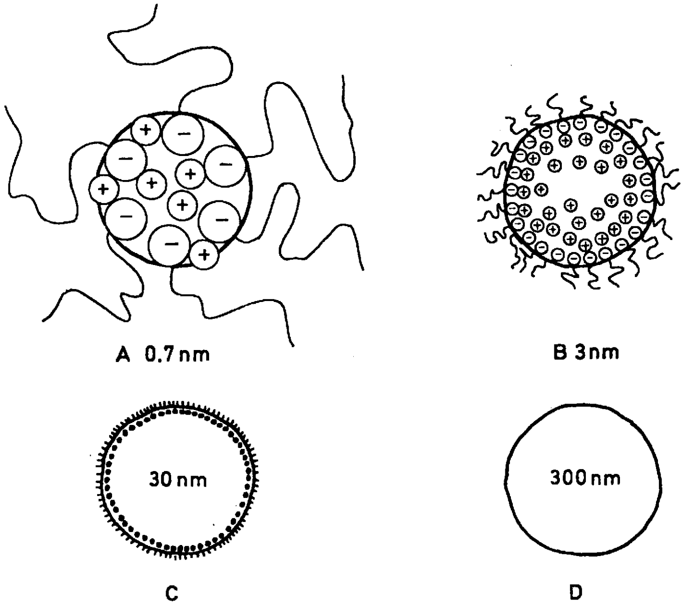

FIG. 1.—Schematic representation of water droplets of various radii (0.7 to 300 nm) in oil with an ionized surfactant at the interface. A may be considered as a water swollen micelle. D comes in the size range of ordinary emulsion droplets. B and C are typical microemulsion droplets. The number of surfactant ions in the surface, *s*, and in the bulk, *s*′, per particle when the surface excess is about 1 ion per 0.5 nm^2 and the bulk concentration about 0.001 mol dm^{-3} is listed.

	A	B	C	D
s	12	225	22 500	2.25×10^6
s'	0.001	0.1	70	70 000

ionic surfactants, I shall assume in this talk that the main surfactant is ionic as in the original cases reported by Schulman. A fairly typical composition is: 33% (by weight) water, 34% toluene, 23% potassium oleate and 10% hexanol, which forms W/O microemulsions with a droplet diameter of about 8 nm. The main questions presenting themselves then are:

(1) What is the significance of the combination of two surfactants, one highly polar (ionic) and one more lipophilic (the alcohol)?

(2) How can the thermodynamic stability and the spontaneous formation be explained?

(3) What determines whether an O/W or a W/O emulsion is formed?

(4) How isodisperse are these systems?

(5) Can similar systems be made with dispersed solids?

3. INTERFACIAL TENSION AND ADSORPTION

Schulman[4] in his later papers postulates that the main feature of microemulsions was a zero interfacial tension between the two phases, or rather a negative interfacial tension at the original composition of the two phases which would lead to a spontaneous extension of the interface and adsorption of surfactant until the remaining concentration of surfactant had become so low that the interfacial tension would rise to zero or to a positive value.

This aspect explains the necessity of using two rather different surfactants. Aqueous solutions of surfactants such as K-oleate generally show a dependence of surface tension or interfacial tension, γ, as sketched in fig. 2.

At low concentrations the surfactant is adsorbed at the air–water and at the oil–water interface and the surface (or interfacial) tension starts to decrease. Even before the surface tension has decreased very much the (γ, log c) curve achieves a steep, nearly constant slope, indicating that the adsorption is saturated. The Gibbs isotherm, eqn (3.1) gives the relation between γ, the amount adsorbed per unit area, Γ_i, and the chemical potential μ_i of component, i,

$$\left(\frac{\partial\gamma}{\partial\mu_i}\right)_{p,T,n_j\neq i} = -\Gamma_i = \frac{\partial\gamma}{2RT\partial\ln a_i} \simeq \frac{\partial\gamma}{2RT\partial\ln c_i} \tag{3.1}$$

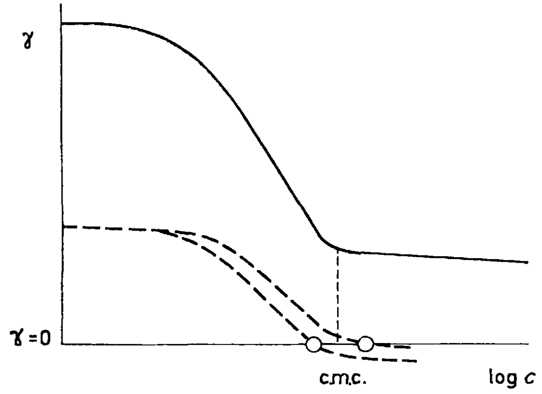

FIG. 2.—Showing how a combination of two surfactants may lower the interfacial tension to zero and to potentially negative values. The drawn line gives the interfacial tension for a surfactant with a c.m.c. The dotted lines refer to the same surfactant, but used after the interfacial tension has been lowered by a cosurfactant. The two dotted curves refer to slightly different affinities of the surfactant for the interface covered with cosurfactant.

where a_i is the activity of i and c_i its concentration. The factor 2 in the denominator arises from the dissociation of the ionic surfactant. For a nonionic surfactant and also for an ionic surfactant in the presence of an excess of a nonsurface active electrolyte, the factor 2 drops out. The decrease in γ with increasing c stops rather suddenly at the critical micelle concentration (c.m.c.). Above this concentration any further addition of surfactant is used to form micelles and although c_i still increases, a_i remains nearly constant.

