equation for binary bulk diffusion

$$N_T = x_T(N_T + N_G) - D_{TG}\frac{P_o}{R_gT}\frac{dx_T}{dr} \qquad (A3)$$

where the molar fluxes N_T, N_G refer to the D_4-pore network and hence are given by

$$N_i = \frac{f\gamma_i}{3}r \quad (i = G, T)$$

Introducing these expressions in (A3) and solving with the condition $x_T = 0$ at $r = R_p$, we obtain

$$x_T = \frac{\gamma_T}{\gamma_T + \gamma_G}\left\{ 1 - \exp\left[-\overline{B}'\left(1 - \frac{r^2}{R_p{}^2}\right)\right] \right\} \qquad (A4)$$

where

$$\overline{B}' = \frac{(1+\delta)}{2}\frac{\overset{\bullet}{D}_{GK}}{\overset{at}{D}_{TG}}\overline{B}$$

The maximum value of x_T is given by

$$x_T(0) = \frac{\gamma_T}{\gamma_T + \gamma_G}(1 - e^{-\overline{B}'}) \qquad (A5)$$

so that the criterion for small composition gradients becomes

$$\overline{B}' << 1 \qquad (A6)$$

According to (A2) the condition (A6) also insures small relative pressure gradients.

To examine the conditions under which (A6) is valid, we take the following example: $T = 800°K$, $R_p = 50$ μm, $\epsilon_4 = 0.015$, weight loss = 20% in 10 s (half of which is gases and half is tar). Using molecular weights $M_G = 25$, $M_T = 250$ and coal particle density 1.2 g/cm³, we compute $\gamma_G = 4.8 \times 10^{-4}$ gmols/cm³s, $\gamma_T = 0.48 \times 10^{-4}$ gmols/cm³s, $D_{GK} = 2.74$ cm²/s, $\overset{at}{D}_{TG} = 0.48$ cm²/s, $f = 0.33$, $\delta = 0.1$ so that $\overline{B} = 0.005$, $\overline{B}' = 0.015$. On the other hand, taking $T = 900°K$ the rates are larger by a factor 3-5 so that $\overline{B}' \sim 0.04$-0.08. If, on the other hand, we take $T = 900°K$ and $R_p = 100$ μm, $\overline{B} \sim 0.06$-0.11, $\overline{B}' \sim 0.16$-0.34, marking a departure from uniform conditions. Under conditions at which $\overline{B}' \not\ll 1$, the use of an effective radius as defined by Equation (5) underestimates the internal build-up of pyrolysis products.

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Thermodynamics of Microemulsions: Combined Effects of Dispersion Entropy of Drops and Bending Energy of Surfactant Films

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A theory of dilute microemulsions is presented which includes for the first time both the entropy of dispersion of the drops and energy effects associated with bending the surfactant films at the drop interfaces. It yields expressions for drop size for (a) a dilute microemulsion in equilibrium with an excess bulk phase, e.g., an oil-in-water microemulsion in equilibrium with excess oil and (b) dilute oil-continuous and water-continuous microemulsions in equilibrium and containing equal amounts of surfactant. In the latter case, our theory indicates that existence of the two microemulsion phases sometimes is favored over a layered or lamellar phase, even though the "natural curvature" of the surfactant films is zero, corresponding to a perfectly flat film.

SCOPE

"Microemulsions are dispersions of one liquid in another which have very small drops (< 0.1 μm) and are often thermodynamically stable. They have been used in such applications as cutting oils and pesticides and are currently of great interest in connection with processes for increasing recovery of petroleum from underground reservoirs.

An important property of a microemulsion is its drop size. Existing theory indicates that drop size has a large effect on the interfacial tensions a microemulsion makes with other phases it contacts. Interfacial tension, in turn, has a strong influence on process success for the petroleum recovery situation. Thus, a theory which could predict drop size in microemulsions would be of considerable interest.

Other researchers have shown that both the entropy of dispersion of the many small drops and the energy required to bend the surfactant films at the drop interfaces are important in determining drop size in microemulsions. But no existing theory includes both effects. Such a theory is presented here.

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CONCLUSIONS AND SIGNIFICANCE

A very simple model applicable to dilute microemulsions has been developed to predict drop size as a function of surfactant concentration, the "natural" radius of curvature of the surfactant films at the drop interfaces, and film compressibility. This theory is the first to include both the entropy of dispersion of the drops and the bending energy of the surfactant films. The former increases with decreasing drop size when a given amount of surfactant is present, while the latter is minimized when drop radius equals the natural radius of curvature.

Analysis shows that a minimum in total system free energy occurs for a drop radius somewhat smaller than the natural radius for an oil-in-water microemulsion in equilibrium with excess oil or vice versa. More flexible surfactant films and lower surfactant concentrations favor smaller drops. When the surfactant is equally soluble in oil and water and when surfactant films are quite flexible, our theory predicts that the free energy of oil-continuous and water-continuous microemulsions in equilibrium is less than that when a layered or lamellar phase is present.

Dispersions of one fluid in another occur in many industrial applications. Typical liquid-liquid dispersions or emulsions contain drops greater than about 0.1 μm in diameter. They are thermodynamically unstable in the sense that coalescence of drops produces a reduction in system free energy. In some cases, effective emulsion lifetime may be quite long, however, owing to appreciable energy barriers which must be overcome before coalescence can occur.

Less common than conventional emulsions are "microemulsions." Typical microemulsions contain drops smaller than 0.1 μm in diameter and are thermodynamically stable. They have been used, for instance, as waxes, dry cleaning solutions, cutting oils, and pesticides (Prince 1977). Microemulsions are currently receiving considerable attention because of their importance in processes being developed to increase recovery of oil from underground reservoirs (Healy et al. 1976, Hwan et al. 1979).

The thermodynamic stability of microemulsions may appear surprising at first glance. As in the case of ordinary emulsions, separation into two bulk phases would greatly reduce interfacial area and, if interfacial tension is positive, interfacial free energy as well. If interfacial tension is negative, however, the interfacial area increase due to dispersion would actually decrease system free energy, and, dispersion should occur spontaneously. Schulman, responsible for much of the early work on microemulsions, considered that this mechanism was responsible for microemulsion formation (Schulman and Montagne 1961).

Rehbinder and coworkers (Rehbinder 1957, Likhtman et al. 1964) recognized that interfacial tension need not actually be negative for spontaneous dispersion to occur. It is necessary only that tension be low enough that the free energy decrease (due to the entropy of dispersion) outweigh the increase in interfacial free energy (due to dispersion). This idea has been developed and improved models have been constructed by Ruckenstein (Ruckenstein and Chi 1975, Ruckenstein 1976), who also considers interaction among drops, and by Reiss (1975). In more recent work, Ruckenstein (1978*a*, *b*) shows that another major contribution to the thermodynamic stability of microemulsions is the free energy decrease which occurs when a surfactant molecule leaves a bulk phase to adsorb at the surface of a drop.

