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Theory of Interfacial Tensions in Multicomponent Systems

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A quantitative theory of interfacial tension in multicomponent systems has been derived from the scaling theory of critical phenomena. This theory is closely related to that previously presented for the quantitative interpretation of phase-volume behavior of such systems near critical points. The interfacial tension theory involves only one additional undetermined parameter once the phase-volume behavior has been determined. It should facilitate the organization and interpretation of interfacial tension data and can be used to interpolate between interfacial tension measurements. The theory has been applied, with good agreement, to experimental results in a simple, ternary, two-phase liquid mixture, as well as to multicomponent three-phase surfactant systems of the type employed in tertiary oil recovery. For the surfactant systems, a combination of the theory for the phase-volume behavior and that for the interfacial tension behavior provides a strong theoretical basis for the heretofore empirical relationship between interfacial tension and "volume uptake" of oil or water into the microemulsion phase. This empirical "volume uptake function" has been used extensively in the literature to characterize surfactant systems for enhanced oil recovery. More importantly, the comparison of the results for the surfactant systems with those of the ternary system separates the two important functions of surfactant action. One is associated directly with the surface active nature of the molecule and the other is associated with the solvent character of the material which makes critical points accessible at moderate temperatures and pressures.

Introduction

The use of surfactants to increase oil recovery from subterranean reservoirs¹⁻⁸ has led to a renewed interest in interfacial phenomena.^{3-6,9-21} Interfacial tension as related to the capillary number^{5,22,23} has been shown to be a key factor in displacement of residual oil.^{5,22,24} In many of the systems^{5,6} studied, optimal oil recovery has been strongly correlated with phase behavior. Consequently, improved methods of describing phase behavior in multicomponent systems have been developed.²⁵⁻²⁷ These methods have been used to obtain a systematic method for optimizing surfactant systems for oil recovery.²⁸ In addition, the rate of emulsion coalescence has been shown to correlate strongly with phase behavior.²⁹ Thus, an intimate relationship between interfacial tensions and phase behavior is to be expected.

Previously,²⁷ we have shown that the shapes of phase-volume diagrams^{6,29,30} can be interpreted in terms of the modern theory of critical phenomena.^{31,32} Here we show how the interfacial tensions near critical points are related to the associated phase-volume diagrams. It will be seen that only one additional adjustable parameter, a scale factor for interfacial tension, is required to fit interfacial tension data once the phase-volume behavior has been characterized. In principle, the interfacial tensions can be calculated from molecular interactions with no adjustable parameters by using recently developed microscopic theories of interfacial tensions in multicomponent systems.³³⁻³⁹ Such calculations are still too ambitious for the multicomponent systems considered here, so we must content ourselves with semiempirical theories for the time being.

Recently, Healy and Reed⁵ have proposed a strictly empirical relationship between interfacial tensions in surfactant systems and volume of water or oil present in the microemulsion phase relative to the volume of surfactant. Here, we shall see that such a relationship does indeed exist, although not of the empirical form employed by Healy and Reed.

Theory

The Behavior of Interfacial Tensions Near Critical Points. The equations describing the behavior of inter-

TABLE I: Summary of Definitions and Values for Critical Exponents

exponent	definition	value	quantity
α	$c_v \sim T - T_c ^{-\alpha}$	1/8	constant volume specific heat
β	$\rho_L - \rho_v \sim T_c - T ^\beta$	5/16	shape of coexistence curve
ν	$\xi \sim T_c - T ^{-\nu}$	5/8	correlation length

facial tensions near critical points in multicomponent systems can be derived by methods similar to those employed previously²⁷ to determine the behavior of phase-volume diagrams. As before, we consider a ternary system in a two-phase region at constant pressure and temperature, although the results are valid for a system of any number of components since variation of a single composition variable in an N component, two-phase system is equivalent to holding temperature, pressure, and $N - 2$ chemical potentials constant. This situation is thermodynamically equivalent to a variation along a single compositional path in a ternary system. We label the components by $i = 1, 2$, and 3 and express all thermodynamic variables in terms of the chemical potential (μ_1) of component 1. From the scaling theory of critical phenomena^{36,39} the interfacial tension between two phases near a critical point must approach zero according to