As Wagner,[5] among others, has pointed out, it is not an unfortunate accident that the concentration at which the interface is saturated and the c.m.c. are close together. The surroundings of a detergent ion or molecule at a saturated interface and in a micelle are rather similar. Consequently, their standard free energies are nearly equal and they are formed at nearly the same concentration of single molecules, so that it is rarely possible to reach zero or potentially negative interfacial tension with only one surfactant.

However, the effects of more than one surfactant may be cumulative, as follows directly from surface thermodynamics.

The differential of the Gibbs energy, dG, may be written

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \gamma\mathrm{d}A + \Sigma\mu_i\mathrm{d}n_i \tag{3.2}$$

where A is the area of the interface and other symbols have their usual meaning. Adding $\mathrm{d}(\mu_i n_i)$ for one component (either the surfactant or the cosurfactant) to both sides we derive easily:

$$\left(\frac{\partial\gamma}{\partial\mu_i}\right)_{T,p,\,\text{all } n_j \text{ except } n_i, A} = -\left(\frac{\partial n_i}{\partial A}\right)_{T,p,\mu_i,\,\text{all } n_j \text{ except } n_i} = -\Gamma_i. \tag{3.3}$$

Using eqn (3.3) first for the cosurfactant, (i = co) and then for the surfactant (i =sa) (or the other way around) we have

$$\gamma = \gamma_0 - \left[\int_{c(\mathrm{co})=0}^{c(\mathrm{co})} \Gamma_{\mathrm{co}}\,\mathrm{d}\mu_{\mathrm{co}}\right]_{T,p,c(\mathrm{sa})=0} - \left[\int_{c(\mathrm{sa})=0}^{c(\mathrm{sa})} \Gamma_{\mathrm{sa}}\,\mathrm{d}\mu_{\mathrm{sa}}\right]_{T,p,n(\mathrm{co}),n_{\mathrm{oil}},n_{\mathrm{water}}} \tag{3.4}$$

We see from eqn (3.4) that upon addition of the second surfactant the interfacial tension will decrease further, the essential requirement being a not too small adsorption of the second surfactant. Whether it replaces the first surfactant or is absorbed in addition to it is immaterial, just as it is not essential for the two surfactants to form a surface complex.

If the two surfactants are of the same type, *e.g.*, both water soluble anionic surfactants, they will form mixed micelles and this will lower the activity of the second surfactant added and decrease both its Γ and dμ. But if they are rather different in nature, *e.g.*, one mostly water soluble and the other mostly oil soluble, they will only slightly affect each other's activity and their combined effect on the interfacial tension may be large enough to bring the interfacial tension down to zero and potentially below zero at finite concentrations.

4. CONSEQUENCES OF ZERO INTERFACIAL TENSION

When the conditions for negative interfacial tension are reached, the interface will expand, adsorbing both surfactants in the process until their activities are lowered to such values that $\gamma = 0$. As a rule this implies that the remaining concentration of the ionic surfactant is below the c.m.c., since above the c.m.c. its activity is nearly constant.

Then all but a small fraction of this surfactant is in the interface and thus the interfacial area is equal to the amount of this surfactant times its molar area (in the presence of the co-surfactant). The molar area is of the order of 0.5 $\text{nm}^2 \times N_{\text{Av}}$.

In certain combinations of amounts of the various components the large total interfacial area involved might be arranged in lamellar form, these systems showing the properties of liquid crystals. At other concentrations typical low viscosity, isotropic transparent microemulsions are found, the huge interfacial area being comprised of the surfaces of a large number of very small droplets.

One might wonder why, at $\gamma = 0$, these droplets are spherical, as there seems to be no driving force to bring such a droplet to the shape of minimum area. However, a microemulsion droplet contains most of its soap ions in the surface and very few in the bulk. Even a small deformation will increase the surface area with a concomitant decrease in adsorption density. A compensation of this decrease by further adsorption from the bulk would lead to a rather large decrease in the bulk concentration and to a strong rise in the interfacial tension, which would drive the shape back to spherical. We may consider this as a manifestation of the Gibbs–Marangoni effect. It also explains why microemulsion droplets behave to a good approximation as hard spheres.[6]

The situation $\gamma = 0$ would be determined by the composition of the two bulk phases and that of the interface, the last named one being controlled by the composition of the bulk phases. These conditions are expected to be at most only slightly dependent on the droplet size. Therefore, when stable microemulsions can be obtained, macroemulsions may also be thermodynamically stable, provided the composition of the bulk phases is the same as in the microemulsions.

