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Interfacial Tension of Critical Liquid Mixtures in the Presence of a Surfactant

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The interfacial tension of a liquid–liquid interface in the critical region has been obtained as a function of the surfactant concentration on the basis of the Landau–Ginzburg model for critical phenomena. It is shown that surfactants may reduce significantly the interfacial tension in addition to the well-known near-critical reduction.

KEY WORDS: critical phenomena; interfacial tension; Landau theory; surfactant solutions.

1. INTRODUCTION

The problem of reducing the interfacial tension of a liquid–liquid (e.g., oil–water) interface is important in a great variety of practical applications. There exist two main different methods to reduce the interfacial tension, namely, either by going close to the critical consolute point or by adding surface-active agents to the system.

According to the classical theory of critical phenomena, the free energy F has, in the critical region, a Landau–Ginzburg expansion of the form [1]

$$F = (k_B T/r_0^3) \int dV(\alpha\tau\varphi^2 + u\varphi^4 + b_1 r_0^2(\nabla\varphi)^2 + \cdots) + F_0 \qquad (1)$$

where φ is the order parameter whose average value is proportional to the difference of the densities (or concentrations) of the coexisting phases; $\tau = (T - T_c)/T_c$ is the reduced deviation of temperature T from the critical

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temperature T_c; V is the volume; k_B is Boltzmann's constant; r_0 is the characteristic molecular size (in a simple case r_0^3 is the molecular volume); α, u, and b_1 are system-dependent constants, and F_0 is the "regular part" of the free energy.

Asymptotically close to the critical temperature the interfacial tension σ behaves as [2]:

$$\sigma = (1/3)(ub_1)^{1/2}\, \varphi_0^3 \propto |\tau|^{3/2} \tag{2}$$

where φ_0 is the average value of φ.

The addition of surfactant molecules to the system provides an alternative mechanism for decreasing the interfacial tension. We have considered the case where these two effects are combined. It allows us to use the Landau–Ginzburg expansion for the free-energy density as well as many simplifying assumptions which become valid in the critical region. As a result, we have obtained a rather simple explicit expression for the interfacial tension.

2. FORMULATION OF THE MODEL

We consider a ternary system, consisting of water (1), oil (2), and surfactant molecules. "Oil" means any hydrocarbon or even a mixture of hydrocarbons and alcohols. The corresponding composition variables are denoted c_1, c_2, and c and may be mole fractions, densities, or volume fractions. In the following we consider the latter case, to account partially for excluded volume effects, but nevertheless, we use the term "concentration" for simplicity. We assume that both the oil and the water molecules are characterized by the same size r_0, while the surfactant molecule is N times longer ($l = Nr_0$), where N is large compared to unity but not so large as in the case of polymers (typically $N \simeq 10$–20). We neglect compressibility effects, so that

$$c_1 + c_2 + c = 1$$

It should be noted that in this case the system can be described with the help of two independent composition variables, for example, $\rho = c_2 - c_1$ and c.

For small values of ρ the excess free energy of the system under consideration may be written in the Landau–Ginzburg-like form [3]

$$F - F_0 = (k_B T/r_0^3) \int dV[(1-c)\ln(1-c) + (c/N)\ln c - (1/2)a_1\rho^2 + (1/12)\rho^4$$
$$+ (1/2)c\rho^2 + (1/2)a_2c^2 + \varepsilon\rho c + b_1 r_0^2(\nabla\rho)^2 + d_1 l^2(\nabla c)^2 + \cdots] \tag{3}$$

Here a_1, a_2, and ε are related to intermolecular interaction constant χ_1 (oil–surfactant), χ_2 (water–surfactant), and χ_{12} (oil–water):

$$a_1 = \chi_{12}/2 - 1; \qquad a_2 = \chi_{12}/2 - \chi_1 - \chi_2; \qquad \varepsilon = \chi_1 - \chi_2$$

b_1 and d_1 are dimensionless coefficients. We neglect all higher-order terms in ρ and c in this expansion.

In the following, we neglect for the sake of simplicity the asymmetric term proportional to ε in Eq. (3) allowing for the solubility of surfactant to be the same in both phases (oil-rich and water-rich).