Besides the source of thermodynamic stability, workers in this field have been much interested in whether microemulsions were of the oil-in-water or water-in-oil type. At least since Winsor's early work (1948), phase continuity has been thought to depend on the "natural curvature" of the surfactant films at the drop interfaces. If an ionic surfactant is present, for example, long-range electrical repulsion in dilute electrolyte solutions acts to increase the distance between surfactant ions in the film, and the natural curvature is that of an oil-in-water system (Figure 1). But if the range of electrical repulsion is much shorter, as in concentrated electrolyte solutions, and if considerable oil penetrates the portion of the film occupied by the hydrocarbon chains of the surfactant, the resulting natural curvature favors a water-in-oil system. Schulman et al. (1959) also recognized this effect, Murphy (1966) analyzed bending properties of interfaces, and Robbins (1976) recently incorporated them into a theory of microemulsions.

Phase equilibrium studies show that, under appropriate circumstances, microemulsions can exist in equilibrium with excess oil, excess water, or both simultaneously. Adamson (1969) presented a thermodynamic analysis of microemulsions. A key idea of his was that the chemical potential of water inside the drops of a water-in-oil microemulsion must equal the chemical potential of water in the bulk aqueous phase in equilibrium with the microemulsion. His particular analysis, based on a difference in concentration of various ions in the two water regions, cannot be applied to oil-in-water microemulsions or to microemulsions made with nonionic surfactants. Robbins (1976) included Adamson's basic idea of equality of chemical potentials in his recent work, which is more general and can be used for these other types of microemulsions.

No existing analysis, however, considers both natural curvature and entropy of dispersion effects, although the available evidence strongly suggests that both are im-

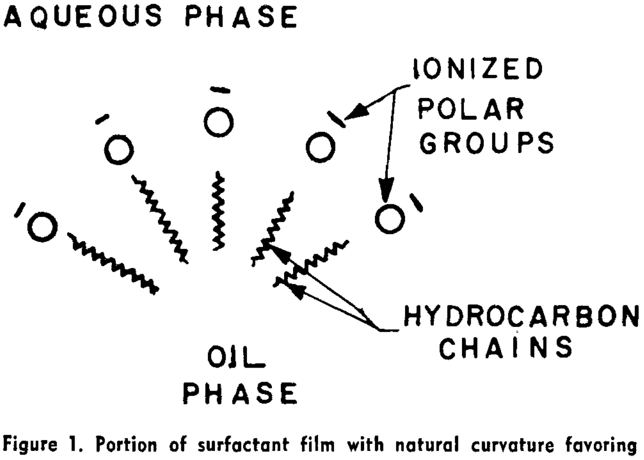

Figure 1. Portion of surfactant film with natural curvature favoring oil-in-water microemulsion.

portant. Here we develop an analysis which includes both effects in its predictions of drop size—a property of microemulsions important in its own right and because of its relation to the ability to produce the ultralow interfacial tensions so important in oil recovery (Miller et al. 1977).

The analysis here deals with two situations where a relatively small amount of surfactant and relatively large amounts of oil and water are present. When the surfactant is much more soluble in one bulk phase than the other, the equilibrium situation involves coexistence of a microemulsion and an excess bulk phase (e.g., an oil-in-water microemulsion and excess oil for a water-soluble surfactant). In this case, the analysis predicts that, when interaction among drops is small, drop diameter is always less than that corresponding to the natural curvature. While bending energy must be supplied to produce drops with the smaller diameter, this effect is more than offset by the increased entropy associated with a larger number of smaller drops.

The second situation we consider is that of a surfactant which is equally soluble in oil and water and whose films at oil-water interfaces therefore have no natural tendency to bend and form either oil drops or water drops. At first glance, one might expect the surfactant to occur in a layered or lamellar structure in such systems, and in some, it doubtless does. Here too, however, the theory predicts that, if drop interaction is small and if the surfactant films are sufficiently flexible, system free energy can be reduced by forming drops, so that at equilibrium oil-continuous and water-continuous microemulsions can coexist.

We note that at higher surfactant concentrations than considered here, the structure of microemulsion phases is not clear in systems where natural curvature is very small. Possible structures based on both drops and lamellae have been suggested, as has a bicontinuous structure containing neither drops nor lamellae (Scriven 1976, Talmon and Prager 1977, 1978). This question shall not be considered here.

DILUTE MICROEMULSION IN EQUILIBRIUM WITH EXCESS BULK PHASE—BASIC THERMODYNAMICS

We consider equilibrium in a system contains substantial amounts of both oil and water, but relatively little surfactant. Experiments show that, in many systems of this kind, appreciable ranges of conditions exist where either (a) an oil-in-water microemulsion containing virtually all the surfactant present is in equilibrium with excess oil or (b) a water-in-oil microemulsion containing virtually all the surfactant present is in equilibrium with excess water. For example, situation (a) occurs at low temperatures and situation (b) at high temperatures in systems containing oil, water, and a nonionic surfactant, polyoxyethylene nonylphenylether (Saito and Shinoda 1970). At intermediate temperatures, a different situation exists: a single microemulsion phase in equilibrium with both excess oil and excess water.

For clarity in presenting the analysis, we consider the particular case of a dilute oil-in-water microemulsion in equilibrium with excess oil. Given these equilibrium phases, our analysis seeks to predict drop size in the microemulsion phase. The drops are assumed to contain all the surfactant and all the solubilized oil but no water. Under these conditions we can write the differential dG_m of the Gibbs free energy of the microemulsion in the following form, using Hill's (1963, 1964) thermodynamics of small systems

$$dG_m = -S_m dT + V_m dp + \mu_w dn_w + \mu_s{}^d dn_s{}^d + \mu_o{}^d dn_o{}^d + E dN \qquad (1)$$

Here the superscript d denotes values for the drops, so that $n_s{}^d$ is, for example, the total amount of surfactant in all the drops. Also V_m is the total volume of the microemulsion, N is the total number of drops, and E is defined by

$$E \equiv \left(\frac{\partial G_m}{\partial N}\right)_{T,p,n_w,n_s{}^d,n_o{}^d} \qquad (2)$$

Other symbols are listed in the notation section below. For the bulk oil phase

$$dG_o = -S_o dT + V_o dp + \mu_o dn_o \qquad (3)$$

We seek the conditions for equilibrium at constant temperature, pressure, and total amount of each component in the system. Noting that conservation of oil requires $dn_o{}^d = -dn_o$, we readily obtain

$$dG_m + dG_o = 0 = (\mu_o{}^d - \mu_o)\, dn_o{}^d + E dN \qquad (4)$$

Clearly $\mu_o{}^d = \mu_o$ and $E = 0$ if (4) is to be satisfied for all possible changes from the equilibrium state.

