

Theory of Interfacial Phase Transitions in Surfactant Systems

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The spin-1 Ising model, which is equivalent to the three-component lattice gas model, is used to study wetting transitions in three-component surfactant systems consisting of an oil, water, and a nonionic surfactant. Phase equilibria, interfacial profiles, and interfacial tensions for three-phase equilibrium are determined in mean field approximation, for a wide range of temperature and interaction parameters. Surfactant interaction parameters are found to strongly influence interfacial tensions, reducing them in some cases to ultralow values. Interfacial tensions are used to determine whether the middle phase, rich in surfactant, wets or does not wet the interface between the oil-rich and water-rich phases. By varying temperature and interaction parameters, a wetting transition is located and found to be of the first order. Comparison is made with recent experimental results on wetting transitions in ternary surfactant systems.

KEY WORDS: Water-oil-surfactant systems; interfacial composition profiles and tensions; wetting transition; Ising model.

1. INTRODUCTION

In recent years, much effort has been devoted to the understanding of wetting phenomena, which are of great industrial importance and scientific interest.⁽¹⁻³⁾ Of particular importance are ternary surfactant systems containing an oil, water, and a surfactant. Surfactant molecules are amphiphilic and thus generally prefer to lie at the oil-water interface, whose interfacial tension can be strongly reduced by the presence of even a small amount of surfactant.

This paper is dedicated to J. K. Percus in honor of his 65th birthday.

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Under appropriate thermodynamic conditions, ternary surfactant systems may exhibit three liquid phases in equilibrium, namely an upper oil-rich phase denoted α , a lower water-rich phase denoted γ , and a middle surfactant-rich phase denoted β .

Based on recent experimental observations,⁽⁴⁻⁷⁾ it has been suggested that in the three-phase region of ternary nonionic surfactant systems, the chain length of the surfactant plays a key role in determining whether the middle surfactant-rich phase wets or does not wet the oil-water interface. In particular, systems with a short-chained surfactant, such as C_4E_1 and C_4E_2 , are found to exhibit wetting middle phases at all temperatures,^(4,5) for which the middle phase β spreads at the oil-rich and water-rich $\alpha\gamma$ interface in the form of a macroscopically thick layer, as shown in Fig. 1a. On the other hand, systems with a surfactant of relatively long chain length, such as C_8E_3 , are found to exhibit nonwetting middle phases at all temperatures,^(6,7) the β phase forming a lens at the $\alpha\gamma$ interface, as depicted in Fig. 1b. These observations led us to conjecture⁽⁸⁾ that for a surfactant of intermediate chain length, there may exist a well-defined temperature which separates the wetting from the nonwetting regimes. At such a temperature, an interfacial phase transition occurs, which is called a wetting transition. This conjecture has been experimentally confirmed in our laboratory,^(8,9) and wetting transitions have been found in three ternary mixtures containing a surfactant of intermediate chain length: water/*n*-tetradecane/ C_6E_2 , water/*n*-hexadecane/ C_6E_2 , and water/*n*-octadecane/ C_6E_2 , where C_iE_j is the nonionic surfactant polyoxyethylene alcohol $C_iH_{2i+1}(CH_2OCH_2)_jOH$. Enhanced videomicroscopy photographs of some of our experiments on the system water/*n*-hexadecane/ C_6E_2 are shown in Fig. 2, where the middle surfactant-rich phase is seen to form a nonwetting lens below 49.4°C and a wetting film above 49.4°C. The thick interface seen at the top of each of Figs. 2a-2d is that separating the oil-rich phase from air.

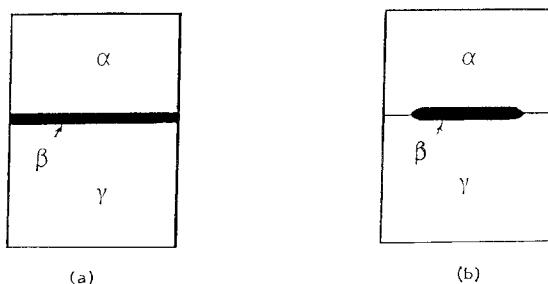
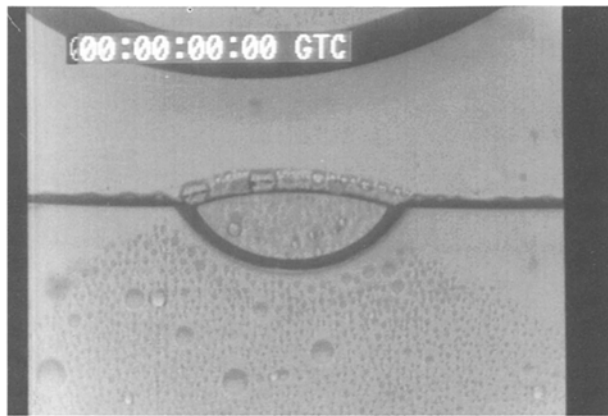
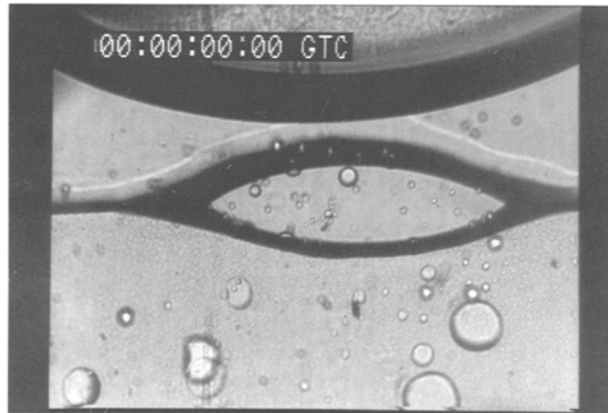


Fig. 1. Schematic illustration of three liquid phases at coexistence: (a) wetting; (b) non-wetting.