$$\gamma = \bar{\gamma}_0 \epsilon_1^\phi \quad (1)$$

where $\epsilon_1 = |\mu_1 - \mu_1^c|/\mu_1^c$, μ_1^c is the chemical potential of component 1 at the critical point, $\bar{\gamma}_0$ is a scale factor, and ϕ is a critical exponent. According to scaling theory^{36,39} the critical exponent is given by

$$\phi = 2\nu \quad (2)$$

where ν is the critical exponent describing the divergence of the correlation length.³¹ A summary of the definitions and values of some critical exponents is given in Table I.

As before,²⁷ we eliminate μ_1 as a variable in terms of $\bar{c}_1 = c_1 + \bar{c}_1/2$, c_1 and \bar{c}_1 being the concentrations of component 1 in the two phases. From eq 3 of ref 27, the reduced chemical potential is given by

$$\epsilon_1 = \left| \frac{\bar{c}_1 - c_1^c}{A_1} \right|^{1/(1-\alpha)} \quad (3)$$

where c_1^c is the concentration of component 1 at the critical point and A_1 is a scale factor. Substituting into eq 1 we obtain

$$\gamma = \frac{\bar{\gamma}_0}{|A_1|^{1/(1-\alpha)}} |\bar{c}_1 - c_1^c|^{2\nu/(1-\alpha)} \quad (4)$$

Again, we consider a linear path through the ternary diagram defined by the composition coordinates (\hat{c}_1, \hat{c}_3) satisfying

$$\hat{c}_1 - c_1^c = \delta \hat{c}_1 + M(\hat{c}_3 - c_3^c) \quad (5)$$

where M is a constant. For this path, it was shown in ref 27 (eq 24) that

$$\bar{c}_1 - c_1^c = \frac{\delta \hat{c}_1 + \left(M - \frac{\bar{B}_1}{\bar{B}_3} \right) (\hat{c}_3 - c_3^c)}{1 - \frac{\bar{B}_1}{\bar{B}_3} \bar{A}_3} \quad (6)$$

where \bar{B}_1 , \bar{B}_3 , and \bar{A}_3 are constants. From the definition of c_3^c in eq 26 of ref 27, eq 6 becomes

$$\bar{c}_1 - c_1^c = \frac{\left(M - \frac{\bar{B}_1}{\bar{B}_3} \right) (\hat{c}_3 - c_3^c)}{1 - \bar{B}_1/\bar{B}_3} \quad (7)$$

Thus, eq 4 becomes

$$\gamma = \gamma_0 |\hat{c}_3 - c_3^c|^{2\nu/(1-\alpha)} \quad (8)$$

where

$$\gamma_0 = \frac{\bar{\gamma}_0}{|A_1|^{1/(1-\alpha)}} \left| M - \frac{\bar{B}_1}{\bar{B}_3} \right|^{2\nu/(1-\alpha)}$$

Since the label 3 is arbitrary, we can drop it along with the “ $\hat{}$ ” symbol. Thus, we have

$$\gamma = \gamma_0 |c - c^c|^{2\nu/(1-\alpha)} \quad (9)$$

Equation 9 describes the behavior of interfacial tension as a function of concentration near a critical point. It should apply to any composition variable in a multicomponent system. When used to calculate experimental tensions, it contains two adjustable parameters. However, when employed in conjunction with the equations of ref 27 fit to phase-volume diagrams, the parameter c^c can be determined independently, leaving γ_0 as the only unknown parameter. Since γ_0 plays the role of a scale factor, one would not expect it to be related to the phase-volume behavior. In the following sections eq 9 will be seen to give excellent agreement with interfacial tension measurements in a ternary system and in several surfactant systems of the type employed in tertiary oil recovery. It will be seen there that γ_0 is, in some sense, a measure of the “surface activity” of the molecules present in a system, i.e., for surfactant systems γ_0 should be much lower than for systems not containing surfactants. We will return to this point later.