Let us consider $\mu_o{}^d$ defined by

$$\mu_o{}^d = \left(\frac{\partial G_m}{\partial n_o{}^d}\right)_{T,p,n_w,n_s{}^d,N} \qquad (5)$$

To evaluate this quantity, we must provide a more detailed physical model of the microemulsion. Accordingly, we assume that total microemulsion free energy G_m can be expressed as

$$G_m = G_m{}^w + G_m{}^o + G_m{}^i + G_m{}^d \qquad (6)$$

Here $G_m{}^w$ is the free energy of the continuous water phase; $G_m{}^o$ is the free energy of the oil within the drops, which we assume can be treated as a bulk oil phase; $G_m{}^i$ is the free energy of the drop interfaces, which we assume can be treated as an ordinary interface between bulk phases; and $G_m{}^d$ is the free energy associated with the existence of a dispersed phase. Among other things, $G_m{}^d$ includes the configurational entropy of dispersion of the drops and the energy of interaction among them.

Now, the total Gibbs free energy G_m of the microemulsion is defined by

$$G_m = U_m - TS_m + pV_m \qquad (7)$$

with p the imposed external pressure. Hence $G_m{}^o$ is given by the same expression with U_m, S_m, V_m replaced by $U_m{}^o$, $S_m{}^o$, $V_m{}^o$. With this definition $G_m{}^o$ is simply the product of the number of moles of oil $n_o{}^d$ and the ordinary chemical potential of the oil phase at T and p. As the latter equals the bulk oil phase chemical potential μ_o, we have

$$\left(\frac{\partial G_m{}^o}{\partial n_o{}^d}\right)_{T,p,n_w,n_s{}^d,N} = \mu_o \qquad (8)$$

For the interfacial free energy we use Murphy's (1966) expression written for the special case of a spherical interface of radius a

$$\left(\frac{\partial G_m{}^i}{\partial n_o{}^d}\right) = \gamma\left(\frac{\partial \mathcal{S}}{\partial n^{od}}\right) - \frac{2\mathcal{S}\mathcal{H}}{a^2}\left(\frac{\partial a}{\partial n_o{}^d}\right) \qquad (9)$$

In this equation, γ is the interfacial tension between the drops and water, $\mathcal{S}$ is the total interfacial area of the drops and $\mathcal{H}$ is the "bending stress" of the interface. Since, according to Murphy's (1966) derivation, the bending stress is basically the derivative of interfacial free energy with respect to curvature at constant area, it is the term in $\mathcal{H}$ which accounts for the energy required to bend the interfacial film. This effect is generally considered to be important in microemulsions, as indicated above. Further information below about its detailed definition and evaluation is given below. Here we simply note that Robbins (1976) included bending effects in his theory.

For the dilute microemulsions considered here, we assume that all drops have the same radius a and use the virial equation of state to evaluate $G_m{}^d$, retaining only the second virial coefficient B_2 (Hill 1960)

$$G_m{}^d = -NkT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V_m e}{N} \right] + NkT \frac{N}{V_m} B_2 \tag{10}$$

where m is the mass of a drop and B_2 is given by

$$B_2 = -\frac{1}{2} \int_0^\infty [\exp(-U(r)/kT) - 1] \, 4\pi r^2 dr \tag{11}$$

where $U(r)$ = potential energy of interaction between drops with centers separated by a distance r. The first term of (10) is the free energy at infinite dilution, while the second term corrects for the finite size of the drops and for drop interaction.

Combining Equations (5)-(10), noting that the free energy of the water $G_m{}^w$ does not depend on $n_o{}^d$, and recognizing that $\mathcal{S} = 4\pi a^2 N$ and $V_o{}^d = (4\pi a^3 N/3)$ by basic geometry, we find

$$\mu_o{}^d = \mu_o + v_o\left(\frac{2\gamma}{a} - \frac{2\mathcal{H}}{a^2} \right) - \frac{NkTv_o}{V_m}\left(1 + \frac{3}{2} \frac{V_m}{V_o{}^d} \right) + \frac{N^2kT}{V_m} \frac{\partial B_2}{\partial n_o{}^d} - \frac{N^2kTv_oB_2}{V_m{}^2} \tag{12}$$

where v_o is the molar volume of the oil. Using (12), we find that the equilibrium condition $\mu_o{}^d = \mu_o$ yields the following relationship between the interfacial tension γ and bending stress $\mathcal{H}$

$$0 = +\left(\frac{2\gamma}{a} - \frac{2\mathcal{H}}{a^2} \right) - \frac{NkT}{V_m}\left(1 + \frac{3}{2} \frac{V_m}{V_o{}^d} \right) + \frac{N^2kT}{V_m v_o} \left(\frac{\partial B^2}{\partial n_o{}^d} \right)_{T,p,n_w,n_s{}^d,N} - \frac{N^2kTB_2}{V_m{}^2} \tag{13}$$

Another equation which must be satisfied is the force balance at the drop interface, which has the form (Murphy 1966)

$$p_o{}^d - p = \frac{2\gamma}{a} - \frac{2\mathcal{H}}{a^2} \tag{14}$$

Here $p_o{}^d$ is the pressure of the oil inside the drops. Note that this equation reduces to the usual Laplace equation of capillarity for a drop when the term in the bending stress $\mathcal{H}$ is negligible. By making several calculations, we find that the terms in (13) proportional to (NkT) are usually small so that, to a good approximation

$$\gamma \cong \frac{\mathcal{H}}{a} \tag{15}$$

$$p_o{}^d \cong p \tag{16}$$

Hence these equations, which are used in Robbins' (1976) analysis, are reasonable in many cases, but not exact. He obtained them by assuming that (16) followed directly from the equilibrium condition $\mu_o = \mu_o{}^d$ and then applying (14).

It remains to determine the implications of the other equilibrium condition obtained from (4), viz., $E = 0$. Now E is given by (2) and, as before, we can use (6) to break the total microemulsion free energy G_m into its various component parts. Carrying out the differentiation and simplifying, we find

$$0 = \frac{4}{3}\pi a^2 \left(\gamma + \frac{2\mathcal{H}}{a} \right) + \frac{5}{2} kT - kT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V_m e}{N} \right] + \frac{2NkT}{V_m} B_2 + \frac{N^2kT}{V_m} \left(\frac{\partial B_2}{\partial N} \right)_{T,p,n_w,n_s{}^d,n_o{}^d} \tag{17}$$

Ruckenstein and Chi's (1975) analysis also contained an equation minimizing system free energy with respect to the number of drops. Equation (17) differs from their equation in that it uses dilute solution expressions for entropy of dispersion and drop interactions, and especially in that it includes the term in bending stress $\mathcal{H}$. Robbins (1976) had no expression analogous to (17) in his analysis.