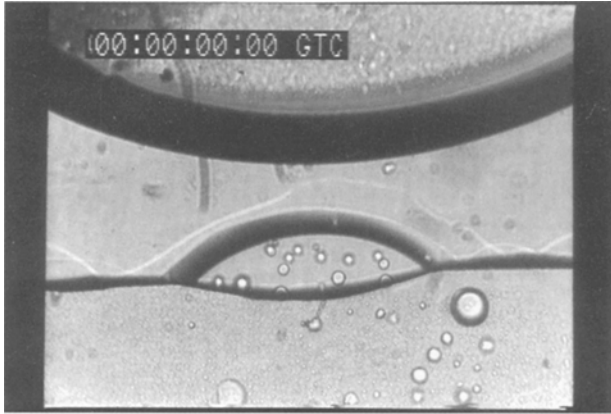


(a)



(b)

Fig. 2. Nonwetting middle surfactant-rich phase in water-*n*-hexadecane- C_6E_2 system at (a) $T=24.3$, (b) 28.6 , (c) 37°C ; and (d) wetting middle surfactant-rich phase in water-*n*-hexadecane- C_6E_2 system at $T=50^\circ\text{C}$.



(c)



(d)

Fig. 2. (Continued)

The theoretical study of the wetting behavior of a three-component surfactant system amounts to the description of the temperature and composition dependences, at a given pressure, of the tensions of the interfaces between the oil-rich and water-rich phases, $\sigma_{\alpha\gamma}$, between the oil-rich and surfactant-rich phases, $\sigma_{\alpha\beta}$, and between the surfactant-rich and water-rich phases, $\sigma_{\beta\gamma}$. Whether the system is in a wetting or in a nonwetting regime can be directly inferred by comparing the tensions of the various interfaces. When a system is in a wetting regime in which the β phase completely wets the $\alpha\gamma$ interface, the interfacial tensions obey Antonow's rule^(10,11)

$$\sigma_{\alpha\gamma} = \sigma_{\alpha\beta} + \sigma_{\beta\gamma} \quad (1)$$

When a system is in a nonwetting regime, in which the β phase partially wets the $\alpha\gamma$ interface, the interfacial tensions are related by Neumann's inequality⁽¹²⁻¹⁴⁾

$$\sigma_{\alpha\gamma} < \sigma_{\alpha\beta} + \sigma_{\beta\gamma} \quad (2)$$

In order for a system to undergo a transition from a wetting regime, described by Eq. (1), to a nonwetting regime, described by Eq. (2), the difference between the interfacial tensions

$$\Delta\sigma = \sigma_{\alpha\gamma} - (\sigma_{\alpha\beta} + \sigma_{\beta\gamma}) \quad (3)$$

should change from zero to a negative value, as thermodynamic conditions are varied.

The microscopic structure and interfacial properties of surfactant systems represent a difficult and yet unsolved problem. Two theoretical approaches have recently been used to determine interfacial tensions in surfactant systems: the first is based on a phenomenological model,⁽¹⁵⁻¹⁸⁾ while the second is based on microscopic models.⁽¹⁹⁻²⁷⁾ For our purposes, the latter approach, which is based on statistical mechanics, is more promising than the former, for it directly deals with intermolecular forces and can therefore account for their effects on the microscopic structures, phase equilibria, and interfacial properties of multicomponent mixtures. Using a lattice gas model,⁽¹⁹⁾ equivalent to a spin- $\frac{1}{2}$ Ising model,⁽²²⁾ a wetting transition was located in a three-component surfactant system with three liquid phases in equilibrium. However, this model suffers from a major drawback in that the surfactant molecules are constrained to always lie at the oil-water interface. Subsequently, a more suitable microscopic model, the spin-1 Ising model, was studied and wetting and nonwetting regimes were located in a three-component surfactant system with four

liquid phases in equilibrium.^(24,25) Several other microscopic models of three-component surfactant systems have been proposed,^(21,23,27,28) but their wetting properties have not been investigated.

In this paper, we analyze the spin-1 Ising model to study the wetting properties of three-component surfactant systems and interpret our recent experiments on wetting transitions in ternary nonionic surfactant systems.^(8,9)

2. MODEL

Consider a three-component mixture consisting of species a (oil), b (water), and c (surfactant), the molecules of which are located on the lattice sites of a simple cubic lattice. Each lattice site is occupied by one and only one molecule of either species. If we consider only nearest-neighbor interactions, the general form of the Hamiltonian is^(24,25,29)

$$\begin{aligned} \mathcal{H} = & - \sum_{\alpha} \sum_{\beta} E_{\alpha\beta} \sum_{\langle ij \rangle} P_i^{\alpha} P_j^{\beta} - \sum_{\alpha} \mu_{\alpha} \sum_i P_i^{\alpha} \\ & - L \sum_{\langle ijk \rangle} [(P_i^a P_j^c P_k^a + P_i^b P_j^c P_k^b) \\ & - (P_i^a P_j^c P_k^b + P_i^b P_j^c P_k^a)] \end{aligned} \quad (4)$$

where $\alpha, \beta = a, b, c$; P_i^{α} is an occupation variable which is equal to one if site i is occupied by species α , and zero otherwise; $E_{ij} = E_{ji}$ is the interaction energy for a pair of molecules i and j ; $\langle ij \rangle$ denotes nearest-neighbor sites, while $\langle ijk \rangle$ denotes triplets of nearest neighbor sites along a line; the sums are over all possible pairs and triplets of molecules, respectively. μ_i is the chemical potential of species i , and L measures the strength of the surfactant interactions. The term containing L in Eq. (4) accounts for three-body interactions; it reduces the energy of the configuration acb or bca of three molecules along a line, and increases the energy of the configurations aca and $bc b$. Note the competition between the two-body terms, which favor like molecules to lie at arbitrary distances from one another, and the three-body term, which favors the surfactant to lie between oil and water rather than to be surrounded by any one species. The first two terms of Eq. (4) represent the Hamiltonian of Blume *et al.*⁽²⁹⁾ The last term in Eq. (4) was introduced by Schick and Shih.⁽²⁴⁾

In the magnetic transcription of the lattice gas, the three-component lattice gas model is equivalent to a spin-1 Ising model, in which each lattice site is occupied by a spin variable S_i , which can assume the values 1, -1 , or 0, representing the three components a , b , and c , respectively. In terms of these spin variables, the Hamiltonian (4) assumes the form

$$\begin{aligned} \mathcal{H} = & -J \sum_{\langle ij \rangle} S_i S_j - K \sum_{\langle ij \rangle} S_i^2 S_j^2 \\ & - C \sum_{\langle ij \rangle} (S_i S_j^2 + S_i^2 S_j) - H \sum_i S_i \\ & + D \sum_i S_i^2 - L \sum_{\langle ijk \rangle} (1 - S_j^2) S_i S_k \end{aligned} \quad (5)$$

where the spin variables are related to the occupation number variables by

$$\begin{aligned} P_i^a &= S_i(1 + S_i)/2 \\ P_i^b &= -S_i(1 - S_i)/2 \\ P_i^c &= 1 - S_i^2 \end{aligned}$$