The Behavior of the Densities of the Phases Near Critical Points. It is well known^{31,32} that the densities of the near-critical phases can also be described by scaling relations. Sufficiently near the critical point, the densities

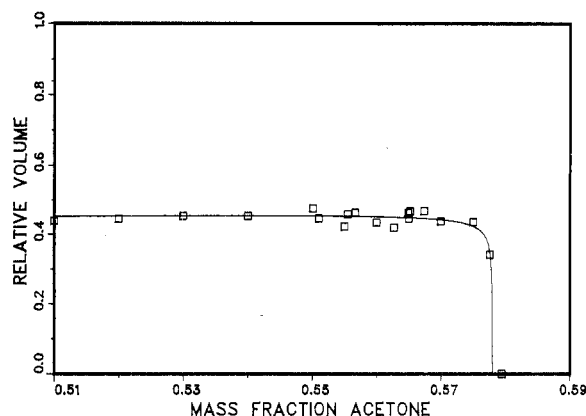


Figure 1. Phase-volume diagram for a 2:1 water-chloroform ratio in the water-acetone-chloroform system.

must satisfy equations analogous to eq 2 and 3 of ref 27, i.e.

$$\rho - \bar{\rho} = \bar{B}\epsilon_1^\beta \quad (10)$$

$$\rho + \bar{\rho} = 2\rho^c + 2\bar{A}\epsilon_1^{1-\alpha} \quad (11)$$

where β and α are the coexistence curve and specific heat critical exponents, respectively.^{31,32} Using eq 3 and 7 and dropping the subscripts and “ $\hat{}$ ” symbol as before, we obtain

$$\rho - \bar{\rho} = B|c - c^c|^{\beta/(1-\alpha)} \quad (12)$$

$$\rho + \bar{\rho} = 2\rho^c + 2A(c - c^c) \quad (13)$$

The concentration enters linearly into eq 13 since the densities and concentrations are thermodynamic density variables⁴⁰ and must, therefore, be described by the same critical exponents. In the following sections eq 9, 12, and 13 will be seen to give excellent agreement with experiments in multicomponent systems.

Comparison with Experiments in a Ternary System

In this section we shall show that the theory of the previous section can be applied to interfacial tensions and densities in a ternary system. We consider the ternary system, discussed previously,²⁷ containing chloroform, acetone, and water. The phase-volume diagram for this system at 25 °C is given in Figure 1 for the path determined when the acetone concentration is varied at a 2:1 ratio by weight of water to chloroform. This path was seen previously²⁷ to pass very near to the plait point in this system. The squares denote the experimental points and the solid curve is calculated from eq 33 of ref 27 with $c^c = 0.57799$, $\bar{c}^c = 0.57798$, and $\lambda = 43.88$.

The interfacial tensions corresponding to the experimental points were measured on a pendant drop⁴¹ interfacial tensiometer. These experimental results are given in Figure 2 along with the least-squares fit to the data using eq 9 with $c^c = 0.57799$. The best fit is obtained with $\gamma_0 = 37.98$ and is seen to be in good agreement with the experiments. As we shall see in the next section, this value of γ_0 is considerably larger than that obtained when surfactants are present. The corresponding densities of the phases are plotted in Figure 3 along with the least-squares fit to eq 12 and 13 with $c^c = 0.57799$. The best fit is obtained with $B = 0.056$, $\rho_c = 0.9241$, and $A = -0.3705$. Again, the agreement with experiments is good.

Comparison with Experiments in Systems Containing Surfactants

Interfacial Tensions. Here we apply the theory to surfactant systems of the type employed in tertiary oil

TABLE II: Fit Parameters for Surfactant Systems

oil	F_o	c^o	\bar{c}^o	λ	$ c^o - \bar{c}^o $
tetradecane					
upper phase	0.305	0.02906	0.02906	2047	7.1×10^{-8}
lower phase	0.486	0.01511	0.01522	-31.2	1.1×10^{-3}
hexadecane					
upper phase	0.350	0.04125	0.04125	42730	6.6×10^{-13}
lower phase	0.513	0.01801	0.01807	-5.76	6.0×10^{-5}
1-phenyltetradecane					
upper phase	0.206	0.03000	0.03000	1023	1.5×10^{-6}
lower phase	0.657	0.01571	0.01580	3.95	9.0×10^{-5}