Such macroemulsions would not appear to be different from ordinary kinetically stabilized emulsions: they would be turbid, they would cream or sediment, but they would not coalesce, since that would decrease the interfacial area and make the interfacial tension negative. The fairly high concentration of alcohol or other cosurfactant in the oil phase might, of course, be a drawback for practical applications.

One difference between such macroemulsions and the corresponding microemulsions might be that the van der Waals attraction between the droplets would be stronger in the macroemulsions, possibly leading to local coalescence in W/O emulsions, so as to invert them into O/W emulsions. These, by virtue of the longer range of the electrostatic repulsion, would then be thermodynamically and kinetically stable.

5. GIBBS ENERGY OF THE SYSTEM

The condition $\gamma = 0$ is not sufficient to describe and understand microemulsions, however important it may be to explain the driving force towards their formation.

For thermodynamic stability the Gibbs energy of the total system must achieve a minimum value. This Gibbs energy contains several terms as discussed by Ruckenstein and Chi.[7] We follow the same line of thought, although our treatment is rather different in its details from that in ref. (7).

The first contribution to the Gibbs energy of a microemulsion, ΔG_1, refers to the Gibbs energy of mixing of surfactant and water and of cosurfactant and oil. To keep our equations reasonably simple, we shall assume that the mutual solubilities of water and oil, of the surfactant in oil and of the cosurfactant in water are negligible. Thus we have

$$\Delta G_1 = n_{\text{w}}(\mu'_{\text{w}} - \mu^{\ominus}_{\text{w}}) + n'_{\text{sa}}(\mu'_{\text{sa}} - \mu^{\ominus}_{\text{sa}}) + n_0(\mu'_0 - \mu^{\ominus}_0) + \\ + n'_{\text{co}}(\mu'_{\text{co}} - \mu^{\ominus}_{\text{co}}) \qquad (5.1)$$

The primes refer to the final situation in which most of the surfactant ($\Gamma_{sa}A$) and a great portion of the cosurfactant ($\Gamma_{co}A$) have disappeared from the solutions into the interface. The original amounts of surfactant and cosurfactant are n_{sa} and n_{co}, respectively.

The second term, ΔG_2, refers to the interfacial area and is

$$\Delta G_2 = \gamma_{\text{final}}\, A + (n_{sa} - n'_{sa})\mu'_{sa} + (n_{co} - n'_{co})\mu'_{co}. \tag{5.2}$$

We split γ_{final}, the final interfacial tension which is close to zero, into $\gamma_{\text{uncharged}}$, the interfacial tension that would obtain if no electrical double layer had been formed, at otherwise unchanged compositions of solutions and interface, and an electrical term $\int\psi_0 d\sigma$, where ψ_0 is the surface potential and σ the surface charge density.

$$\gamma_{\text{final}} = \gamma_{\text{uncharged}} + \int_0^\sigma \psi_0 d\sigma \quad . \tag{5.3}$$

Splitting γ_{final} into these two contributions is useful since $\gamma_{\text{uncharged}}$ presumably is based on short range effects and thus to a first approximation independent of the curvature of the interface, whereas the electrical term encompasses long range effects and is therefore a function of the radius, a, of the particles.

Finally, there is a second free energy of mixing term, ΔG_3, due to the mixing of the droplets (say of water) into the continuous phase (oil). We are dealing with concentrated emulsions and thus we have to take non-ideal behaviour into account. Vrij *et al.*[6] have shown that the Percus-Yevick[8]–Carnahan-Starling[9] approximation for hard spheres applies rather well to the light scattering of oil continuous microemulsions. We have therefore applied the same theory, starting with the equation for the osmotic pressure, Π, of a hard sphere suspension in the form

$$\Pi = RT\frac{\varphi}{V_{hs}}\frac{1 + \varphi + \varphi^2 - \varphi^3}{(1 - \varphi)^3} \tag{5.4}$$

where V_{hs} is the molar volume of the hard spheres and φ their volume fraction.

From Π we derive μ (dispersion medium), then $d\mu_{hs}$ using the Gibbs–Duhem relation and μ_{hs} by integration. The final result for ΔG_3 is:

$$\Delta G_3 = n_{hs} RT\left(\ln\varphi - 1 + \varphi\frac{4 - 3\varphi}{(1 - \varphi)^2} + \ln\frac{V_o}{V_{hs}}\right) \quad . \tag{5.5}$$

The detailed calculation is given in the appendix.