The coupling parameters in (5) are related to the interaction energies of (4) by^(24,25,29)

$$\begin{aligned} J &= (E_{aa} + E_{bb} - E_{ab})/4 \\ K &= [E_{aa} + E_{bb} + 2E_{ab} + 4E_{cc} - 4(E_{ac} + E_{bc})]/4 \\ C &= (E_{aa} - E_{bb} - 2E_{ac} + 2E_{bc})/4 \\ H &= [\mu_a - \mu_b + 6(E_{ac} - E_{bc})]/4 \\ D &= [2\mu_c - \mu_a - \mu_b - 6(E_{ac} + E_{bc} - E_{cc})]/2 \end{aligned} \quad (6)$$

In Eqs. (5) and (6), J is an interaction parameter which distinguishes between components a and b ; K is an interaction parameter which distinguishes between components c and b and a , and which, in surfactant systems, is a measure of the strength of the surfactant. D represents the chemical potential of the surfactant and H is a measure of the magnetic field. C and H are the symmetry-breaking terms which ensure that the compositions of species a and b are not the same. Note that in (5) those terms which are spin-independent are ignored, for they clearly have no influence on the phase equilibrium. Furthermore, in order to promote phase separation, L is taken to be negative, while J and K are always positive. Further details on this model can be found in refs. 24, 25, and 29.

For the symmetric case in which there is no difference between components a and b (oil and water), $C = H = 0$, so that $\mu_a = \mu_b$, and the Hamiltonian (6) becomes

$$\begin{aligned} \mathcal{H} = & -J \sum_{\langle ij \rangle} S_i S_j - K \sum_{\langle ij \rangle} S_i^2 S_j^2 \\ & + D \sum_i S_i^2 - L \sum_{\langle ijk \rangle} (1 - S_j^2) S_i S_k \end{aligned} \quad (7)$$

The free energy corresponding to the Hamiltonian (7) cannot be evaluated analytically without approximation. Within the mean field approximation, in which the thermal expectation values are defined by

$$M_i = \langle S_i \rangle \quad \text{and} \quad Q_i = \langle S_i^2 \rangle$$

the reduced free energy of a system which is not translationally invariant in the z direction and is described by Hamiltonian (7) can be expressed as

$$\Phi/N\bar{J} = \sum_{z=-\infty}^{\infty} \Phi_z \quad (8)$$

with

$$\begin{aligned} \Phi_z = & (6M_z^2 + M_z \Delta^2 M_z)/12 + k(6Q_z^2 + Q_z \Delta^2 Q_z)/12 \\ & + l[(9M_z^2 + M_z \Delta^2 M_z) - (6M_z^2 Q_z + M_z^2 \Delta^2 Q_z) \\ & - (12M_z^2 Q_z + 2M_z Q_z \Delta^2 M_z)]/18 \\ & - t \ln[1 + 2 \cosh(a_z) \cdot e^{b_z}] \end{aligned} \quad (9)$$

and

$$M_z = 2 \sinh(a_z) / [e^{-b_z} + 2 \cosh(a_z)] \quad (10)$$

$$Q_z = 2 \cosh(a_z) / [e^{-b_z} + 2 \cosh(a_z)] \quad (11)$$

$$\begin{aligned} a_z = & \{ (6M_z + \Delta^2 M_z) + l[36M_z(1 - Q_z) \\ & + 4(1 - Q_z) \Delta^2 M_z - 3M_z \Delta^2 Q_z] / 6 \} / 6t \end{aligned} \quad (12)$$

$$b_z = [k(6Q_z + \Delta^2 Q_z) - \Delta - l(9M_z^2 + M_z \Delta^2 M_z) / 3] / 6t \quad (13)$$

where

$$\Delta^2 M_z = M_{z+1} + M_{z-1} - 2M_z \quad (14)$$

$$\Delta^2 Q_z = Q_{z+1} + Q_{z-1} - 2Q_z$$

Here, z denotes the height of a given lattice plane, N is the number of such planes, and t is the reduced temperature. In order to be consistent with the notations of Blume *et al.*,⁽²⁹⁾ the variables in the above equations are defined as

$$k = \bar{K}/\bar{J}; \quad l = \bar{L}/\bar{J}$$

$$t = k_B T/\bar{J}; \quad \Delta = D/\bar{J}$$

with

$$\bar{J} = qJ; \quad \bar{K} = qK; \quad \bar{L} = q \cdot L \tag{15}$$

q is the coordination number of the lattice ($q=6$ for the simple cubic lattice) and k_B is Boltzmann's constant. For given values of the interaction parameters and of the temperature, the free energy can be determined by first solving Eqs. (10)–(14) numerically for M_z and Q_z at each lattice plane z , and then substituting their values into Eq. (9).

For a spatially uniform phase, the terms in Eqs. (8)–(14) become independent of z , and Eq. (8) reduces to⁽²⁹⁾

$$\Phi/N\bar{J} = M^2/2 + kQ^2/2 + l(1 - 2Q)M^2/2 + t \ln(1 - Q) \tag{16}$$

For three phases to coexist at given t , Δ , k , and l , there are three different values of (M, Q) corresponding to identical free energies of the coexisting α , β , and γ phases. In most cases, the values of (M_i, Q_i) are determined numerically from Eqs. (10)–(14) and Eq. (16), and can also be related to the compositions of the individual components in each phase through

$$X_o = (Q + M)/2 \tag{17a}$$

$$X_w = (Q - M)/2 \tag{17b}$$

$$X_s = 1 - Q \tag{17c}$$

where X_o , X_w , and X_s are the compositions of oil (denoted above by a), water (denoted above by b), and surfactant (denoted above by c), respectively.

The tensions σ_{ij} of the planar interface separating the i and j phases can be directly evaluated from

$$\sigma_{ij} = \sum_{z=-\infty}^{\infty} (\Phi_z - \Phi_B) \quad (i \neq j) \tag{18}$$

where $i = \alpha, \beta, \gamma$ and $j = \alpha, \beta, \gamma$. Φ_B is the free energy of one of the bulk phases, with boundary conditions $\Phi_z = \Phi_i(M_i, Q_i)$ as $z \rightarrow \infty$ and $\Phi_z = \Phi_j(M_j, Q_j)$ as $z \rightarrow -\infty$. Note that for the symmetrical case of equivalent a and b species, one clearly has $\sigma_{\alpha\beta} = \sigma_{\beta\gamma}$ and, of course, $\sigma_{ij} = \sigma_{ji}$.