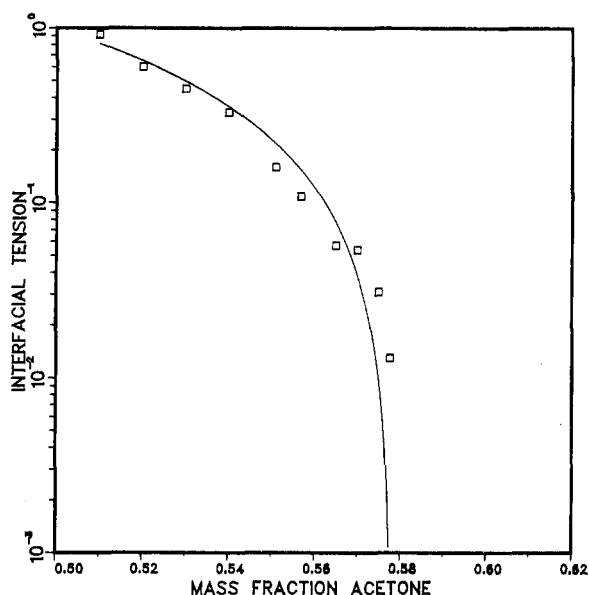


Figure 2. Interfacial tension for a 2:1 water-chloroform ratio in the water-acetone-chloroform system.

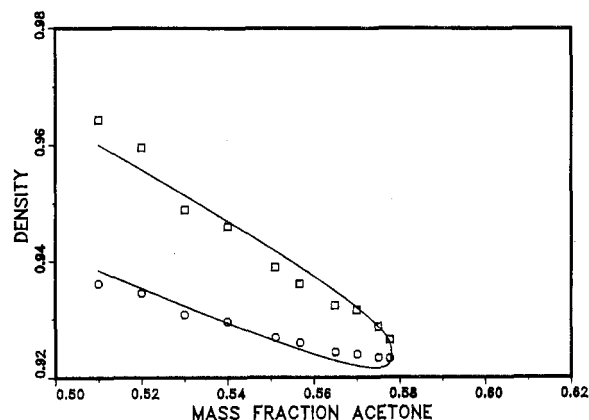


Figure 3. Density of phases for a 2:1 water-chloroform ratio in the water-acetone-chloroform system.

recovery. The phase-volume diagrams as a function of salinity for three such systems discussed previously²⁷ are presented in Figures 4-6. These systems all contain surfactant systems consisting of the sodium sulfonate extracted from Witco TRS 10-410 petroleum sulfonate and isobutyl alcohol in brine solutions which are equilibrated with three different hydrocarbons, tetradecane, hexadecane, and 1-phenyltetradecane. The fit parameters for these curves are summarized in Table II. In all cases the fits were determined by assuming that the shape of the lower curve corresponds to a microemulsion-aqueous phase critical end point while that for the upper curve corresponds to a microemulsion-oil phase critical end point.²⁷

The interfacial tensions for these systems were measured on a spinning drop interfacial tensiometer.^{9,42} The oil phase vs. microemulsion phase and aqueous phase vs.

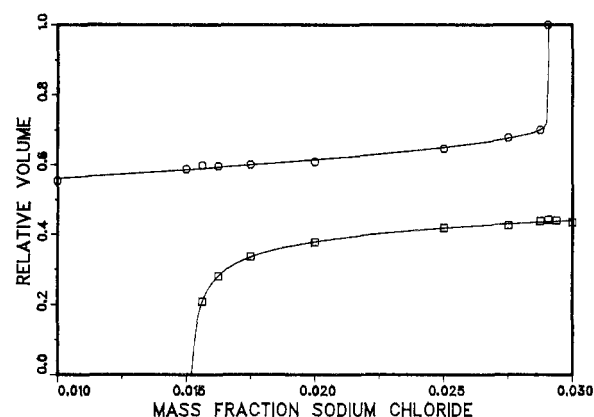


Figure 4. Phase-volume diagram for the system with tetradecane as the oil.