The total Gibbs energy of the microemulsion, leaving out the standard terms for the individual components is then:

$$\begin{aligned}&\Delta G_{\text{microemulsion}} = \Delta G_1 + \Delta G_2 + \Delta G_3 = \\ &n_w\mu_w' + n_{sa}\mu'_{sa} + n_o\mu'_o + n_{co}\mu'_{co} + (\gamma_{\text{uncharged}} + \textstyle\int \psi_0 d\sigma)A \\ &+ n_{hs} RT\left(\ln\varphi - 1 + \varphi\frac{4 - 3\varphi}{(1 - \varphi)^2} + \ln\frac{V_o}{V_{hs}}\right) \quad .\end{aligned} \tag{5.6}$$

At equilibrium dG must be zero and d^2G positive. To a first approximation A, $n'_{sa} = n_{sa} - \Gamma_{sa}A$, and $n'_{co} = n_{co} - \Gamma_{co}A$ are variable, $\gamma_{\text{uncharged}}$ depends on n'_{sa} and n'_{co}, n_{hs} can be related to A, but $\int\psi_0 d\sigma$ depends on Γ_{sa} which we may assume to be constant in the region of saturation adsorption and depends only slightly on a which itself is proportional to A^{-1}.

We may then write for $\mathrm{d}G_{\text{microemulsion}}$

$$\mathrm{d}G_{\text{microemulsion}} = \underbrace{n_{\mathrm{w}}\mathrm{d}\mu'_{\mathrm{w}} + n'_{\mathrm{sa}}\mathrm{d}\mu'_{\mathrm{sa}}}_{\text{(I)}} + \underbrace{n_0\mathrm{d}\mu'_0 + n'_{\mathrm{co}}\mathrm{d}\mu'_{\mathrm{co}}}_{\text{(II)}}$$

$$+ \underbrace{\Gamma_{\mathrm{sa}}A\mathrm{d}\mu'_{\mathrm{sa}} + \Gamma_{\mathrm{co}}A\mathrm{d}\mu'_{\mathrm{co}} + A\mathrm{d}\gamma}_{\text{(III)}} + \gamma_{\text{uncharged}}\,\mathrm{d}A +$$

$$+ (\textstyle\int \psi_0 \mathrm{d}\sigma)\mathrm{d}A + \frac{A^2kT\mathrm{d}A}{12\pi(n_{\mathrm{w}}V_{\mathrm{w}})^2}\left[\ln\varphi - 1 + \varphi\frac{4-3\varphi}{(1-\varphi)^2} + \ln\frac{V_0}{V_{\mathrm{hs}}}\right] \tag{5.7}$$

where the relation $n_{\mathrm{hs}}\,N_{\mathrm{Av}} = A^3/36\pi(n_{\mathrm{w}}V_{\mathrm{w}})^2$ has been used to eliminate n_{hs}.

The terms (I) and (II) are zero on account of the Gibbs–Duhem relation and (III) is zero according to the Gibbs adsorption isotherm. Consequently,

$$\mathrm{d}G = \mathrm{d}A\left[\gamma_{\text{uncharged}} + \textstyle\int\psi_0\mathrm{d}\sigma + \frac{A^2kT}{12\pi(n_{\mathrm{w}}V_{\mathrm{w}})^2}\left(\ln\varphi - 1 + \varphi\frac{4-3\varphi}{(1-\varphi)^2} + \right.\right.$$

$$\left.\left. + \ln\frac{V_0}{V_{\mathrm{hs}}}\right)\right] \tag{5.8}$$

The three terms are rather unequal in magnitude. The last term is always negative. It can be transformed by using $A \sim n_{\mathrm{sa}}/\Gamma_{\mathrm{sa}}$ and for a rather high ratio of soap to water, $n_{\mathrm{sa}}/n_{\mathrm{w}} = 0.04$ (corresponding to a mass ratio of about 0.7) and $\varphi = 0.5$, it has the value -0.2 dyn cm^{-1}. For $\varphi = 0.1$ the value would be -0.5 dyn cm^{-1}, and φ would have to be below 10^{-5} to make this term equal to -1.0 dyn cm^{-1}.

The electrical Gibbs energy per unit area of the double layer is quite high at the high charge densities involved, so high that no simple theory will give a precise value. If it is assumed that most of the energy is present in a molecular condenser (Stern-layer) with a capacity of 15μF cm^{-2} (order of magnitude found at a mercury–water interface) then at a charge density of 1 elementary charge per 0.5 nm^2, $\int\psi_0\mathrm{d}\sigma$ becomes

$$\int\psi_0\mathrm{d}\sigma = \frac{1}{2}\,\frac{\sigma^2}{\text{capac.}} = 340 \text{ dyn cm}^{-1} \tag{5.9}$$

and the corresponding potential difference would be 2.1 V. Such a large potential would certainly force a large fraction of the counterions in between the charged heads of the ionic surfactant and decrease the effective charge density to between 50% to 10% of its value, thus reducing the potential to several hundred mV and the (positive) contribution to the interfacial tension to 50 dyn cm^{-1} or less.