Note that $a_1 > 0$ and that the system is in the two-phase region below the critical temperature T_c. To obtain the coexistence curve and, hence, the value of T_c, we may use the following conditions:

$$\mu_\rho^{(1)} = \mu_\rho^{(2)}; \qquad \Pi^{(1)} = \Pi^{(2)}; \qquad \mu_c^{(1)} = \mu_c^{(2)}$$

where

$$\Pi = F - \mu_\rho \rho - \mu_c c; \qquad \mu_c = \partial F/\partial c; \qquad \mu_\rho = \partial F/\partial \rho$$

the superscripts (1) and (2) denote two coexisting phases. These conditions are equivalent to the quality of the three chemical potentials. Here μ_ρ and μ_ρ are the so-called exchange potentials and Π is the osmotic pressure. From Eq. (3) we obtain

$$-\rho^{(1)} = +\rho^{(2)} = \rho_0, \qquad \rho_0^2 = 3(a_1 - c_0), \qquad c^{(1)} = c^{(2)} = c_0 \tag{4}$$

where ρ_0 and c_0 are the equilibrium values of ρ and c in the bulk phases. At the critical point $\rho_0^2 = 0$. In the absence of the surfactant $(c_0 = 0)$ $\rho_0^2 \propto a_1 \propto |\tau|$ and expansion given by Eq. (3) is equivalent to expansion given by Eq. (1).

In the homogeneous system (one-phase region), all concentrations are independent of position if the thermal fluctuations are neglected. This one-phase region is situated above the critical temperature T_c. Below T_c, where demixing into oil-rich and water-rich domains takes place, the system becomes inhomogeneous and the specificity of amphiphillic molecules manifests itself in the tendency of "sticking" to oil–water interfaces with the corresponding orientational ordering, following the geometry of the surface. Both these specific features of surfactant molecules are readily accounted for with the help of a vector order parameter, coupled with the density (or concentration) gradient of the solvent [4]. Such coupling leads in the first approximation to the extra interaction term in Eq. (3), which reduces the free energy:

$$F_{\text{int}} = (k_B T/r_0^3) \int (-\lambda l^2 c(\nabla\rho)^2)\, dV \tag{5}$$

where $\lambda > 0$ is a dimensionless coupling constant.

This particular interaction enabled us to describe self-assembly processes in surfactant solutions [4] and proved to be useful in getting new insight into microemulgation and micellization problems. In that case, the inhomogeneities of a solution (gradients of "density") were associated with fluctuations, while in the case under consideration we relate the gradient terms to the macroscopic interface region.

The interfacial tension σ is defined as the difference per unit area of the interface between the actual total free energy of the system and that which it would have if there were no interface:

$$\begin{aligned}\sigma &= \int dz\{f[\rho(z), c(z)] - f(\rho_0, c_0) - \partial f/\partial\rho_0(\rho-\rho_0) - \partial f/\partial c_0(c-c_0)\}\\ &= (k_B T/r_0^3)\int_{-\infty}^{\infty} dz\, W(\rho, c, \rho_z, c_z) \qquad (6)\end{aligned}$$

Here f is the free energy density, while ρ_z and c_z are the gradients in the z-direction perpendicular to the surface.

The dimensionless excess free energy density W satisfies the Euler–Lagrange minimization equations:

$$\begin{aligned}\frac{\partial W}{\partial \rho} - \frac{d}{dz}\left(\frac{\partial W}{\partial \rho_z}\right) &= 0\\ \frac{\partial W}{\partial c} - \frac{d}{dz}\left(\frac{\partial W}{\partial c_z}\right) &= 0\end{aligned} \qquad (7)$$

The relations given by Eq. (7) allow one to determine composition profiles $\rho(z)$ and $c(z)$, as well as to calculate σ.

Defining

$$\eta(z) = \rho(z)/\rho_0$$

we obtain from Eqs. (3), (5), and (7)

$$\begin{aligned}W = {} & (1-c)\ln[(1-c)/(1-c_0)] + (c/N)\ln(c/c_0) + (a_2/2)(c-c_0)^2\\ & + (\rho_0^2/2)(c-c_0)(\eta^2-1) + (\rho_0^4/12)(\eta^2-1)^2 + (b_1-\lambda N^2 c)r_0^2\rho_0^2\eta_z^2\\ & + d_1 l^2 c_z^2 \qquad (8)\end{aligned}$$

$$\begin{aligned}&(1/N)\ln(c/c_0) - \ln[(1-c)/(1-c_0)] + a_2(c-c_0) + (\rho_0^2/2)(\eta^2-1) - \lambda l^2\rho^2\eta_z^2\\ &\quad = 2d_1 l^2 c_{ee} \qquad (9)\end{aligned}$$

$$(\rho_0^2/3)\,\eta(\eta^2-1) + (c-c_0)\eta = 2(b_1-\lambda N^2 c)r_0^2\eta_{zz} - \lambda l^2 c_z\eta_z \qquad (10)$$

where $c_{zz} = \partial^2 c/\partial z^2$ and $\eta_{zz} = \partial^2\eta/\partial z^2$.