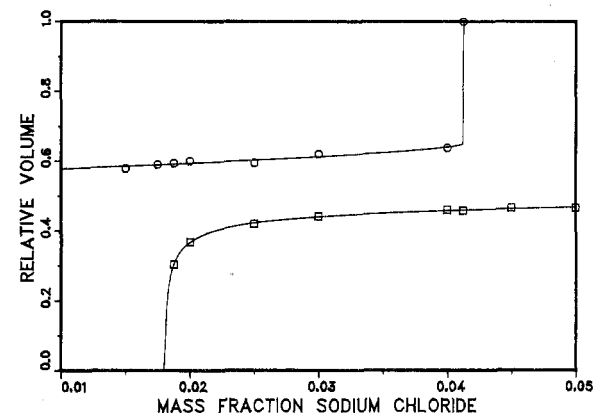


Figure 5. Phase-volume diagram for the system with hexadecane as the oil.

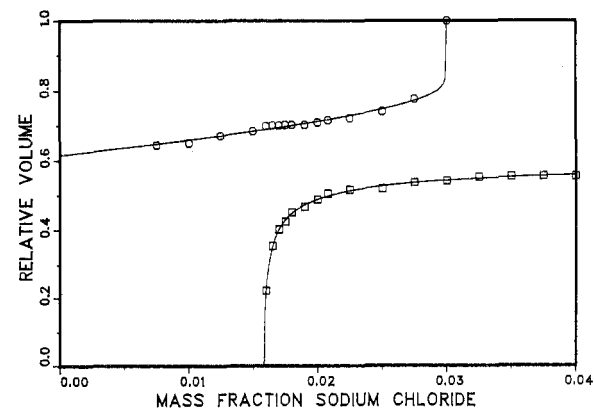


Figure 6. Phase-volume diagram for the system with 1-phenyltetradecane as the oil.

microemulsion phase tensions are plotted in Figure 7 for the system containing tetradecane as the oil. The solid lines were obtained from the best fits to eq 9, fixing $c^o = 0.0151$ for the aqueous-microemulsion curve and $c^o = 0.0291$ for the oil-microemulsion curve since these values

TABLE III: Fit Parameters for Interfacial Tensions and Densities

system	γ_0	ρ_c	A	B
chloroform-acetone-water	37.98	0.9241	-0.3705	0.0564
surfactant-tetradecane	12.94	0.9774	-4.516	0.8513
aqueous-microemulsion	5.40	0.7916	-4.424	0.8224
oil-microemulsion	13.53	0.9787	-2.347	0.6563
surfactant-hexadecane	4.07	0.8027	-2.4378	0.6541
aqueous-microemulsion	12.15	0.9910	-2.589	0.4741
oil-microemulsion	5.37	0.8706	-3.044	0.5254

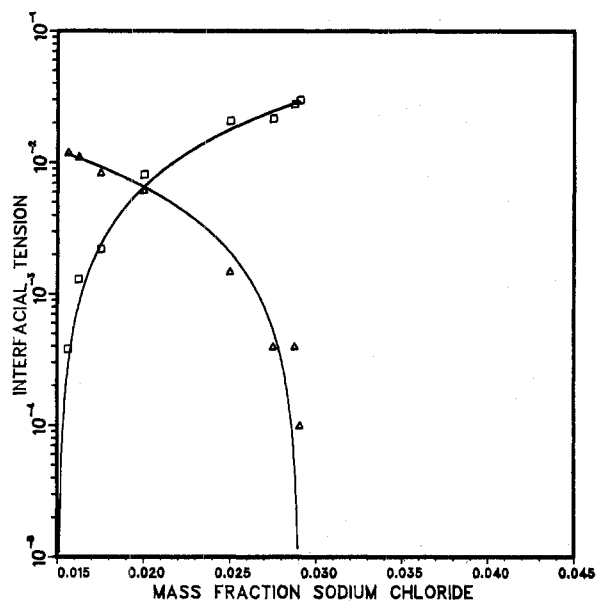


Figure 7. Interfacial tensions for the system with tetradecane as the oil.