This still requires $\gamma_{\text{uncharged}}$ to have a high negative value in order to reach $\mathrm{d}G = 0$.

The conclusion so far must be that in a microemulsion the interfacial tension, including the electrical term has very low, but slightly positive values. The small variations in the total interfacial tension required to balance variations in the free energy of mixing (osmotic) term can be easily obtained by small variations in n'_{sa}, and n'_{co}, leading to variations in $\gamma_{\text{uncharged}}$.

6. OIL-IN-WATER OR WATER-IN-OIL

So far it has not been necessary to specify whether an O/W or a W/O microemulsion was the stable one. Several factors are playing a role here. The osmotic term increases with increasing φ and thus favours the situation in which the phase with the smaller volume fraction forms the droplets, with in addition a small advantage for the oil phase to form the droplets because $V_{\text{oil}} > V_{\text{water}}$.

For W/O emulsions the hard sphere volume is only slightly larger [see ref. (6)] than the water volume, since the hydrocarbon tails of the surfactant may interpenetrate to a certain extent, when two droplets come close together.

For O/W emulsions, on the other hand, the repulsion between double layers may easily have a range of several times $1/\kappa$ ($1/\kappa$ = Debye length), and unless the electrolyte concentration (other than the ionized surfactant) is very high, it would increase the hard sphere radius by 5 nm or more. This factor works in favour of the W/O emulsion, especially for small droplets.

Furthermore, establishing a curvature of the adsorbed layer at a given adsorption will be easier with water as the droplet phase, since in this case the hydrocarbon tails of the surfactant will have more freedom to move around than when they are inside the drop. Consequently, other things being equal the interfacial tension will be slightly lower for W/O than for O/W emulsions.

It has been mentioned earlier that van der Waals forces would work in favour of O/W emulsions, but only when the droplets are large.

A unique preference does not exist, but on the whole W/O emulsions will be favoured with small drops, O/W with large drops. However, since the difference in stability between the two possible forms is not large, small specific effects such as packing of the interfacial layer and the volume fraction may become decisive factors.

7. DROPLET SIZE DISTRIBUTION

Finally, we arrive at the issue of the isodispersity. If at a given total interfacial area the particles all have the same size, that size is determined by the following two equations (for a W/O emulsion).

$$4\pi n_{\mathrm{hs}} a^2 N_{\mathrm{Av}} = A \tag{7.1}$$

and

$$\frac{4\pi}{3} n_{\mathrm{hs}} a^3 N_{\mathrm{Av}} = n_{\mathrm{w}} V_{\mathrm{w}} \tag{7.2}$$

where we neglect for simplicity the term $n'_{\mathrm{sa}} V_{\mathrm{sa}}$ in the total volume of the droplets. Solving these equations for a and n_{hs} leads to

$$a = \frac{3n_{\mathrm{w}} V_{\mathrm{w}}}{A} \text{ and } n_{\mathrm{hs}} = A^3/36\pi N_{\mathrm{Av}}(n_{\mathrm{w}} V_{\mathrm{w}})^2. \tag{7.3}$$

However, the same area and the same volume can be obtained with a particle size distribution about the above radius. The kind of distribution and its width will depend on the differences in Gibbs energy amongst the particles of different sizes.

Transfer of water or surfactant from one droplet to other droplets (keeping the total area, the total volume and n'_{sa} constant) does not change the total Gibbs energy. Neither would a moderate deviation from isodispersity change the osmotic term, since it is mainly determined by φ, which stays constant and n_{hs}, which changes little. Also $\gamma_{\mathrm{uncharged}}$ remains the same, but now the secondary effects of the particle radius on the electric term become important.

The radial dependence of the standard Gibbs energy per particle, $E(a)$, is then

$$\frac{\partial E(a)}{\partial a} = \frac{\partial}{\partial a}\{[\gamma_{\mathrm{uncharged}} + (\textstyle\int \psi_0 \mathrm{d}\sigma)_a]4\pi a^2\} \tag{7.4}$$

As mentioned above, there is no completely satisfactory way of estimating the electrical free energy for these very highly charged double layers, but we may assume that starting at some distance from the surface the double layer behaves as if it emanated from a lower surface charge density, *e.g.*, from 1 elementary charge per 200 Å^2 or 500 Å^2 (75 to 90% of the charge compensated very close to the head groups).

When we consider the diffuse part of the double layer inside a spherical drop and assume as a first approximation that the Debye–Hückel linearization may be applied, then the potential ψ would have to satisfy the equation

$$\nabla^2\psi = \kappa^2\psi \tag{7.5}$$

with

$$\kappa^2 = 2F^2c/\varepsilon\varepsilon_0 RT \tag{7.6}$$

assuming that a concentration c of monovalent electrolytes is present.