In general, Equations (13) and (17) must be solved simultaneously to determine the number of drops present, drop size, and the amount of solubilized oil at equilibrium. When (13) and (14) simplify to (15) and (16), the latter pair of equations may be substituted into (17) to obtain the equilibrium condition

$$0 = \frac{4\pi a\mathcal{H}}{kT} + \frac{5}{2} - \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V_m e}{N} \right] + \frac{2NB_2}{V_m} + \frac{N^2}{V_m} \left(\frac{\partial B_2}{\partial N} \right)_{T,p,n_w,n_s{}^d,n_o{}^d} \tag{18}$$

Note that both the contribution of the bending stress and that of the drop entropy and interaction are important. If the latter is neglected, for example, Equations (15) and (18) can be satisfied only for $\gamma = \mathcal{H} = 0$. But with a bending stress $\mathcal{H}$ of zero, the surfactant film would assume its "natural" radius of curvature at equilibrium. As we show later, drop radius often differs significantly from the natural radius when calculated from our more general procedure. Moreover, since the dispersion entropy effect is a key factor in the basic thermodynamic stability of microemulsions, any theory omitting it should apply only for a limited range of conditions.

On the other hand, if bending effects are neglected altogether, (15) requires that interfacial tension γ vanish, and (17) can be satisfied only if interactions between drops just cancel the entropy of dispersion—a rather unsatisfying general result though perhaps true in some special cases. Even if there is no bulk oil phase in equilibrium with the microemulsion so that (15) does not apply, the situation considered by Ruckenstein and Chi (1975), the neglect of the bending term $(2\mathcal{H}/a)$ in (17) in comparison with the interfacial tension term γ, is probably not justified under many conditions. Thus, it is important that both natural curvature (bending) effects and the configurational entropy of drop dispersion be included in a realistic theory of microemulsions containing surfactants.

A SIMPLE MODEL FOR INTERFACIAL TENSION AND BENDING STRESS

Following several previous workers (Schulman and Montagne 1961, Prince 1969, Robbins 1976), we choose as a model of the surfactant film at the drop interfaces a

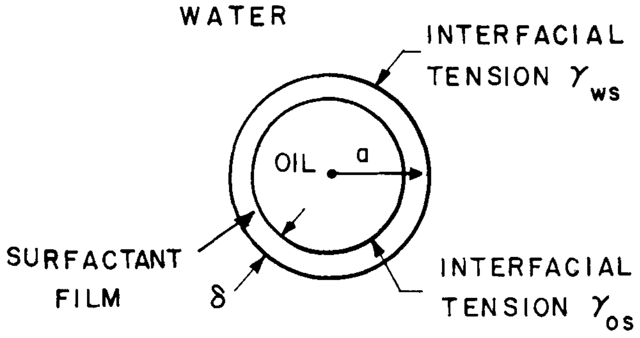

Figure 2. Simplified model of a drop in a microemulsion.

layer of uniform thickness δ having a tension γ_{ws} with the aqueous phase and γ_{os} with the oil phase. Drop radius a is taken at the mid-point of the film (see Figure 2). In accordance with the definitions of interfacial tension γ and bending stress $\mathcal{H}$ given by Murphy (1966) based on a Gibbs' reference surface at $r = a$, we write

$$\gamma = \gamma_{ws}\left(1+\frac{\delta}{2a}\right) + \gamma_{os}\left(1-\frac{\delta}{2a}\right) \qquad (19)$$

$$\mathcal{H} = \frac{\delta}{2}\left(\gamma_{ws} - \gamma_{os}\right) \qquad (20)$$

An additional term in γ proportional to $(\delta/a)^2$ has been neglected. Note that γ is basically the sum of interfacial tensions at the inner and outer surfaces of the surfactant film, while $\mathcal{H}$ is basically their net moment about a point on the film mid-plane.

Next, suppose that there exists some interfacial area per molecule $\mathcal{S}_m^*$ and radius of film curvature a^* for which $\gamma = 2\gamma^*$ and $\mathcal{H} = 0$. This radius a^* corresponds to the natural curvature of the film where there is no tendency for bending. From (19) and (20), we see that $\gamma_{ws} = \gamma_{os} = \gamma^*$ under these conditions. Now suppose that γ_{ws} and γ_{os} obey the following equations

$$\gamma_{ws} = \gamma^* + K_{ws}\left(\frac{\mathcal{S}_m - \mathcal{S}_m^*}{\mathcal{S}_m^*}\right) + d_{ws}\left(\frac{1}{a} - \frac{1}{a^*}\right) \qquad (21)$$

$$\gamma_{os} = \gamma^* + K_{os}\left(\frac{\mathcal{S}_m - \mathcal{S}_m^*}{\mathcal{S}_m^*}\right) - d_{os}\left(\frac{1}{a} - \frac{1}{a^*}\right) \qquad (22)$$

Here K_{ws} and K_{os} are the interfacial compressional moduli (reciprocal interfacial compressibilities) of the interfaces between the surfactant film and the aqueous and oil phases, respectively. Both K_{ws} and K_{os} are assumed constant here over the range of $\mathcal{S}_m$ which is of interest. The parameters d_{ws} and d_{os}, also assumed to be constant, indicate how γ_{ws} and γ_{os} change with drop radius a at constant area per molecule $\mathcal{S}_m$. The latter is measured at the film mid-plane.