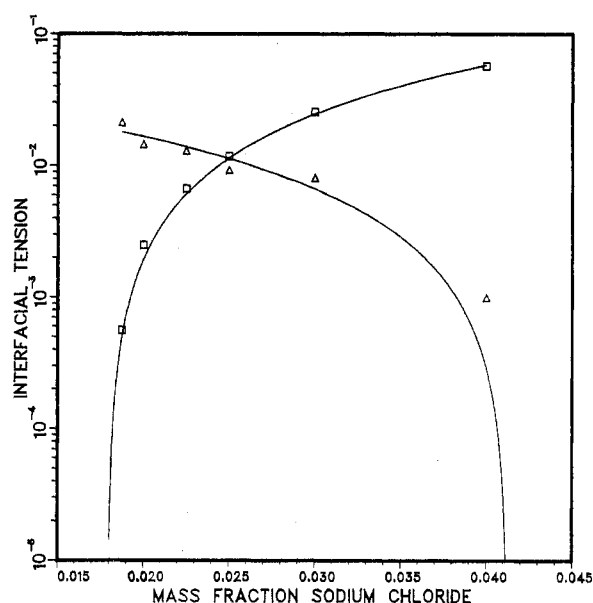


Figure 9. Interfacial tensions for the system with hexadecane as the oil.

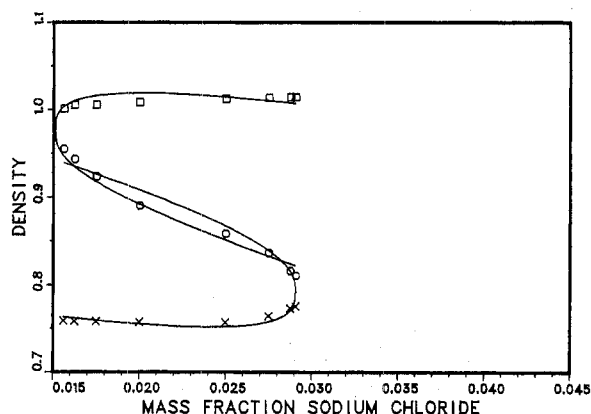


Figure 8. Densities of phases for the system with tetradecane as the oil.

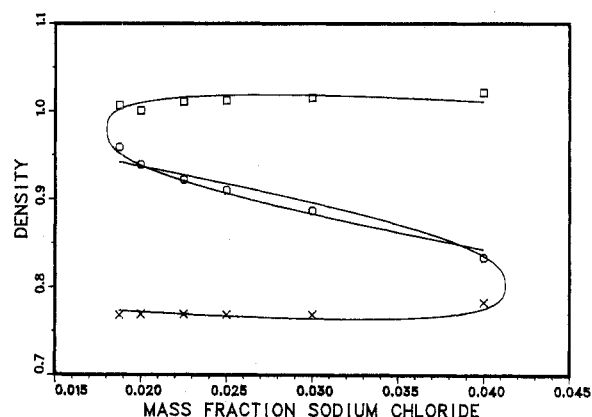


Figure 10. Densities of phases for the system with hexadecane as the oil.

were obtained from the fits to the phase-volume diagram. The best fits were obtained with $\gamma_0 = 12.94$ for the aqueous-microemulsion curve and $\gamma_0 = 5.40$ for the oil-microemulsion curve. The agreement with experiments is good for both cases, further substantiating that the aforementioned critical phenomena do indeed occur in this system.

We observe that the scale factor γ_0 is almost an order of magnitude lower for the oil-microemulsion tension and a factor of 3 lower for the aqueous-microemulsion tension than that for the water-acetone-chloroform system. This suggests that the manifestation of the surface activity of the surfactant molecule is to reduce the scale of interfacial tensions in a given system. The other important role of the surfactant is its cosolvating property which makes

possible critical mixing of water and oil at relatively low concentrations. This is seen for the present systems where the near-critical behavior is obtained at an overall surfactant and cosurfactant concentration of 4% while an acetone concentration of nearly 60% was necessary to induce critical mixing of water and chloroform.