The solution of eqn (7.5) inside a spherical drop is

$$\psi = \frac{P \sinh \kappa r}{r} \tag{7.7}$$

with P equal to:

$$P = \frac{a^2\Gamma' F}{\varepsilon\varepsilon_0(\kappa a \cosh \kappa a - \sinh \kappa a)} \tag{7.8}$$

where Γ' is that portion of the surface charge density (in moles per unit area) that is not compensated very close to the surface.

Levine and Robinson[10] give a better approximation starting from the non-linearized Poisson–Boltzmann equation instead of from eqn (7.5), but it is more complicated. The main point in my discussion is to show the basic line of thought.

In our linearized case the electrical contribution to the surface Gibbs energy is

$$\int\psi_0 \mathrm{d}\sigma = \frac{1}{2}\,\psi_{\mathrm{surf}}\,\sigma = \frac{a(\Gamma' F)^2}{2\varepsilon\varepsilon_0(\kappa a \coth \kappa a - 1)} \quad . \tag{7.9}$$

For a certain value of $a = a_0$ the electrical term in eqn (7.4) just compensates $\gamma_{\mathrm{uncharged}}$ and therefore

$$\gamma_{\mathrm{uncharged}} = -(\int\psi_0 \mathrm{d}\sigma)_{a0} \quad . \tag{7.10}$$

Using now eqn (7.4), (7.10) and (7.9) we can write for $E(a_0 + \Delta a)$

$$\begin{aligned} E(a_0 + \Delta a) &= 4\pi a^2 \frac{\mathrm{d}}{\mathrm{d}a}(\int\psi_0 \mathrm{d}\sigma)\Delta a = \\ &= -\frac{2\pi(\Gamma' F)^2}{\varepsilon\varepsilon_0\kappa^2}\left(1 + \frac{2}{\kappa a} + \ldots\right)\Delta a \end{aligned} \tag{7.11}$$

where we have asumed that $\kappa a \gg 1$ so that we may approximate

$$\kappa a \coth \kappa a - 1 = \kappa a - 1 + 2 \;\; \kappa a \mathrm{e}^{-2\kappa a} + \ldots \quad . \tag{7.12}$$

The particle size distribution function $f(a) = \mathrm{d}n_{\mathrm{hs}}/\mathrm{d}a$ is a Boltzmann distribution

$$f(a) = \mathrm{d}n_{\mathrm{hs}}/\mathrm{d}a = f(a_0)\exp(-E/kT) = f(a_0)\exp(+\Delta a/\Delta a_{\mathrm{w}}) \tag{7.13}$$

with Δa_{w}, the width of the distribution equal to

$$\Delta a_{\mathrm{w}} = \varepsilon\varepsilon_0\kappa^2 kT/2\pi(\Gamma' F)^2 \tag{7.14}$$

which results in an exponential distribution with a sharp cut-off at the large particle size as sketched in fig. 3.

The distribution becomes narrower with decreasing κ (*i.e.*, with decreasing electrolyte concentration) and with increasing surface charge. Its width, expressed as Δa_w, is independent of the average particle size. To give an idea of the numerical value of Δa_w, we estimate it for a fairly high electrolyte concentration (0.1 mol dm^{-3} of a 1–1 electrolyte) and a surface charge density created by $\Gamma' = 1$ monovalent ion per 200 Å^2. Then Δa_w is equal to

$$\Delta a_w[0.1 \text{ mol dm}^{-3} \text{ (1–1 electrolyte)};\ \Gamma' = (N_{Av} \times 200 \text{ Å}^2)^{-1}] = 0.7 \text{ Å} \quad . \qquad (7.15)$$

The conclusion is that the distribution is narrow, the narrower the lower the electrolyte concentration and the higher the surface charge. Although the calculation contains admittedly rather drastic approximations, the conclusion may be expected to hold also for more accurate calculations.

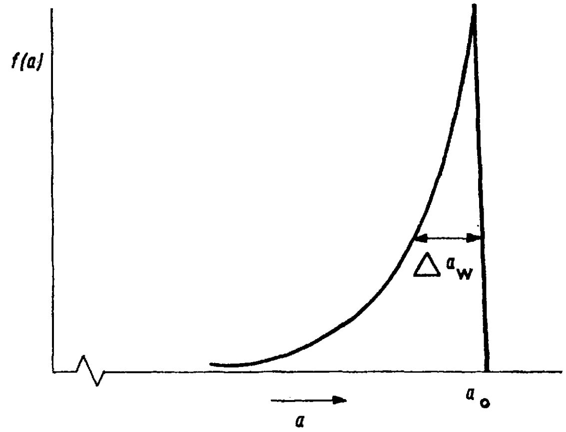

FIG. 3.—Particle size distribution function with a width Δa_w. At the radius a_0 the interfacial tension ($\gamma_{\text{uncharged}} + \int \psi_0 d\sigma$) is just zero [*cf.* eqn (7.10) and (7.14)].