To deduce the main features of the dependence of σ on c_0, we shall simplify Eqs. (9) and (10) as much as possible. Specifically, we put

$$c_{zz} \cong 0 \tag{11}$$

For small values of the average surfactant concentration $c_0 \ll 1$, keeping in mind that, at least in the critical region, the local concentration $c(z)$ should not differ much from c_0, we may rewrite Eqs. (8)–(10) in the following form:

$$\begin{aligned} W \cong{} & (a_c/2)(c-c_0)^2 + (\rho_0^2/2)(c-c_0)(\eta^2-1) + (\rho_0^4/12)(\eta^2-1)^2 \\ & + [b_1 - c\lambda N^2] r_0^2 \rho_0^2 \eta_z^2 \end{aligned} \tag{12}$$

$$a_c(c-c_0) + (\rho_0^2/2)(\eta^2-1) - \lambda l^2 \rho_0^2 \eta_z^2 = 0 \tag{13}$$

$$(\rho_0^2/3)\,\eta(\eta^2-1) + (c-c_0)\eta = 2b_1 r_0^2 \eta_{zz} - \lambda l^2 c_z \eta_z \tag{14}$$

where

$$a_c = a_2 + 1/(1-c_0) + 1/N_0 \cong a_2 + 1 + 1/Nc_0 \tag{15}$$

From Eq. (13) we obtain

$$c - c_0 = (\rho_0^2/a_c)[(1-\eta^2)/2 + \lambda l^2 \eta_z^2] \tag{16}$$

$$c_z = (\rho_0^2/a_c)\,\eta_z(2\lambda l^2 \eta_{zz} - 1) \tag{17}$$

Substituting Eqs. (16) and (17) into Eq. (14), we obtain

$$\begin{aligned} & (\rho_0^2/3)\,\eta(\eta^2-1) + \eta(\rho_0^2/a_c)[(1-\eta^2)/2 + \lambda l^2 \eta_z^2] \\ & \quad = 2b_1 r_0^2 \eta_{zz} - 2\lambda l^2 c_0 \eta_{zz} - \lambda l^2 (\rho_0/a_c)\,\eta_z^2 (2\lambda l^2 \eta_{zz} - 1) \end{aligned} \tag{18}$$

The solution of Eq. (18) yields the interfacial profile $\eta(z)$, which in turn, after substitution into Eqs. (16) and (6), gives an expression for the interfacial tension σ in the approximation considered. Unfortunately Eq. (18) cannot be solved analytically. To obtain qualitative insight into the problem, we omit all higher-order terms proportional to $\rho_0^2 \eta_z^2$ in Eq. (18). Then the solution of Eq. (18) is reduced to a traditional "kink" approximation:

$$\eta = th(z/\xi) \tag{19}$$

where ξ plays the role of correlation length, which determines the thickness of the interface:

$$\xi^2 = 12\tilde{b}_1 r_0^2/(\rho_0^2 \tilde{u}) \tag{20}$$

with

$$\tilde{b}_1 = b_1 - \lambda N^2 (c_0 + \rho_0^2/2a_c), \qquad \tilde{u} = 1 - 3/2a_c \tag{21}$$

As follows from Eq. (20) the correlation length ξ diverges when ρ_0 tends to zero at the critical point. Since at $Nc_0 \ll 1$, $a_c \simeq 1/Nc_0$, the factor $\tilde{u} \simeq 1 - 3Nc_0/2$. Thus at $\rho_0 = \text{constant}$ the larger N, the thicker the interface. The factor $\tilde{u}$ is proportional to the effective coefficient of the fourth-power term in the Landau expansion of the free energy. Indeed, substituting Eqs. (16) and (17) into Eq. (12) yields

$$W = (1/12)(1 - 3/2a_c)\,\rho_0^4(1 - \eta^2)^2 + \tilde{b}_1 r_0^2 \rho_0^2 \eta_z^2 \tag{22}$$

At sufficiently large values of c_0, $\tilde{b}_1$ and $\tilde{u}$ may approach zero. The point where $\tilde{b}_1 = 0$ is called the Lifshitz point [5], and that with $\tilde{u} = 0$ is the tricritical point [2]. To consider these two cases one needs to take the higher-order terms in the expansion given by Eq. (3) into account. The specific character of the surfactant manifests itself in the reduction of $\xi^2 \propto \tilde{b}_1(c_0)$ resulting from the tendency of surfactant molecules to order at the interface and, thus, to pull oil and water molecules closer to the interface.