The densities of the three phases are plotted in Figure 8 along with the solid curves obtained from the least-squares fit to eq 12 and 13 with the appropriate c^0 's taken from Table II. The calculated curves for the microemulsion do not mesh with one another since they are only valid in the region of the critical end points and do not properly account for the transition from one critical region to another. Nevertheless, the agreement between theory and experiment is good in the regions of applicability. The

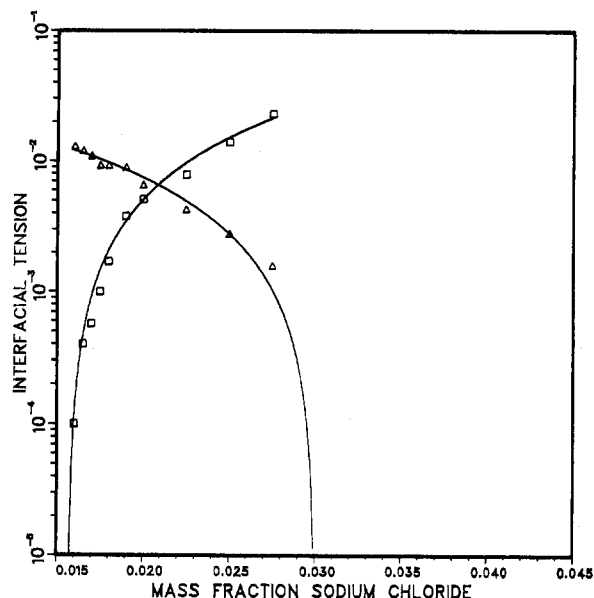


Figure 11. Interfacial tensions for the system with 1-phenyltetradecane as the oil.

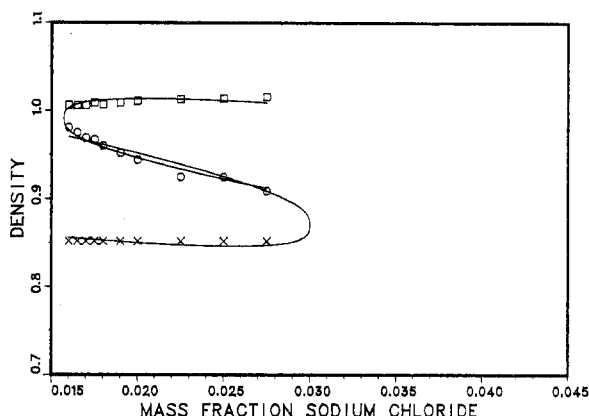


Figure 12. Densities of phases for the system with 1-phenyltetradecane as the oil.

fit parameters for the densities are given in Table III. The interfacial tensions and densities for the surfactant systems containing hexadecane and 1-phenyltetradecane are given in Figures 9–12. The fit parameters for all the curves are summarized in Table III. Again the agreement with experiments is good for both tensions and densities. A few observations about Table III are worth noting. The γ_o 's corresponding to the aqueous–microemulsion tensions are all essentially the same (12.9 ± 0.7). Likewise, the oil vs. microemulsion γ_o 's are all essentially the same (4.9 ± 0.8). This may reflect that the three oils have effective alkane carbon numbers (EACN)⁴³ which are close to one another rather than reflecting a true insensitivity of the γ_o 's to the choice of oil. The fact that the γ_o 's for the oil–microemulsion phases are consistently lower than the γ_o 's for the water–microemulsion phases suggests that the surfactant system considered here is too oleophilic. Also note that A's and B's are essentially the same for both branches for a given oil.

Interpretation in Terms of "Volume Uptake". Recently, Healy and Reed^{4,5} have suggested that the interfacial tensions of multiphase surfactant systems are closely related to the volumes of oil or water present in the microemulsion. As we shall see, such a dependence is a direct consequence of the considerations discussed here. Equations similar to (12) and (13) apply for any phase composition variables c and \tilde{c} or any function of composition

variables sufficiently near a critical point.