3. RESULTS AND DISCUSSION

3.1. Phase Diagram

In order to study the wetting properties of the Hamiltonian (5) and locate its possible wetting transitions, it is first necessary to determine its three-phase equilibria over as wide a range as possible of the temperature

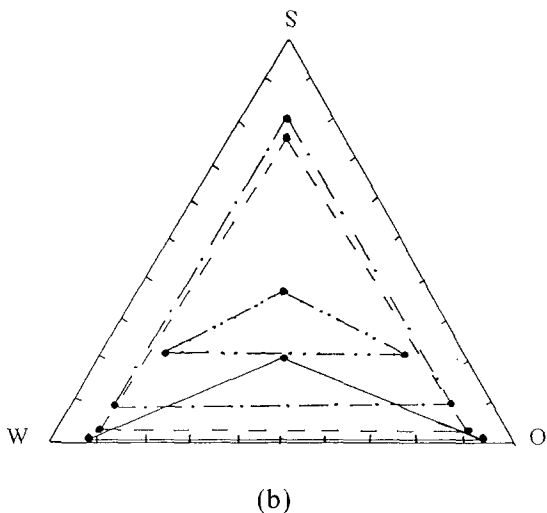
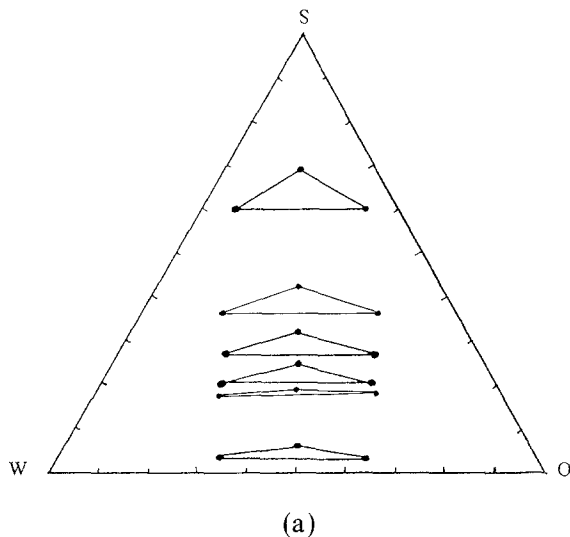


Fig. 3. Phase diagrams for oil-rich, water-rich, and surfactant-rich phases in equilibrium for (a) $t = 0.97t_{\text{tcp}}$: triangles from top to bottom refer to $(k=0, l=0)$, $(k=1, l=0)$, $(k=2, l=0)$, $(k=2.88, l=0)$, $(k=3.8, l=0)$, and $(k=2.88, l=-2.0)$; (b) for a fixed $t = 0.6457$ (in units of \bar{J}): $(-\cdots)$ $(k=2.0, l=0)$, (\cdots) $(k=2.88, l=0)$, (\cdots) $(k=2.88, l=-2.0)$, $(-)$ $(k=2.88, l=-4.0)$, (c) for $(k=2.88, l=0)$: $(-)$ $t = 0.93t_{\text{tcp}}$; $(---)$ $t = 0.89t_{\text{tcp}}$; and (\cdots) $t = 0.49t_{\text{tcp}}$; and (d) properties of the bulk surfactant-rich phase as a function of temperature for $k=2.88, l=0$: $(-)$ composition of oil; (\cdots) composition of surfactant; (\cdots) free energy of the bulk phase.

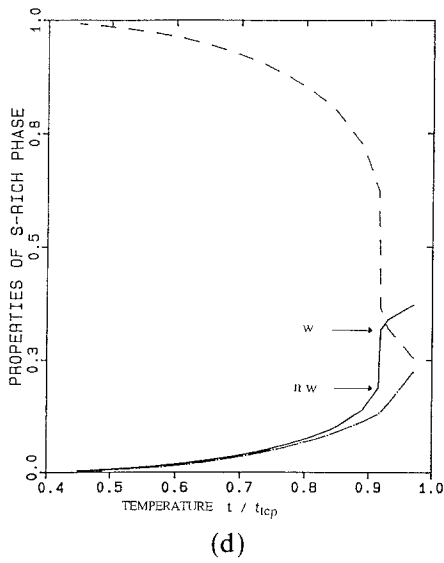
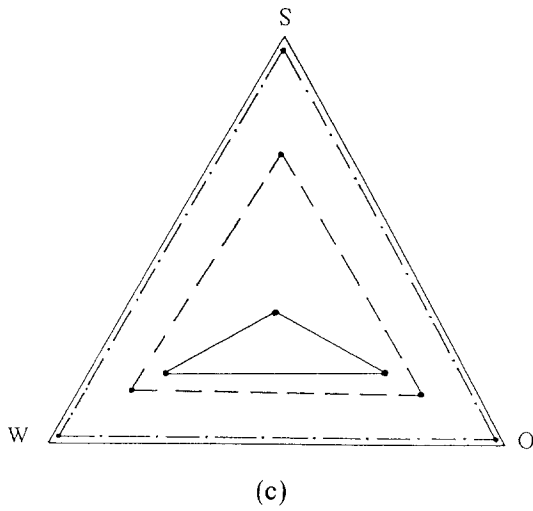


Fig. 3. (Continued)

and surfactant parameters k and l . In Fig. 3a, we show a typical phase diagram for three-phase compositions. The effect of the variation of the interaction parameter k is shown at a fixed temperature $t = 0.97t_{\text{tcp}}$, where t_{tcp} denotes the tricritical temperature,⁽²⁹⁾ which differs for each (k, l) . It is seen that for $k = 0$, the amount of surfactant is too large (68%) to dissolve oil and water. However, when k is increased, the temperature increases and the composition of the surfactant in the middle phase gradually decreases, to 22% for $k = 3.8$ and $l = 0$. In fact, by allowing for three-body interactions, that is, by increasing the strength of the amphiphile, the surfactant content in the middle phase can be drastically reduced: for example, it drops to 6% for $k = 2.88$ and $l = -2$. These results are consistent with those of Schick and Shih.⁽²⁴⁾

Figure 3b shows the explicit effect of k and l on the compositions of three-phase equilibria at the given temperature $t = 0.6457$, which is significantly lower than the temperature $t = 0.97t_{\text{tcp}}$ of Fig. 3a. Unlike in Fig. 3a, surfactant content in the middle phase increases with k ; but, as in Fig. 3a, it can be substantially reduced by taking three-body interactions into account ($k = 2.88$, $l = -2$ and -4). This suggests that at the temperature considered, entropic effects are more pronounced than energy effects, and correspondingly stronger surfactant interactions are needed to overcome them.