Substituting Eq. (19) into Eq. (6) we arrive at the following expression for interfacial tension:

$$\sigma = (4/3^{1/2})(k_B T/r_0^2)\,\rho_0^3(\tilde{u}\tilde{b}_1)^{1/2} \tag{23}$$

As can be seen from Eq. (23) there exist two mechanisms which reduce the interfacial tension: the approach to the critical point or the nearness of the tricritical point and the reduction of the effective square-gradient coefficient $\tilde{b}_1$. The first mechanism has been discussed in the literature [3, 6] and can be observed in principle in any ternary solution, while the second mechanism is due only to the presence of surfactant. When the bulk surfactant concentration c_0 is sufficiently small, so that $Nc_0 \ll 1$, we may put $a_c^{-1} \cong Nc_0$ according to Eq. (15). One can then write

$$\sigma(c_0) = (4/3^{1/2})(k_B T/r_0^2)\,\rho_0^3\{(1 - 3Nc_0/2)[b_1 - \lambda N^2 c_0(1 + N\rho_0^2/2)]\}^{1/2} \tag{24}$$

As can be seen from Eq. (24) the reduction of $\sigma(c_0)$ as small c_0 results mainly from the $\tilde{b}_1(c_0)$ factor if the coupling constant λ is sufficiently large. The typical behavior of $\sigma(c_0)$ is presented in Fig. 1. The parameters of Eq. (24) are chosen as follows:

$$N = 10, \qquad \rho_0 = [3(0.01 - c_0)]^{1/2}$$

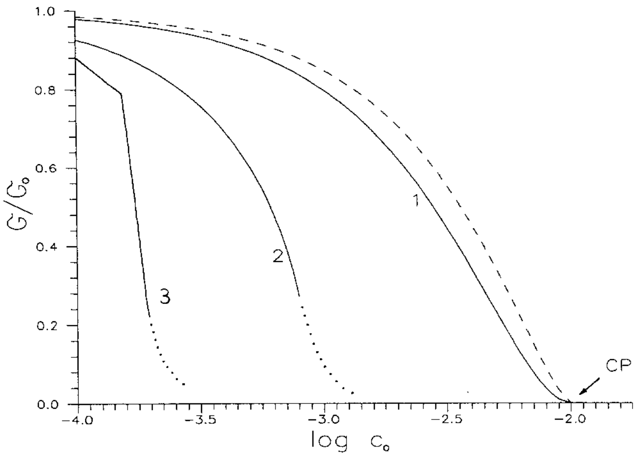

Fig. 1. Interfacial tension σ (normalized to its value σ_0 at $c_0 = 0$) as a function of the surfactant concentration c_0 according to Eq. (24). The dashed curve corresponds to the absence of a specific coupling between amphiphiles and interface ($\lambda = 0$); curve 1 corresponds to a moderate coupling ($\lambda = 1$); curve 2 corresponds to a strong coupling ($\lambda = 10$); curve 3 corresponds to the coupling constant, depending on the local concentration $c(\mathbf{r})$; and CP is the critical point.

Thus, the critical surfactant concentration is 0.01. Curves 1 and 2 correspond to a moderate ($\lambda = 1$) and a strong ($\lambda = 10$) coupling, respectively. In the latter case, the Lifshitz point is situated below the critical point. Curve 3 corresponds to the coupling constant, depending on the local concentration $c(\mathbf{r})$. In this case the "phase transition" at the interface results in the discontinuity of the slope of the dependence $\sigma(c_0)$. The variety of such transitions was demonstrated and studied in detail in Ref. 7.

In the vicinity of the Lifshitz point $\tilde{b}_1 = 0$, Eq. (24) for the interfacial tension is not valid anymore. To obtain the concentration dependence of σ in this region, one must take the higher-order terms in the gradient expansion given by Eq. (3) into account. The result of the corresponding evaluation is shown by the dotted curves in Fig. 1. Consideration of the case $\tilde{b}_1 < 0$ in more detail will be published elsewhere.

3. CONCLUSION

On the basis of the Landau–Ginzburg model for the free energy of a ternary oil–water–surfactant system below the critical consolute point and using the simple model for the interaction between amphiphillic molecules and density inhomogeneities, we have elucidated the explicit dependence of the oil–water interface tension σ on the surfactant concentration c_0. The dependence of σ on c_0 in a near-critical solution is strongly affected by the interplay of two different mechanisms, both leading to a reduction of the interfacial tension with an increase in the surfactant concentration. The first mechanism is the well-known critical reduction resulting in vanishing the interfacial tension at the critical point. The second can be called the "Lifshitz-point" mechanism leading to the renormalization of the gradient-term coefficient in the Landau–Ginzburg expansion of the free energy. We believe that at low surfactant concentrations, the main role is played by the latter of these mechanisms.

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