One can estimate d_{ws} and d_{os} by assuming that the main effects of a decrease in drop radius at constant mean film area $\mathcal{S}_m$ are an expansion of the outer surface of the film and a corresponding compression of the inner surface. For an oil-in-water microemulsion the ratio of the area $\mathcal{S}_{ws}$ at the film-water interface to the area $\mathcal{S}$ at the film mid-plane is given by

$$\frac{\mathcal{S}_{ws}}{\mathcal{S}} = \frac{\left(a + \frac{\delta}{2}\right)^2}{a^2} \cong 1 + \frac{\delta}{a} \qquad (23)$$

If drop radius changes from a^* to a at constant $\mathcal{S}$, then

$$\frac{\mathcal{S}_{ws} - \mathcal{S}_{ws}^*}{\mathcal{S}} = \delta\left(\frac{1}{a} - \frac{1}{a^*}\right) \qquad (24)$$

The corresponding change in γ_{ws} is given by

$$\Delta\gamma_{ws} = K_{ws}\delta\left(\frac{1}{a} - \frac{1}{a^*}\right) \Big/ \left(1 + \frac{\delta}{a^*}\right) \qquad (25)$$

Hence, we obtain

$$d_{ws} = K_{ws}\delta \Big/ \left(1 + \frac{\delta}{a^*}\right) \qquad (26)$$

By a similar argument for the oil-film interface,

$$d_{os} = (K_{os}\delta)/(1 + \delta/a^*) \qquad (27)$$

Substituting (21) and (22) into (19) and (20) yields

$$\gamma = 2\gamma^* + \left(\frac{\mathcal{S}_m - \mathcal{S}_m^*}{\mathcal{S}_m^*}\right)\left[K_{ws}\left(1 + \frac{\delta}{2a}\right) + K_{os}\left(1 - \frac{\delta}{2a}\right)\right] + \left(\frac{1}{a} - \frac{1}{a^*}\right) \left[d_{ws}\left(1 + \frac{\delta}{2a}\right) - d_{os}\left(1 - \frac{\delta}{2a}\right)\right] \qquad (28)$$

$$\mathcal{H} = \frac{\delta}{2}\left[(K_{ws} - K_{os})\left(\frac{\mathcal{S}_m - \mathcal{S}_m^*}{\mathcal{S}_m^*}\right) + (d_{ws} + d_{os})\left(\frac{1}{a} - \frac{1}{a^*}\right)\right] \qquad (29)$$

These expressions may be used to calculate γ and $\mathcal{H}$ for use in the equations of the preceding section provided the necessary parameters can be evaluated.

For simplicity we made calculations below for the special case of equal compressional moduli, i.e., $K_{ws} = K_{os} = K$. Substituting this condition, (26) and (27) into (29),

$$\mathcal{H} = \frac{K\delta^2}{1 + \frac{\delta}{a^*}}\left(\frac{1}{a} - \frac{1}{a^*}\right) \qquad (30)$$

When the approximate condition (15) holds, the interfacial tension γ at equilibrium is also readily obtained in terms of the equilibrium drop radius a.

SURFACTANT EQUALLY SOLUBLE IN OIL AND WATER

The basic thermodynamic analysis presented above can be readily adapted to the case of a surfactant equally soluble in oil and water. For a system quite dilute in surfactant and containing equal volumes of oil and water, the equilibrium state consists of coexisting oil-continuous and water-continuous microemulsions. If densities of the two continuous phases are equal, the number and size of drops and the amount of solubilized material are equal for the two microemulsions. Under these conditions and again using the approximations (15) and (16), the equilibrium condition is found to be (18), with the volume V_m of each microemulsion being exactly half the volume of the entire system, and the derivative of the virial coefficient in the last term being taken at constant amounts of oil, water, and surfactant in each microemulsion.

The model presented above for calculating interfacial tension γ and bending stress $\mathcal{H}$ may also be used in this case. Since there is zero natural curvature ($a^* \to \infty$), the terms proportional to $(1/a^*)$ are set equal to zero in equations such as (30).

TABLE 1. PARAMETERS HELD CONSTANT IN CALCULATION OF MICROEMULSION DROP SIZE

Surfactant film thickness $\delta = 2$ nm
Temperature $T = 300$K
$\mathcal{S}_m^*$ (in uncompressed film) $= 50 \times 10^{-20}$ m²/molecule
Density $\rho = 10^3$ kg/m³
Interfacial tension $2\gamma^*$ in uncompressed film $= 10^{-2}$ mN/m

RESULTS

We have made calculations using (15), (18), and (30) of drop size in microemulsions under various conditions. In determining the second virial coefficient B_2 we used Hamaker's formula (Hamaker 1937) for London-van der Waals interactions between spheres. We assumed, as a first approximation, that no interpenetration of surfactant films of adjacent drops could occur. Under these conditions the interaction energy between two drops is given by

$$U(\xi) = \begin{cases} -\dfrac{A_H}{12}\left[\dfrac{1}{\xi^2 + 2\xi} + \dfrac{1}{\xi^2 + 2\xi + 1} + 2 \ln \dfrac{\xi^2 + 2\xi}{\xi^2 + 2\xi + 1}\right] & \text{for } \xi \geqq \xi_m \\ \infty \quad \text{for } \xi < \xi_m & \end{cases} \tag{31}$$

where A_H is the Hamaker constant, and ξ is defined in terms of the distance r between the centers of the drops

$$\xi = \frac{r - 2a}{2a} \tag{32}$$

The minimum possible value ξ_m occurs when r has the value $(a + \delta/2)$, in view of our previous statement that a is the radius to the mid-point of the surfactant film which has a thickness δ. Equation (31) is used to calculate B_2 from (11).

Equation (31) applies to microemulsions containing nonionic surfactants, although it could readily be extended to include the electrical repulsion between particles which exists for ionic surfactants. For simplicity we consider only the nonionic surfactant case here.

The parameters used in the calculations are given in Table 1. Basically, we calculated drop size as a function of surfactant concentration for various values of natural radius of curvature a^*, surfactant film compressional modulus K, and Hamaker constant A_H. In all cases, we consider microemulsions formed at room temperature by a surfactant having films 2 mm thick with an area of 0.5 nm² per surfactant molecule. Note that while we simply select reasonable values for a^* and K in using the theory here, an important topic for future research is to relate these parameters to the molecular structure of the surfactant molecules present.

Figure 3 shows predicted variation of drop size with surfactant concentration for three different values of a^*. For all three curves, drops are taken as noninteracting ($A_H = 0$) and a constant value of film compressional modulus K is used. It is clear from the curves that drop size increases as the natural radius of curvature a^* increases, the expected result. Moreover, for each value of a^* drop radius a increases with increasing surfactant concentration. Nevertheless, a remains significantly below a^* even for the highest values of surfactant concentration plotted, which in all three cases correspond to situations where the volume fraction of drops in the microemulsion is between 10% and 15%.