Figure 3c shows the variation with temperature of the compositions of three-phase equilibria for given interaction parameters $k = 2.88$ and $l = 0$. As can be seen, a decrease in the temperature has a dramatic effect on the phase diagram, and more surfactant is required to dissolve oil and water. For these values of the interaction parameters, the effect of varying temperature on the bulk phase free energy, as well as on the compositions of oil and surfactant in the surfactant-rich phase, have also been investigated, and the results are shown in Fig. 3d. Free energy and surfactant composition are found to be continuously decreasing functions of the temperature, whereas oil composition is a continuously increasing function of the latter.

The present microscopic model reproduces qualitatively many of the features of three-phase equilibria of surfactant systems observed in experiments. For example, the results shown in Fig. 3 are found to be in accord with those of recent experiments,⁽³⁰⁾ in which long-chained surfactants are found to be more effective in mutually dissolving oil and water than are short-chained surfactants.

3.2. Interfacial Tensions

The tensions of the interfaces $\alpha\gamma$, $\alpha\beta$, and $\beta\gamma$ along the three-phase coexistence line are evaluated in mean field approximation as described in

Section 2, and the results are shown in Fig. 4 as a function of temperature. Only a symmetric Hamiltonian, in which $C = H = 0$, has been considered. As is evident from the figure, the tensions $\sigma_{\alpha\gamma}$ and $\sigma_{\alpha\beta} = \sigma_{\beta\gamma}$ are larger at low temperatures than at high temperatures. As the tricritical point of the mixture is approached, the tensions $\sigma_{\alpha\gamma}$ and $\sigma_{\alpha\beta} = \sigma_{\beta\gamma}$ decrease, ultimately vanishing at the tricritical point itself. Also shown in Fig. 4 are the values $\sigma_{\alpha\gamma}^{\circ}$ of $\sigma_{\alpha\gamma}$ in the absence of surfactant. At sufficiently low temperatures, where two-phase equilibria of oil-rich and water-rich phases are encountered, $\sigma_{\alpha\gamma}$ approaches $\sigma_{\alpha\gamma}^{\circ}$, as expected.

If the surfactant molecules are long-chained, the interaction energy is greatly reduced, resulting in ultralow values of the interfacial tensions. For example, the interfacial tensions $\sigma_{\alpha\gamma}$ and $\sigma_{\alpha\beta} = \sigma_{\beta\gamma}$ at $t = 0.97t_{\text{tcp}}$ are equal to 0.0016 and 0.0008, respectively, for $k = 2.88$ and $l = 0$, while they drop to 0.0010 and 0.0005, respectively, for $k = 2.88$ and $l = -2.0$. Likewise, at a fixed temperature $t = 0.6457$, $\sigma_{\alpha\gamma}$ and $\sigma_{\alpha\beta} = \sigma_{\beta\gamma}$ are equal to 0.1007 and 0.0914, respectively, for $k = 2.88$ and $l = 0$, while they drop to 0.0888 and 0.0778, respectively, for $k = 2.88$ and $l = -2$.

Once the values of $\sigma_{\alpha\gamma}$ and $\sigma_{\alpha\beta} = \sigma_{\beta\gamma}$ are known as functions of temperature and interaction parameters, it is straightforward, as seen from Eqs. (1)–(3), to determine whether a wetting transition occurs. The variation of $\Delta\sigma = \sigma_{\alpha\gamma} - (\sigma_{\alpha\beta} + \sigma_{\beta\gamma})$ with temperature is also shown in Fig. 4 for a given potential parameter $k = 2.88$, keeping $l = 0$. At the highest tem-

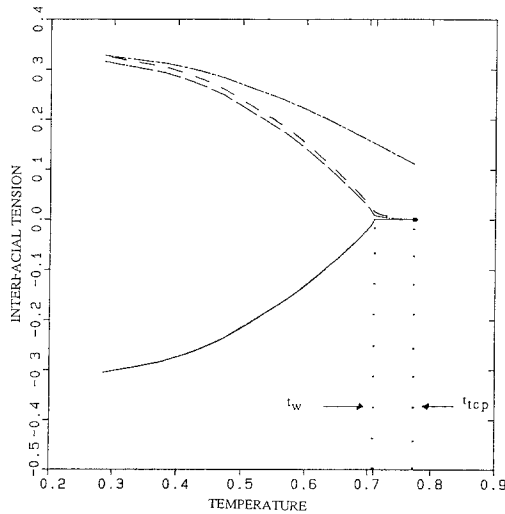


Fig. 4. Wetting–nonwetting transition and interfacial tensions between the phases as a function of temperature ($k = 2.88, l = 0$): (—) $\Delta\sigma$, (---) σ_{ow} , (- - -) σ_{os} , (- · - ·) σ_{ow}° . The solid circle denotes the tricritical point.

perature, which is that of a tricritical point for the above parameters, $\Delta\sigma=0$; that is, the surfactant-rich phase (β) always wets the $\alpha\gamma$ interface, as it obviously must. As the temperature is lowered, the system is found to remain in a wetting regime, with $\Delta\sigma=0$, until a temperature t_w is reached at which a transition from a wetting regime to a nonwetting regime takes place, with $\Delta\sigma$ changing continuously from $\Delta\sigma=0$ to $\Delta\sigma<0$. In units of \bar{J} , the wetting transition temperature t_w is found to be approximately equal to 0.708. As is evident from Fig. 4, the nonwetting regime extends over a range of temperatures lying within the three-phase region. On the scale of Fig. 4, the temperature derivative of $\Delta\sigma$ at t_w is found to be discontinuous, indicating that the transition is first-order.

