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Wetting in mixtures of water, nonionic amphiphiles, and nonpolar solvents

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As is well known, medium- and long-chain alkanes do not spread across H₂O–air interfaces, but shape a lens. In this paper it is shown that the same holds for the upper amphiphile-rich phase in binary H₂O–amphiphile mixtures with medium- and long-chain nonionic amphiphiles that show a (closed) miscibility gap with water. This finding is somewhat unexpected because surfactants form monolayers at H₂O–air interfaces which should facilitate the spreading of the amphiphile-rich phase. This wetting behavior corresponds to that in ternary H₂O–oil–nonionic amphiphile mixtures with a three-phase body, in which the middle amphiphile-rich phase does not spread across the H₂O–oil interface. The results may stimulate further studies on critical-point wetting [for a recent review see, e.g., S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1988), Vol. 12, p. 1.], and may also help clarifying the properties of microemulsions [for a recent review see, e.g., M. Kahlweit, R. Strey, P. Firman, D. Haase, J. Jen, and R. Schomäcker, *Langmuir* 4, 499 (1988)].

I. INTRODUCTION

Following essentially the arguments presented by Cahn,¹ we consider two near-critical liquid phases (a) and (b) in contact with a third noncritical fluid phase (c). Let the density ρ of (b) lie between that of (a) and (c). We then define as “wetting coefficient”

$$w_\sigma \equiv \Delta\sigma/\sigma_{ab}, \quad (1)$$

where $\Delta\sigma \equiv \sigma_{bc} - \sigma_{ac}$ and $\rho_a > \rho_b > \rho_c$. As distance from the critical temperature T_c we, furthermore, define

$$\epsilon \equiv |T - T_c|/T_c \geq 0. \quad (2)$$

σ_{ab} is always positive but vanishes for $\epsilon \rightarrow 0$:

$$\lim_{\epsilon \rightarrow 0} \sigma_{ab} = +0. \quad (3)$$

$\Delta\sigma$, on the other hand, can be either positive or negative, depending on the composition and structure of the interfacial layer at the a/c and b/c interface, respectively. For $\epsilon \rightarrow 0$, however, σ_{ac} and σ_{bc} must approach the same value $\sigma_c > 0$, so that

$$\lim_{\epsilon \rightarrow 0} \Delta\sigma = \pm 0. \quad (4)$$

Assume that for sufficiently small ϵ ,

$$\Delta\sigma = p\epsilon^x \text{ and } \sigma_{ab} = q\epsilon^y, \quad (5)$$

where p can be either positive or negative, whereas q is always positive. Then

$$w_\sigma = (p/q)\epsilon^{x-y}. \quad (6)$$

Excluding the case $x = y$, one may then distinguish between three cases: (1) The first case is

$$x > y. \quad (7)$$

In this case one has $\lim_{\epsilon \rightarrow 0} w_\sigma = \pm 0$, depending on the sign of p . (2) The second case is

$$x < y \text{ and } p < 0. \quad (8)$$

In this case one has $\lim_{\epsilon \rightarrow 0} w_\sigma < -1$. (3) The third case is $x < y$ and $p > 0$. (9)

In this case one has $\lim_{\epsilon \rightarrow 0} w_\sigma > +1$.

Cases (2) and (3) are illustrated schematically on Fig. 1.² It shows σ_{ab} and $\Delta\sigma$ vs ϵ as ordinate. σ_{ab} (solid curve on the right-hand side) is always positive. If $\Delta\sigma > 0$ (dashed curve on the right-hand side), one will find a transition from $0 < w_\sigma < +1$ to $w_\sigma > +1$ at some $\epsilon > 0$ (horizontal dashed line), whereas if $\Delta\sigma < 0$ (dashed curve on the left-hand side), one will find a transition from $-1 < w_\sigma < 0$ to $w_\sigma < -1$.

The relation between w_σ and the thermodynamic stability of the interfaces was discussed in Ref. (3). We recall the results:

Case (i): $w_\sigma \leq -1$,

that is,

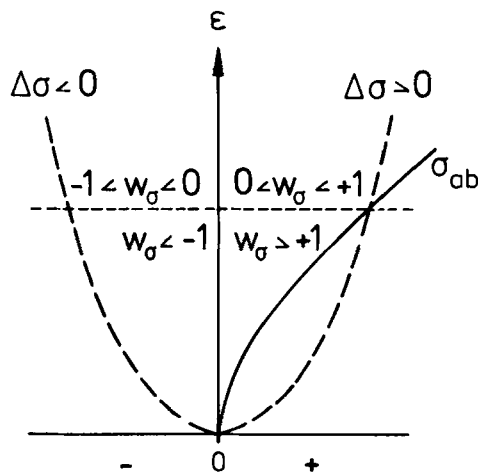


FIG. 1. Nonwetting–wetting transition near a critical point (schematic). For reasons of simplicity we assumed $x < 1$ and $y > 1$.