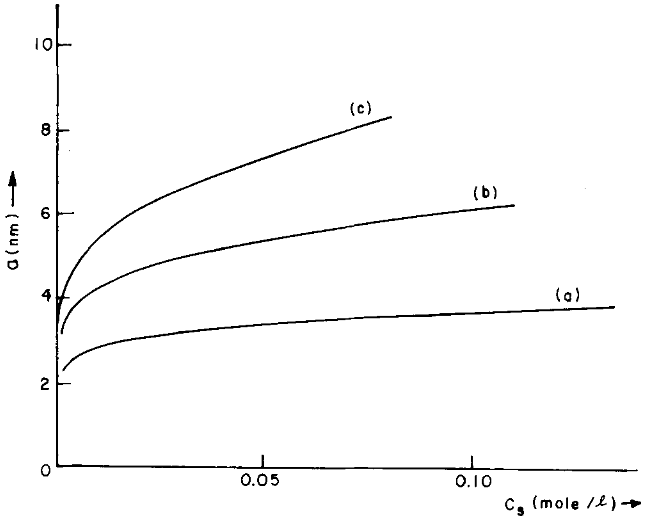

Figure 3. Variation of drop radius a with surfactant concentration C_s for natural radius of curvature a^* equal to (a) 25 nm, (b) 100 nm, (c) ∞. In all cases, Hamaker constant $A_H = 0$, and film compressibility modulus $K = 3$ mN/m.

These results can be explained as follows. One might initially expect that drops would have the natural radius of curvature a^*. At any given surfactant concentration, however, the system can reduce its free energy by forming drops with $a < a^*$. For although bending of the surfactant films to the smaller radius involves an increase in energy, this effect is more than offset by a decrease in free energy caused by an increased number of drops, and hence in the entropy of dispersion. The increased number of drops occurs because decreasing drop size decreases interfacial area per drop, while total interfacial area remains virtually constant, with a fixed amount of surfactant present.

It is particularly noteworthy that a system containing drops has a lower free energy than one containing layers for the case of zero natural curvature ($a^* \rightarrow \infty$). This result indicates that microemulsion phases may sometimes form instead of lamellar liquid crystalline phases, when the surfactant is about equally soluble in oil and water.

As surfactant concentration increases, so does the concentration of drops in the system, and the entropy of dispersion cannot be increased as much by going to smaller drops. Accordingly, equilibrium drop size increases with increasing surfactant concentration.

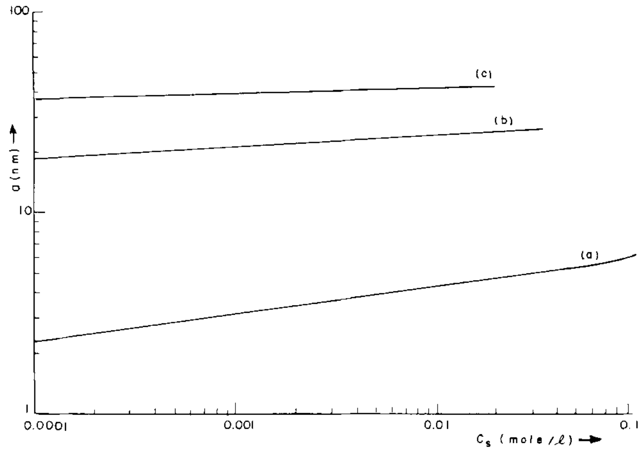

Figure 4. Variation of drop radius a with surfactant concentration C_s for film compressibility modulus K equal to (a) 3, (b) 5, (c) 7 mN/m. In all cases, $A_H = 0$ and $a^* = 100$ nm.

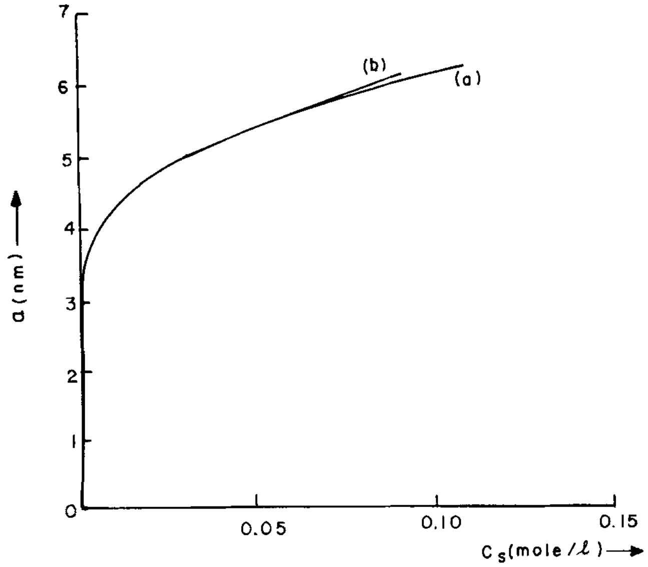

Figure 5. Variation of drop radius a with surfactant concentration C_s for Hamaker constant A_H equal to (a) 0, (b) 3×10^{-20} J. In both cases, $K = 3$ mN/m and $a^* = 100$ nm.

With increasing values of surfactant film compressional modulus K, more energy is required to bend the film from its natural radius a^* to a particular radius a. As a result, equilibrium drop size increases rapidly as K increases, if other parameters are held constant (see Figure 4). Note that all three curves in Figure 4 are again plotted only up to surfactant concentrations where the volume fraction of drops in the microemulsion reaches 10% to 15%. The surfactant concentration corresponding to this situation is naturally smaller for larger drops, so that the curves for larger K terminate at lower surfactant concentrations.

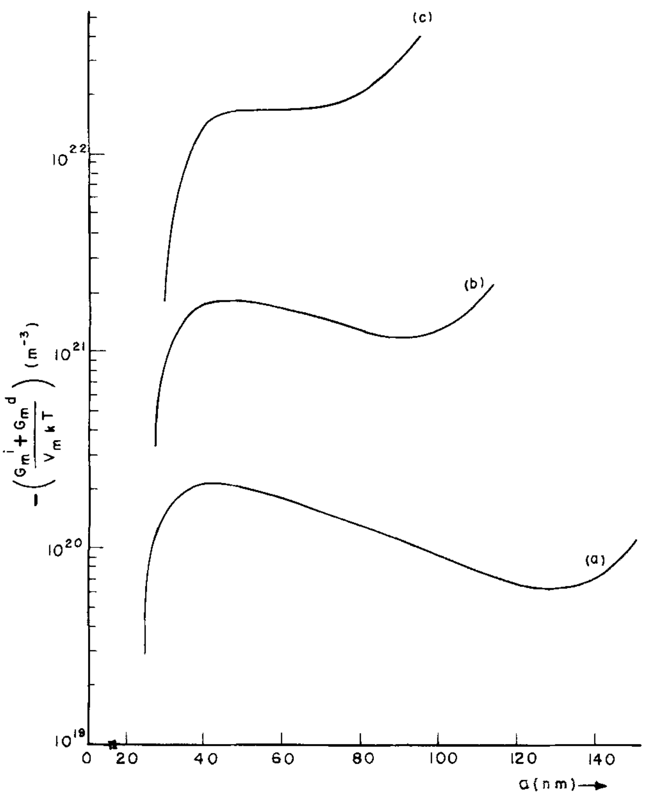

Fig. 6. Variation of magnitude of free energy per unit volume with drop size for surfactant concentration C_s equal to (a) 0.001, (b) 0.01, (c) 0.1 mole/l. In all cases, $A_H = 1 \times 10^{-20}$ J, $K = 5$ mN/m, and $a^* = 100$ nm. As the free energy is negative, a maximum in its magnitude as plotted corresponds to a minimum in free energy.