The effect of the surfactant interaction parameter k on the wetting behavior is illustrated in Fig. 5. As k increases, the nonwetting region expands and is enclosed between the tricritical point temperature and the wetting line ($t_{\text{tcp}} - t_w$). The middle phase is always found to spread across the interface between the oil-rich and water-rich phases provided $k < 1.2$, while it does not wet that interface for $k \gtrsim 1.2$ over a large part of the temperature range. Consequently, long-chained surfactants promote nonwetting over a much larger temperature range, even up to the tricritical point temperature. This result is in agreement with experimental observations.⁽⁶⁻⁹⁾

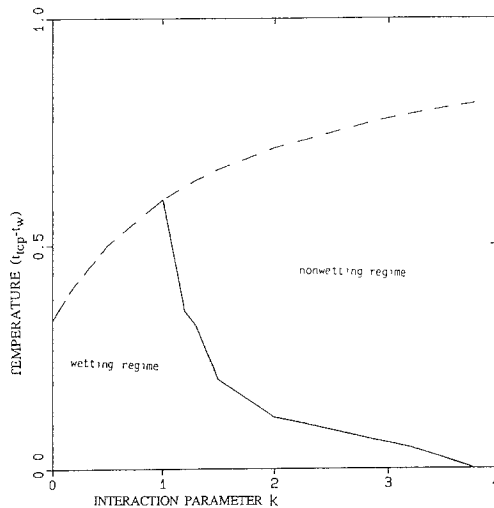


Fig. 5. Range of wetting and nonwetting regimes as a function of the interaction parameter k for $l=0$: (—) wetting line, (---) tricritical temperature line.

In recent theoretical studies,^(16,31) it has been suggested that microscopic structural changes in the bulk surfactant-rich middle phase may be associated to a wetting transition. To test this suggestion, it is useful to consider first how the composition of the surfactant-rich phase varies with temperature from a wetting to a nonwetting regime. From Fig. 3c, in which three-phase compositions are plotted for $k = 2.88$ and $l = 0$, we note that the high-temperature phase diagram ($t = 0.93t_{tcp}$) lies in the wetting regime containing relatively small amounts of surfactant in the middle phase, while the low-temperature phase diagrams ($t = 0.89t_{tcp}$ and $t = 0.49t_{tcp}$) lie in the nonwetting regime containing larger amounts of surfactant. That is to say, a decrease in the temperature is followed by an appreciable increase in the amount of the surfactant in the middle phase, as the system moves from a wetting to a nonwetting regime.

To quantify this point, we determine the individual compositions of the middle phase at two typical temperatures, $t = 0.918t_{tcp}$ and $0.915t_{tcp}$, corresponding to a wetting regime and a nonwetting regime, respectively. The interaction parameters are again $k = 2.88$ and $l = 0$, but the temperature range is now very narrow. For $t = 0.918t_{tcp}$, the compositions in the middle phase are $X_o = X_w = 0.32$ and $X_s = 0.36$, while for $t = 0.915t_{tcp}$, $X_o = X_w = 0.19$ and $X_s = 0.62$. Thus, as one moves from a wetting to a nonwetting regime, a large but continuous change in the compositions of the

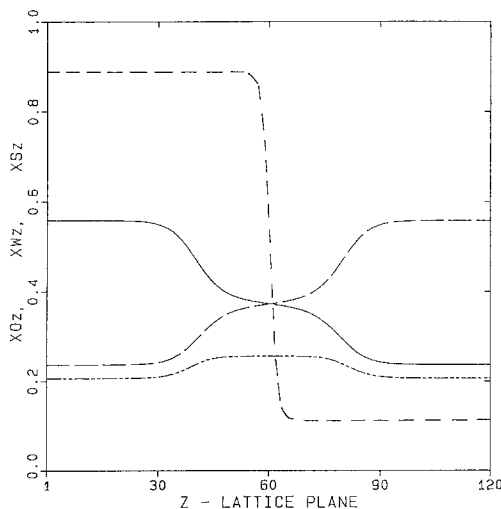


Fig. 6. Composition profiles of oil-rich and water-rich interface at $t = 0.97t_{tcp}$ and for ($k = 2.88, l = 0$): (—) composition of oil, (---) composition of water, (- - -) composition of surfactant, (- - -) composition of oil across oil-water interface in the absence of surfactant.

middle phase occurs, amounting to 41% for each X_o and X_w , and 72% for X_s ; this is also evident from Fig. 2d. However, as the value of k is lowered, this change in the surfactant composition decreases, amounting, for example, to only 2% for $k = 1.5$ and $l = 0$.

Of particular interest is the comparison of the interfacial profiles in the wetting and nonwetting regimes. Figures 6 and 7 show the composition profiles of the $\alpha\gamma$ and $\alpha\beta$ interfaces, whereas Fig. 8 illustrates the free energy profiles for the $\alpha\gamma$ and $\alpha\beta$ interfaces, all at $t = 0.97t_{\text{tcp}}$ for $k = 2.88$ and $l = 0$. Recall that for these values of the parameters, the $\alpha\gamma$ interface is wet by the β phase. As shown in Fig. 6, the composition of oil decreases, whereas that of water increases, symmetrically to that of oil, from that of the bulk oil-rich phase to that of the bulk water-rich phase. On the other hand, the composition of the surfactant is always larger across the interface than it is in the corresponding bulk phases, demonstrating the well-known fact that the surfactant molecules aggregate at the rather thick interface, which leads eventually to oscillations in the density profile; hence, the low value of $\sigma_{\alpha\gamma}$. One could obtain $\sigma_{\alpha\gamma}$ directly by subtracting the free energy of the homogeneous (bulk) phase from that of the inhomogeneous phase (Fig. 8). Also included in Fig. 6 is the composition profile of the oil-water interface in the absence of surfactant; its general features are found to be consistent with earlier investigations.⁽²²⁾ Figure 7 shows composition profiles of the interface between the oil-rich and surfactant-rich phases. The tension of the $\alpha\beta$ interface, as obtained from Fig. 8, is found to be lower than that

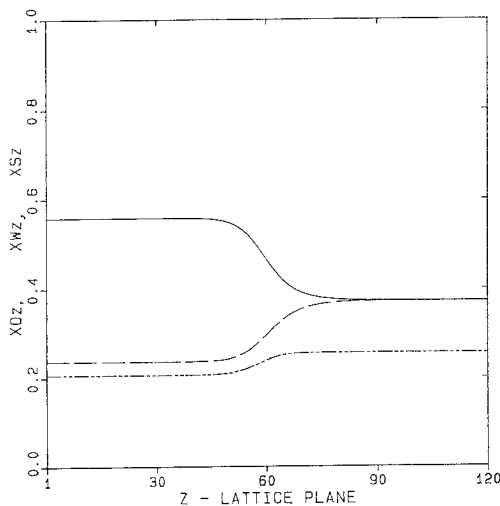


Fig. 7. Composition profiles of oil-rich and surfactant-rich interface at $t = 0.97t_{\text{tcp}}$ and for ($k = 2.88, l = 0$). Key as in Fig. 6.