$$\sigma_{ac} \geq \sigma_{ab} + \sigma_{bc} \quad (10)$$

In this case the a/c interface is unstable. At normal gravity, phase (b) spreads across the a/c interface. Evidently, σ_{ac} cannot be measured exactly. It may, however, be approximated by extrapolating σ_{ac} isotherms to the solubility limit.⁴

$$\text{Case (ii): } -1 < w_\sigma < +1,$$

that is,

$$\sigma_{bc} - \sigma_{ab} < \sigma_{ac} < \sigma_{bc} + \sigma_{ab} \quad (11)$$

In this case all three interfaces are stable. Consequently, phase (b) contracts to a lens leaving part of the a/c interface nonwetted, so that all three interfacial tensions can be measured exactly.

$$\text{Case (iii): } w_\sigma \geq +1, \text{ that is, } \sigma_{bc} \geq \sigma_{ab} + \sigma_{ac} \quad (12)$$

In this case the b/c interface is unstable. Consequently, phase (b) contracts to a globule that floats beneath the a/c interface, being separated from phase (c) by a layer of phase (a). σ_{bc} cannot be measured exactly, but may be approximated by extrapolating σ_{bc} isotherms to the solubility limit.

The shape of the body of (b) in cases (ii) and (iii) depends on the relation between the interfacial tensions, on that between the densities, as well as on that between the volumes of the phases. The above considerations hold irrespective of whether the miscibility gap between the two near-critical phases is one with an upper critical point, or an upper miscibility gap with a lower critical point. Thus, observing the shape of the body of phase (b) as one approaches the critical point, should permit distinguishing which of the above cases holds for a particular liquid mixture. We shall now apply the results of these considerations to two near-critical liquid phases in equilibrium with vapor (air), and in equilibrium with a noncritical third liquid phase.

II. MIXTURES OF WATER AND NONIONIC AMPHIPHILES

In Ref. 3 we discussed the wetting in alkane-water, and in alkane-methanol mixtures in contact with vapor (air). In this paper we study the wetting in mixtures of nonionic amphiphiles and water. As nonionic amphiphiles we chose n -alkyl polyglycolethers, abbreviated by C_iE_j , where i denotes the number of carbon atoms in the hydrophobic "tail" of the amphiphile, and j denotes the number of ethyleneoxid $O(CH_2)_2$ groups in the hydrophilic "head." Because i and j can be varied independently of each other, one may vary the ratio between the repulsive "hydrophobic interaction" between the tails and H_2O , and the attractive "hydrophilic interaction" between the heads and H_2O .

The phase diagram of every binary mixture shows at sufficiently low temperatures a miscibility gap with an upper critical point. In $H_2O-C_iE_j$ mixtures, the hydrophilic interaction between the heads and H_2O makes this critical point, in general, lie below the melting temperature of the mixture. The hydrophilic interaction, however, decreases with rising temperature so that the homogeneous mixture separates again into two liquid phases as one raises temperature. This upper miscibility gap is a "closed loop" with a lower and an upper critical point. The extensions of this loop as well as its position on the temperature scale depend on the outcome of

the competition between the hydrophobic and the hydrophilic interaction between the amphiphile and the solvent. Accordingly, its lower critical temperature drops with increasing i , but rises with increasing j . For sufficiently large i , the loop extends below the melting temperature and may even merge with the lower miscibility gap, whereas for sufficiently large j , the loop lies above the boiling temperature and may even disappear altogether.

A simple example is given by the series C_4E_j . The miscibility gap between n -butanol (C_4E_0) and H_2O extends below the melting temperature. If one adds one $O(CH_2)_2$ group to the head, that is, proceeds to C_4E_1 , the upper loop appears at about 50 °C. If one proceeds to C_4E_2 , the loop disappears altogether. This suggests choosing an amphiphile with a sufficiently large number i and then stepwise increasing j at constant i . This will make the lower critical temperature of the loop rise stepwise from below to above the melting temperature of the mixture.

Experiments in $H_2O-C_iE_j$ mixtures show the interfacial tensions between the two liquid equilibrium phases and air to differ only little, irrespective of the distance from the critical point. This can be interpreted as being caused by the tendency of amphiphiles to adsorb at the H_2O /air interface, with their tails oriented towards the air, and their heads oriented towards the water. Adding an amphiphile to water thus reduces the interfacial tension between the aqueous phase and air until the interface is covered by a close-packed monolayer of the amphiphile. Further increasing concentration enforces the amphiphile to form association colloids (micelles) within the aqueous bulk phase (at temperatures below the loop), or to separate as amphiphile-rich liquid phase (at elevated temperatures). The small difference between the interfacial tensions of the two equilibrium phases against air could thus be explained by assuming the structure of the two interfacial layers to be rather similar, irrespective of the distance ϵ to the critical point. The interfacial tension between the two phases, on the other hand, will increase with increasing ϵ .