The respective volume fractions of water, oil, and surfactant in the microemulsion phase are given by

$$V_w^m = c_w^m / \rho_w \quad (14)$$

$$V_o^m = c_o^m / \rho_o \quad (15)$$

$$V_s^m = c_s^m / \rho_s \quad (16)$$

where c_w^m , c_o^m , and c_s^m are the respective concentrations of water, oil, and surfactant in the microemulsion and ρ_w , ρ_o , and ρ_s are the corresponding bulk densities of the pure components. Thus, by manipulating two equations similar to (12) and (13), we obtain for the "solubility parameters" sufficiently near the appropriate critical end points eq 17 and 18, where V_w^c , V_o^c , and V_s^c are the corresponding

$$\gamma_{mw} = \gamma_{1mw} \left| \frac{V_w^m}{V_s^m} - \frac{V_w^c}{V_s^c} \right|^{2\nu/\beta} \quad (17)$$

$$\gamma_{mo} = \gamma_{1mo} \left| \frac{V_o^m}{V_s^m} - \frac{V_o^c}{V_s^c} \right|^{2\nu/\beta} \quad (18)$$

values of volume fractions at the appropriate critical end points. Equations 17 and 18 are the expected relations between interfacial tensions and "volume uptakes". These are not the only such relationships, however. One could just as well express the interfacial tensions in terms of any other function of composition variables, for example, the volume uptake of surfactant in the water and oil phases.

Healy and Reed⁵ have suggested an empirical relationship between interfacial tension and certain solubility parameters. Under some circumstances this relationship can give a fair approximation to the interfacial tension behavior but it is not rigorously correct for any range of variables. Interfacial tensions can be properly represented in terms of "volume uptakes", however, the actual concentrations of water and oil in the microemulsion phase would need to be measured experimentally to accurately determine these quantities. The commonly used assumption that all the surfactant and alcohol partition into the microemulsion phase is incorrect^{26,28} and leads to significant errors especially near the critical end points. Because of the difficulty in experimentally measuring any concentration, it seems preferable to express interfacial tension as a function of an independent overall composition variable which is more easily controlled (e.g., salt concentration). Furthermore, in practice, it seems that a more effective use of the phase–volume data is to obtain a fit to the phase–volume diagram by using the methods of ref 27 in order to evaluate c^o for each branch, rather than trying to approximate a "volume uptake". Then the c^o 's so obtained can be used in eq 9 to fit the tension data. The principle advantage of this method is that more of the adjustable parameters are associated with the phase–volume measurements which can be performed quickly and accurately as a function of an easily controlled variable such as salinity. The only remaining adjustable parameter, γ_o , can then be determined by relatively few interfacial tension measurements.

Conclusions

We have derived expressions for the interfacial tensions and phase densities for multicomponent systems near critical points based on critical point scaling theory.^{36,39} These equations are intimately related to those derived previously²⁷ to describe the behavior of phase–volume diagrams^{8,29,30} near such critical points. The theory is in

good agreement with experiments in a ternary system containing water, chloroform, and acetone and in surfactant systems of the type employed in tertiary oil recovery.

Probably the most important result of this work is the quantification of two functions of the surfactant in achieving low interfacial tensions. One of these, resulting from the surface-active nature of the molecule, is to reduce the scale of interfacial tensions below that obtained in systems not containing surfactants. The other, associated with the solvent character of the material, is to make critical points accessible at moderate temperatures and pressures. For the systems studied here, the tension scale factor is at least 3 times smaller for surfactant systems than for the nonsurfactant system, and the induced critical phenomena are obtained at a surfactant (plus cosurfactant) concentration roughly 15 times less than the acetone concentration required in the nonsurfactant system.

A secondary conclusion of this work has been to provide a sound theoretical basis for the heretofore empirical relationship between interfacial tension and volumes of water and oil taken into the microemulsion phase of a multiphase surfactant system. Such a relationship has been seen to result naturally from these theoretical considerations. Although the relationship between interfacial tension and "volume uptakes" has been made rigorous, it is more convenient and more accurate to treat an easily controlled composition variable, such as salinity, as an independent variable, rather than one associated with some uncertainty, such as volume uptakes.

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