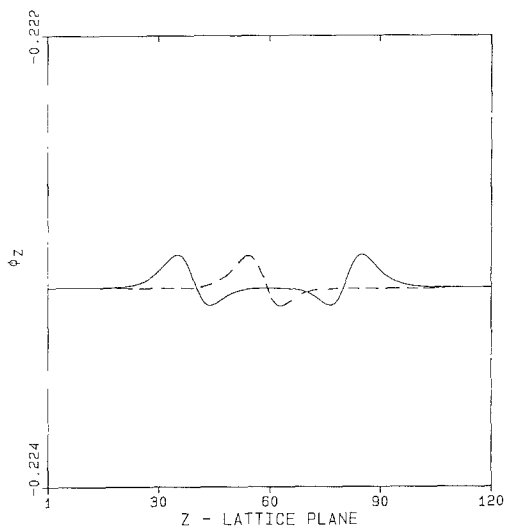


Fig. 8. Free energy profiles of oil-rich, water-rich (—) interface and oil-rich, surfactant-rich interface (---) at $t = 0.97t_{tcp}$ and for $(k = 2.88, l = 0)$.

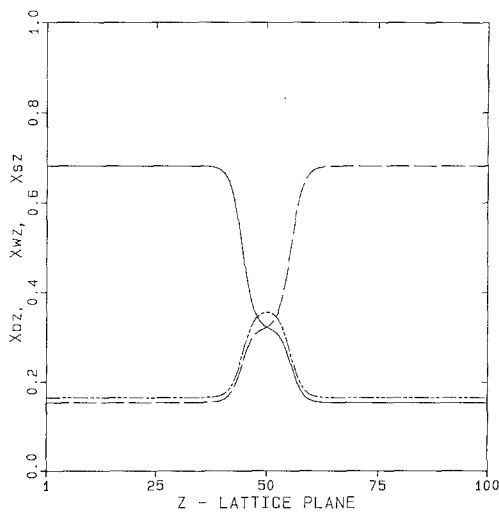


Fig. 9. Composition profiles of oil-rich and water-rich interface at $t = 0.918t_{tcp}$ and for $(k = 2.88, l = 0)$. Key as in Fig. 6.

of the $\alpha\gamma$ interface. Similar results for the profiles of the $\alpha\beta$ and $\alpha\gamma$ interfaces are shown in Figs. 9–11, but now at a lower temperature $t = 0.918t_{\text{tcp}}$, which lies slightly above the wetting transition temperature. As can be seen, a decrease in the temperature amounts to an increased adsorption of surfactant at the $\alpha\gamma$ interface, and hence to large oscillations in the free energy profiles.

We next turn to the nonwetting regime. Figures 12–14 show the composition profiles and free energy profiles of the $\alpha\beta$ and $\alpha\gamma$ interfaces in the nonwetting regime, at the temperature $t = 0.915t_{\text{tcp}}$ for $k = 2.88$ and $l = 0$. The surfactant molecules are found to mostly aggregate at the thin interface, leading to large oscillations in the interfacial free energy, and thereby increasing the interfacial tensions. It thus appears that at low temperatures the middle phase becomes more structured, the change of interfacial composition profiles with temperature being a direct consequence of the adsorption of surfactant molecules at the interface.

Finally, we examine in Fig. 15 the effect of three-body interactions on the wetting transition. The interaction parameters are taken to be $k = 2.88$ and $l = -2.0$. As is clear from comparing Figs. 4 and 15, the inclusion of three-body interactions (l) expands both the wetting and the nonwetting regions, while the general features of the wetting behavior remain the same as in Fig. 4. However, the strong competition between the pair and the

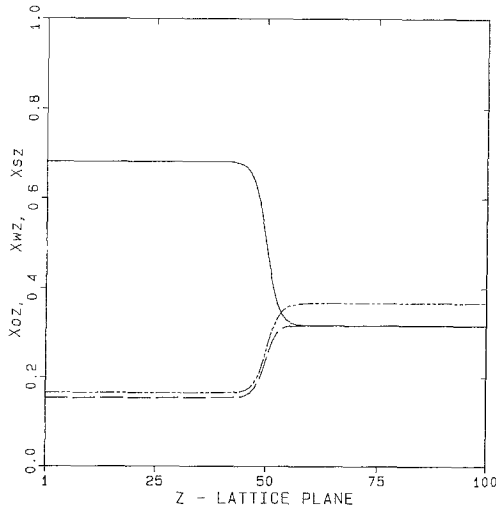


Fig. 10. Composition profiles of oil-rich and surfactant-rich interface at $t = 0.918t_{\text{tcp}}$ and for ($k = 2.88$, $l = 0$). Key as in Fig. 6.

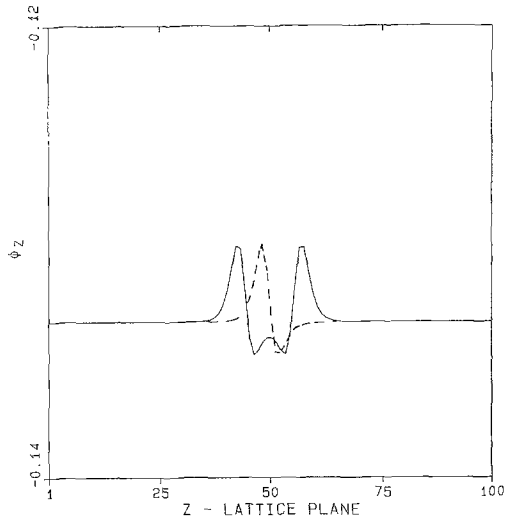


Fig. 11. Free energy profiles of oil-rich, water-rich (—) interface and oil-rich, surfactant-rich interface (---) at $t = 0.918t_{cp}$ and for $(k = 2.88, l = 0)$.