It was mentioned in the discussion after eqn (5.8) that the contribution of the interfacial tension, $\gamma_{\text{uncharged}} + \int \psi_0 d\sigma$, has to be slightly positive to counterbalance the free energy of mixing term. This will remain true for the particle size distribution described above, and in general will require the upper limit of the particle radius to be $a_1 < a_0$. The value a_1 and the number of droplets, $N_{Av} \times n_{hs}$, are found easily from the distribution function, eqn (7.13), the total volume, $n_w V_w$ of the droplets and their total area, A. For a narrow size distribution ($\Delta a_w < a_1$) we have to a good approximation

$$a_1 \approx \langle a \rangle + \Delta a_w \qquad (7.16)$$

$$\langle a \rangle \approx 3 n_w V_w / A \qquad (7.17)$$

$$n_{hs} \approx A^3 / 36 \pi N_{Av} (n_w V_w)^2 . \qquad (7.18)$$

The value $a_0 - a_1$ will depend on the volume fraction, φ; a_0, the radius at which the interfacial tension is exactly zero, adjusts itself by a small change in the free concentrations of the surfactants n'_{sa} and n'_{co}.

Considering now the more general case, without the restriction that κa be large, we derive in the same way as eqn (7.11)

$$\begin{aligned}E(a_0 + \Delta a) &= 4\pi a^2 \frac{\mathrm{d}}{\mathrm{d}a} \frac{a(\Gamma' F)^2}{2\varepsilon\varepsilon_0(\kappa a \coth \kappa a - 1)} \Delta a \\ &= -\frac{2\pi(\Gamma' F)^2}{\varepsilon\varepsilon_0\kappa^2} \frac{1 - \kappa^2 a^2/\sinh^2 \kappa a}{(\coth \kappa a - 1/\kappa a)^2} \Delta a \\ &= -\frac{2\pi(\Gamma' F)^2}{\varepsilon\varepsilon_0\kappa^2} f(\kappa a)\Delta a, \qquad (7.19)\end{aligned}$$

$f(\kappa a)$ has a very limited range, going from 1 for $\kappa a \longrightarrow \infty$ *via* 2.018 for $\kappa a = 3$ and 2.816 for $\kappa a = 1$ to 3.0 for $\kappa a = 0$. For small values of κa, the distribution is narrower by as much as a factor 3 than that predicted by eqn (7.14).

Qualitatively, the results obtained can be understood by noting that even a small microemulsion droplet contains several hundred surfactant ions. A relatively small change in the curvature of the surface leads to a small change in the convergence of the lines of force towards the centre of the (water) droplet and to a small change in the electrical Gibbs energy of the double layer per soap ion. The sum of hundreds of these small differences adds up to many times kT.

It is also evident that the electrical free energy per unit charge in the surface is larger the smaller the droplet, if the double layer is inside the droplet. For an O/W emulsion the double layer would be outside the droplet, and thus the energy per unit charge would increase with increasing droplet size, leading to an exponential particle size distribution with a sharp cut-off at the small particle end.

8. OTHER DISPERSIONS THAT ARE THERMODYNAMICALLY STABLE

A few months ago Stol and de Bruyn,[11] working on the nucleation and growth of oxides and hydroxides, remarked that it might be possible to obtain thermodynamically stable dispersions of solids in cases in which the adsorption of potential determining ions is large enough to lead to a zero (or potentially negative) interfacial tension. If this could be realized systematically it might mean an important breakthrough in the preparation of stable dispersions. The idea need not be limited to potential determining ions, since any additional positive adsorption, *e.g.*, of surfactant ions or molecules would lead to a further decrease in the interfacial tension and increase the chances of obtaining thermodynamic stability.

In looking for confirmation of this postulate, one need not expect spontaneous comminution, but it is conceivable that the growth of particles is stopped by this effect, and even " negative Ostwald ripening " might occur. Favourable conditions are:

(*a*) a low interfacial tension to begin with, and thus preferably a low energy density solid rather than a high energy density one;

(*b*) a very asymmetric point of zero charge, since this would favour high surface potentials;

(*c*) strong adsorption of small molecules (or ions) so that Γ may become large. In " protecting " suspensions by this mechanism, small molecules are better than large, polymeric ones;

(*d*) use of more than one adsorbate;

(*e*) a high electrolyte concentration is favourable in the case of potential determining ions, since this would lead to a high charge density at a given surface potential; but if saturation adsorption of an ionic detergent is reached, then a low electrolyte concentration is preferable since this would give a high surface potential for the given surface charge.

The remarkable stability of silica sols[12] at alkaline pH may be a case of this nature.

9. CONCLUDING REMARKS

The concept of potentially negative, but ultimately positive small interfacial tension explains the formation and thermodynamic stability of at least certain types of microemulsions and possibly other dispersions of solids. Isodispersity can be regarded as a consequence of the change in the electrical contribution to the surface tension with the curvature of the interface.