Increased attraction between drops also causes an increase in drop size. For small drops the effect is quite small, as Figure 5 indicates. For very large drops, attraction can become so great that the second term in (10) involving the virial coefficient B_2 reaches magnitudes comparable to or even larger than the first or entropy term. In this case, our analysis breaks down and a more detailed model for drop entropy and interaction is required.

When drops are sufficiently large, attractive forces sufficiently great, and surfactant concentrations sufficiently high, it can happen that the analysis predicts no equilibrium drop size. Such a case is illustrated in Figure 6. At low surfactant concentrations C_s, the free energy G_m reaches a minimum (or $-G_m$, as plotted, reaches a maximum) for a particular value of drop diameter, here about 40 nm. When C_s increases to 0.1 mole/l, however, no minimum in G_m exists, and free energy decreases continuously with increasing drop size.

The reason is that the total interaction energy among the many, relatively large drops becomes very large and increases with increasing drop size. The same effect is also responsible for the maximum in G_m (minimum in $-G_m$) seen at large drop sizes for low surfactant concentrations in Figure 6. In both cases the virial coefficient becomes so large that the model is inapplicable under these conditions. The result does suggest that phases other than microemulsions, probably liquid crystalline phases, can be expected at high surfactant concentrations. Other results leading to the same conclusion are discussed later.

DISCUSSION

Figure 4 shows clearly that drop size increases rapidly as film compressional modulus K increases, i.e., as the film becomes less compressible or more rigid. For sufficiently large values of K, the energy required to bend the film becomes so great that drop radius a approaches the natural radius of curvature a^*. This result implies that for a fixed but finite value of a^*, solubilization increases with increasing film rigidity. But when $a^* \to \infty$ it indicates that a lamellar liquid crystalline phase is to be expected instead of a microemulsion containing drops. Thus, when natural curvature is zero and the surfactant is nearly equally soluble in oil and water, microemulsion phases should be seen only in systems with rather flexible surfactant films.

For systems containing anionic surfactants addition of a short-chain alcohol as a "cosurfactant" appears to enhance surfactant film flexibility. Salter (1977) demonstrated that solubilization at a given value of a^*, e.g., $a^* \to \infty$, decreases when alcohol is added, an indication, as mentioned above, of increased flexibility. Studies of phase behavior also indicate that adding alcohol reduces the range of compositions where liquid crystalline phases are present (Healy and Reed 1974), a result which is again consistent with increased flexibility.

More flexible films also appear to result from increasing salt concentration in systems containing ionic surfactants. Bourrel et al. (1978) show, for example, that solubilization decreases with increasing NaCl concentration under conditions where $a^* \to \infty$. The increased flexibility presumably results from a decrease in the effective repulsion between surfactant ions in the film owing to the increased screening effect of the salt.

In surfactant systems for enhanced oil recovery, very low interfacial tensions are often seen, when a microemulsion phase occurs for the situation $a^* \to \infty$. As solubilization of oil and water increase under these conditions, interfacial tension decreases (Healy et al. 1976). There are also theoretical reasons for believing that tensions should be lower when solubilization and drop size are larger (Miller et al. 1977). In view of the above results, it appears that the optimum condition for producing low tensions is when the surfactant film is sufficiently flexible to form a microemulsion phase instead of a lamellar liquid crystal—but not so flexible that solubilization and drop size are greatly decreased.

As surfactant concentration and the number of drops per unit volume increase, a point may be reached where the microemulsion separates into two phases, one with a high concentration and one with a low concentration of drops (Miller et al. 1977). Since the present model applies only in dilute systems, it cannot predict such a phase separation. Behavior of this type could be predicted if a more complicated model based, for example, on interacting hard spheres was used.

Whether or not phase separation occurs, surfactant concentration may eventually, in some cases, reach values so high that the drops cannot be packed into the amount of continuous phase present. This situation is most likely to occur when drop size is large. If it does, a surfactant-rich phase having some different structure and presumably liquid crystalline in nature must form. A microemulsion phase may be present as well, however. Here too, a more detailed model of concentrated microemulsions, as well as a model of the liquid crystalline phase, are needed, if quantitative prediction of phase behavior under these conditions is desired.

IN SUMMARY

A theory of microemulsions has been presented, which is the first to include both bending or natural curvature effects and the entropy of dispersion of the drops. While limited to relatively dilute systems, it indicates how drop size depends on such parameters as surfactant concentration, strength of drop interaction, and the compressibility of the surfactant films at the drop interfaces. It indicates that for rather compressible films, drop radius will be appreciably smaller than the natural radius of curvature of the films under the given conditions. In particular, microemulsions containing drops can be favored over lamellar phases (liquid crystals) in some cases where the surfactant is equally soluble in oil and water and there is no natural curvature of the films.

ACKNOWLEDGMENTS

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NOTATION

a = drop radius
a^* = natural radius of curvature
A_H = Hamaker constant
B_2 = second virial coefficient
d = parameter defined by Equations (21), (22),
e = base of natural logarithms
E = parameter defined by Equation (2)
G = Gibbs free energy
$\mathcal{H}$ = bending stress
h = Planck constant
k = Boltzmann constant
K = interfacial compressibility modulus
m = mass of drop
N = number of drops
n = number of moles
p = pressure
r = distance between centers of drops
S = entropy
$\mathcal{S}$ = total surface area of drops
$\mathcal{S}_m$ = area per surfactant molecule
$\mathcal{S}_m^*$ = area per surfactant molecule when film is not compressed
T = absolute temperature
v = molar volume
V = volume

Greek Letters

γ = interfacial tension
γ^* = interfacial tension for $\mathcal{S}_m = \mathcal{S}_m^*$, $a = a^*$
δ = thickness of surfactant film
μ = chemical potential
ξ = dimensionless separation distance between drops

Subscripts

m = microemulsion
o = oil
os = oil-surfactant interface
w = water
ws = water-surfactant interface

Superscripts

d = drop portion of microemulsion

LITERATURE CITED

Adamson, A. W., "A Model for Micellar Emulsions," *J. Coll. Interface Sci.*, 29, 261 (1969).