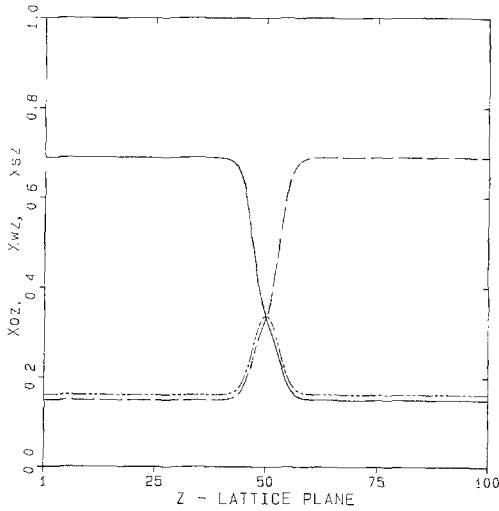


Fig. 12. Composition profiles of oil-rich and water-rich interface at $t = 0.915t_{cp}$ and for $(k = 2.88, l = 0)$. Key as in Fig. 6.

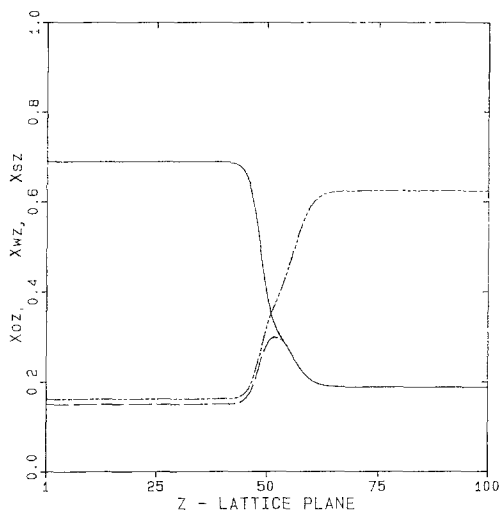


Fig. 13. Composition profiles of oil-rich and surfactant-rich interface at $t = 0.915t_{\text{icp}}$ and for $(k = 2.88, l = 0)$. Key as in Fig. 6.

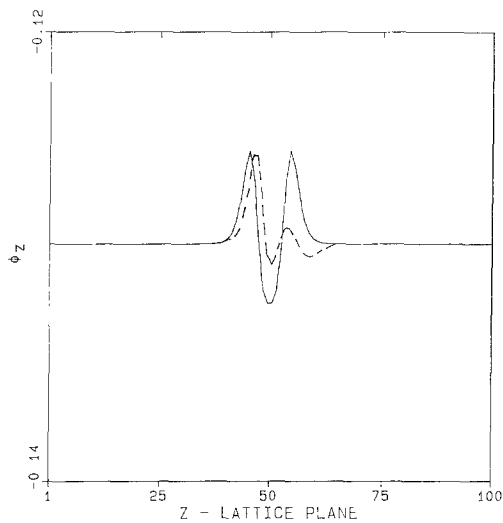


Fig. 14. Free energy profiles of oil-rich, water-rich (—) interface and oil-rich, surfactant-rich (---) interface at $t = 0.915t_{\text{icp}}$ and for $(k = 2.88, l = 0)$.

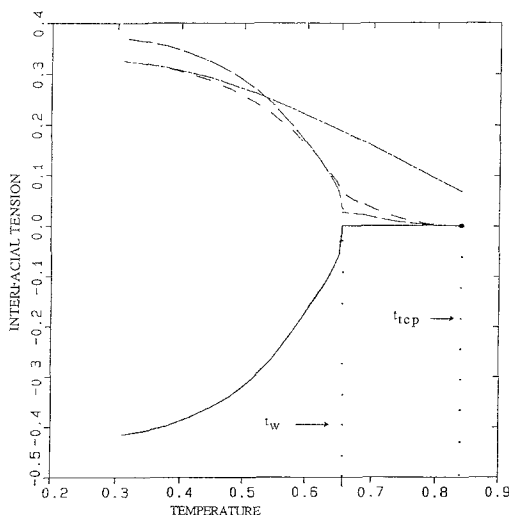


Fig. 15. Wetting–nonwetting transition and interfacial tensions at three-phase equilibrium as a function of temperature for ($k = 2.88$, $l = -2.0$). Key as in Fig. 4.

three-body interactions results in significantly overestimating $\sigma_{\alpha\beta}$ over $\sigma_{\alpha\gamma}$ at lower temperatures, which lie in the nonwetting region and well away from the wetting transition temperature.

4. CONCLUSIONS

A simple lattice gas model has been studied in mean field approximation to determine phase equilibria and interfacial properties of three-component surfactant systems. It is found that as the strength of the amphiphile increases, both the composition of the surfactant in the surfactant-rich middle phase and the interfacial tensions between the phases along the three-phase coexistence line decrease. If the amphiphilic interactions are sufficiently strong, the interfacial tension between the oil-rich phase and the water-rich phase is largely reduced, in some cases to ultralow values. These predictions are in accord with the recent experimental observations^(6,7) that long-chained surfactants are more effective in mutually dissolving oil and water than short-chained surfactants.

The strength of the amphiphile is found to largely affect the wetting behavior of surfactant systems. In the case of a weak surfactant parameter ($k \lesssim 1.2$), the middle phase always wets the interface between the oil-rich and water-rich phases for all temperatures at which three phases coexist. In contrast, for strong surfactant parameter ($k \gtrsim 3.5$), the middle phase does not wet that interface, even up to the tricritical point temperature. For

intermediate surfactant parameter ($1.2 \lesssim k \lesssim 3.5$), wetting transition temperatures are located by continuously varying the temperature in the three-phase region. These results indicate that long-chained surfactants promote nonwetting behavior, and are in qualitative agreement with our experimental observations^(8,9) and those of Langevin *et al.*⁽³²⁾ for surfactant systems consisting of an oil, water, and a nonionic surfactant. The wetting transition is determined to be of the first order. It may be noted that all wetting transitions observed to date, with a possible exception,⁽³³⁾ are found to be first-order.⁽¹⁻³⁾

The variations with temperature and surfactant parameters of phase equilibria, interfacial profiles, and interfacial tensions are consistent with the suggestion^(16,25,31) that wetting transitions in surfactant systems may be associated to structural changes in the surfactant-rich middle phase.

The present model is found to capture many of the qualitative features of phase equilibria and interfacial properties found in experiment. It can be further improved upon by taking into account the asymmetric and higher-neighbor interactions as well as hydrogen-bonding and other effects.⁽²⁵⁾

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