A continuous transition from swollen micelles *via* typical transparent microemulsions to macroemulsions is possible, although in the latter case the thermodynamic stability may be limited by the relatively stronger van der Waals interaction amongst the droplets.

Refinement of the treatment as offered in this paper is possible and desirable. A search for other systems with this type of stability might be rewarding.

In microemulsions stabilized by a nonionic surfactant (*cf.* Shinoda and Friberg)[13] electrical effects as discussed in this paper are absent. Whether such systems are better characterized as swollen micelles or as dispersions of droplets with low interfacial tension is omitted from discussion here.

I gratefully acknowledge constructive criticism by Prof. R. G. Donnelly of the text of this communication.

APPENDIX

DERIVATION OF EXPRESSION FOR THE GIBBS ENERGY OF MIXING OF HARD SPHERES IN A SOLVENT, EQN (5.5)

The relation between the osmotic pressure, Π, and the chemical potential of the solvent, 1, is

$$\mu_1 = \mu_1{}^{\ominus} - \Pi V_1 \tag{A.1}$$

where V_1 is the molar volume of the solvent. Using the value for Π, given in eqn (5.4) we have

$$\mu_1 = \mu^{\ominus}{}_1 - RT\frac{V_1}{V_{\text{hs}}}\varphi\frac{1+\varphi+\varphi^2-\varphi^3}{(1-\varphi)^3} \quad . \tag{A.2}$$

According to the Gibbs–Duhem relation

$$\mathrm{d}\mu_{\text{hs}}/\mathrm{d}\mu_1 = -(1-x)/x \tag{A.3}$$

where x is the mole fraction of hard spheres. The mole fraction is expressed in the volume fraction, φ, by

$$x = \frac{\varphi/V_{\text{hs}}}{\varphi/V_{\text{hs}} + (1-\varphi)/V_1} \quad . \tag{A.4}$$

Then $\mathrm{d}\mu_{\text{hs}}$ can be written

$$\begin{aligned}\mathrm{d}\mu_{\text{hs}} &= +\frac{1-\varphi}{\varphi}\frac{V_{\text{hs}}}{V_1}RT\frac{V_1}{V_{\text{hs}}}\mathrm{d}\left(\frac{\varphi(1+\varphi+\varphi^2-\varphi^3)}{(1-\varphi)^3}\right)\\ &= RT\,\mathrm{d}\left(\frac{1+\varphi+\varphi^2-\varphi^3}{(1-\varphi)^2}\right) + RT\frac{1+\varphi+\varphi^2-\varphi^3}{\varphi(1-\varphi)^3}\mathrm{d}\varphi\end{aligned} \tag{A.5}$$

Integrating of the second term and combining the result with the first term we find:

$$d\mu_{hs} = RT\,d\left(\ln\varphi + \frac{2}{1-\varphi} + \frac{3}{(1-\varphi)^2} - \varphi\right) \tag{A.6}$$

Integrating eqn (A.6) from $\varphi = 0$ to φ leads to

$$\mu_{hs} = RT\left(\ln\varphi + \frac{2}{1-\varphi} + \frac{3}{(1-\varphi)^2} - \varphi\right) - RT\,(\ln\varphi_{\phi\to0} + 5) + \mu^{\ominus}{}_{hs} + RT\ln x_{hs(\phi\to0)} \tag{A.7}$$

Since $(x/\varphi)_{\phi\to0} = V_1/V_{hs}$ we finally have:

$$\mu_{hs} = \mu^{\ominus}{}_{hs} + RT\left(\ln\varphi + \varphi\frac{7-3\varphi-\varphi^2}{(1-\varphi)^2} + \ln\frac{V_1}{V_{hs}}\right) \tag{A.8}$$

The Gibbs energy of mixing can now be written

$$\begin{aligned}\Delta G_3 &= n_1(\mu_1 - \mu^{\ominus}{}_1) + n_{hs}(\mu_{hs} - \mu^{\ominus}{}_{hs}) \\ &= -RT\frac{V_1}{V_{hs}}n_1\varphi\frac{1+\varphi+\varphi^2-\varphi^3}{(1-\varphi)^3} + n_{hs}RT \\ &\quad\times\left(\ln\varphi + \varphi\frac{7-3\varphi-\varphi^2}{(1-\varphi)^2} + \ln\frac{V_1}{V_{hs}}\right)\end{aligned} \tag{A.9}$$

Using $V = n_1V_1 + n_{hs}V_{hs}$, $V_1n_1\varphi/V_{hs}$ can be converted into $n_{hs}(1-\varphi)$. Inserting this in eqn (A.9) we obtain

$$\Delta G_3 = n_{hs}RT\left(\ln\varphi - 1 + \varphi\frac{4-3\varphi}{(1-\varphi)^2} + \ln\frac{V_1}{V_{hs}}\right) \tag{A10}$$

and this is the same as eqn (5.5).

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