Bourrel, M., A. M. Lipow, W. H. Wade, and R. S. Schechter, "Properties of Amphiphile/Oil/Water Systems at an Optimum Formulation for Phase Behavior," Soc. Petrol. Eng. Preprint 7450, Annual Meeting, Houston (1978).

Hamaker, H. C., "The London-van der Waals Attraction Between Spherical Particles," *Physica*, 4, 1058 (1937).

Healy, R. N. and R. L. Reed, "Physicochemical Aspects of Microemulsion Flooding," *Soc. Petrol. Eng. J.*, 14, 491 (1974).

Healy, R. N., R. L. Reed, and D. G. Stenmark, "Multiphase Microemulsion Systems," *Soc. Petrol. Eng. J.*, 16, 147 (1976).

Hill, T. L., *Introduction to Statistical Thermodynamics*, Addison-Wesley, Reading, Mass. (1960).

Hill, T. L., *Thermodynamics of Small Systems*, Vol. 1 and 2, W. A. Benjamin, New York (1963, 1964).

Hwan, R., C. A. Miller, and T. Fort, Jr., "Determination of Microemulsion Phase Continuity and Drop Size by Ultracentrifugation," *J. Coll. Interface Sci.*, 68, 221 (1979).

Likhtman, V. I., E. D. Shchukin, and P. A. Rehbinder, *Physicochemical Mechanics of Metals*, Translated by Israel Program for Scientific Translations (1964), Nijhoff, The Hague (1964).

Miller, C. A., R. Hwan, W. J. Benton, and T. Fort, Jr., "Ultralow Interfacial Tensions and Their Relation to Phase Separation in Micellar Solutions," *J. Coll. Interface Sci.*, 61, 554 (1977).

Murphy, C. L., "Thermodynamics of Low Tension and Highly Curved Interfaces," Ph.D. thesis, University of Minnesota (1966).

Prince, L. M., "A Theory of Aqueous Emulsions. II. Mechanism of Film Curvature at the Oil/Water Interface," *J. Coll. Interface Sci.*, 29, 216 (1969).

Prince, L. M., *Microemulsions, Theory and Practice*, Academic Press, New York (1977).

Rehbinder, P. A., *Proc. 2nd Int. Congr. Surface Activity*, London, 1, 476 (1957).

Reiss, H., "Entropy-induced Dispersion of Bulk Liquids," *J. Coll. Interface Sci.*, 53, 61 (1975).

Robbins, M. L., "Theory for the Phase Behavior of Microemulsions," pp. 713ff in K. L. Mittal (ed.), *Micellization,* *Solubilization and Microemulsions*, Vol. 2, Plenum, New York (1976).

Ruckenstein, E. and J. C. Chi, "Stability of Microemulsions," *J. Chem. Soc. Faraday Trans. II*, 71, 1690 (1975).

Ruckenstein, E., "Stability Phase Equilibria, and Interfacial Free Energy in Microemulsions," pp. 755ff in K. L. Mittal (ed.), *Micellization, Solubilization and Microemulsions*, Vol. 2, Plenum, New York (1976).

Ruckenstein, E., "The Origin of Thermodynamic Stability of Microemulsions," *Chem. Phys. Letters*, 57, 517 (1978).

Ruckenstein, E., "On the Thermodynamic Stability of Microemulsions," *J. Coll. Interface Sci.*, 66, 369 (1978).

Saito, H. and K. Shinoda, "The Stability of w/o Type Emulsions as a Function of Temperature and of the Hydrophilic Chain Length of the Emulsifier," *J. Coll. Interface Sci.*, 32, 647 (1970).

Salter, S. J., "The Influence of the Type and Amount of Alcohol on Surfactant-Oil-Brine Phase Behavior and Properties," Soc. Petrol. Eng., Preprint 6843, Annual Meeting, Denver (1977).

Schulman, J. H., W. Stroeckenius, and L. M. Prince, "Mechanism of Formation and Structure of Microemulsions by Electron Microscopy," *J. Phys. Chem.*, 63, 1677 (1959).

Schulman, J. H. and J. B. Montagne, "Formation of Microemulsions by Amino Alkyl Alcohols," *Ann. New York Acad. Sci.*, 92, 366 (1961).

Scriven, L. E., "Equilibrium Bicontinuous Structures," *Nature*, 263, 123 (1976).

Talmon, Y. and S. Prager, "Statistical Mechanics of Microemulsions," *Nature*, 267, 333 (1977).

Talmon, Y. and S. Prager, "Statistical Thermodynamics of Phase Equilibria in Microemulsions," *J. Chem. Phys.*, 69, 2984 (1978).

Winsor, P. A., "Hydrotropy, Solubilization, and Related Emulsification Processes," *Trans. Faraday Soc.*, 44, 376 (1948).

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Studies in the Synthesis of Control Structures for Chemical Processes

Part I: Formulation of the Problem. Process Decomposition and the Classification of the Control Tasks. Analysis of the Optimizing Control Structures.

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Part I of this series presents a unified formulation of the problem of synthesizing control structures for chemical processes. The formulation is rigorous and free of engineering heuristics, providing the framework for generalizations and further analytical developments on this important problem.

Decomposition is the underlying, guiding principle, leading to the classification of the control objectives (regulation, optimization) and the partitioning of the process for the practical implementation of the control structures. Within the framework of hierarchical control and multi-level optimization theory, mathematical measures have been developed to guide the decomposition of the control tasks and the partitioning of the process. Consequently, the extent and the purpose of the regulatory and optimizing control objectives for a given plant are well defined, and alternative control structures can be generated for the designer's analysis and screening.

In addition, in this first part we examine the features of various optimizing control strategies (feedforward, feedback; centralized, decentralized) and develop methods for their generation and selective screening. Application of all these principles is illustrated on an integrated chemical plant that offers enough variety and complexity to allow conclusions about a real-life situation.

SCOPE

During the last ten years, numerous works have dealt with the design of control systems to regulate specific unit operations (e.g., distillation), to bring a system (e.g., a reactor) back to the desired operating point in some optimal fashion, to guarantee optimal profiles in nonhomogeneous reactors, etc. The interactions between different pieces of equipment in a chemical plant are complex, and do not allow us to regard plant control as a simple extension of unit operations control. These interconnections decrease the number of degrees of freedom, and great care must be taken not to over- or under-specify the control objectives in a process.

All available control theories assume that measured and manipulated variables have been selected, thus not answering one of the basic questions an engineer is facing when designing a plant. Rules of thumb and experience guide the designer's choice of measured and manipulated variables. Naturally, without a systematic procedure, there is no guarantee that all the feasible alternatives are explored, and even less that the best possible structure is chosen. The lack of sound techniques for solving those problems has been criticized frequently, and

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