In liquid mixtures with a surface active substance as one of the components it is, therefore, not appropriate to assume the difference $\Delta\sigma$ between the interfacial tensions of the two near-critical phases against a third noncritical phase to be proportional to the difference $\Delta\rho$ between their densities, because the composition of the interfacial layer that determines the interfacial tension differs, in general, considerably from the composition of the bulk phase that determines the density.

This raises the question whether a drop of the upper amphiphile-rich phase spreads across the liquid/air interface, or whether it contracts to a lens floating at that interface. Denoting the lower aqueous phase by (a), the upper amphiphile-rich phase by (b) and the air by (c), the answer depends on the value of the wetting coefficient

$$w_\sigma = (\sigma_{bc} - \sigma_{ac})/\sigma_{ab}.$$

If $w_\sigma \leq -1$ (case i), the amphiphile-rich phase (b) will spread across the liquid/air interface. If, however, $-1 < w_\sigma < +1$ (case ii), it will contract to a lens. Since

experiment shows that $\sigma_{ac} \approx \sigma_{bc}$, one expects for sufficiently large ϵ , that is, sufficiently large σ_{ab} , case (ii).

For C_4E_0 -H₂O mixtures, the three interfacial tensions have been measured by Carter and Jones.⁵ They found at 25 °C, $\sigma_{ac} = 25.2$, $\sigma_{bc} = 24.6$, and $\sigma_{ab} = 4.0$ mN m⁻¹, thus $w_\sigma = -0.15$. A drop of *n*-butanol saturated with H₂O should thus contract to a lens at the liquid/air interface of H₂O saturated with C_4E_0 . This is confirmed by experiment. It was performed by using an optical quartz cuvette of 1 mm thickness, placed in a water thermostat, and observed through a horizontally mounted microscope. Because photographs are difficult to reproduce, we have copied them as drawings. Figure 2 shows the profile of the C_4E_0 lens at 25 °C. In these mixtures one has $\rho_a \gtrsim \rho_b \gg \rho_c$. For this case we have shown in a semiquantitative calculation,³ that the shape of the lens can be approximated by a sphere with a segment cut off by the liquid/air interface (Fig. 3). For the contact angle φ between that sphere and the liquid/air interface we found

$$\cos \varphi = w_\sigma, \quad (13)$$

which resembles Young's equation for the contact angle between two liquid phases and a plane solid wall, the liquid/air interface playing the role of the solid. For $-1 < w_\sigma < 0$, one has $\varphi > \pi/2$. For $w_\sigma = 0$, the drop shapes a hemisphere ($\varphi = \pi/2$). For $0 < w_\sigma < +1$, one has $\varphi < \pi/2$. Applying Eq. (13) to Fig. 2, one finds in qualitative agreement with the data determined by Carter and Jones $\varphi > \pi/2$, that is, $-1 < w_\sigma < 0$.

We studied the mixture H₂O-*n*-octanol (C_8E_0), finding at 25 °C, $\sigma_{ac} = 29.4$, $\sigma_{bc} = 26.9$, and $\sigma_{ab} = 8.5$ mN m⁻¹, thus $w_\sigma = -0.3$. With this mixture, the lens can be readily observed by placing a drop of octanol on a wafer surface.

In both mixtures the miscibility gaps extend below the melting temperature. Whether these gaps are closed loops or merge with the lower miscibility gap, is difficult to clarify. However, if one chooses the series H₂O- C_8E_j and increases the number *j* of O(CH₂)₂ groups in C_8E_j stepwise from zero, this will make the lower critical temperature of the loop rise until the critical point eventually appears above the melting temperature. For *j* = 0, 1, and 2, the lower critical temperature of the loop lies below zero centigrade, for *j* = 3, however, at 11 °C. At a fixed temperature of experiment, one will thus effectively decrease ϵ by increasing *j*. As a consequence, the interfacial tension σ_{ab} between the two liquid equilibrium phases will decrease with increasing *j*, whereas $\Delta\sigma$ will be less effected due to the amphiphilic nature of C_iE_j .

Figure 4 shows the profiles of the lenses of C_8E_j with *j* = 0, 1, 2, and 3 at 25 °C. As expected, w_σ is negative for C_8E_0 . However, as one increases *j*, w_σ increases to change



FIG. 2. Profile of a lens of *n*-butanol (C_4E_0) floating at the interface between water saturated with butanol and air at 25 °C, copied from a photograph.

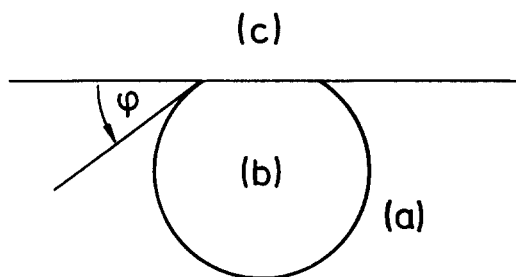


FIG. 3. Globule of phase (b) floating at the *a/c* interface (schematic). For discussion see text.

sign between *j* = 1 and *j* = 2, which implies that $\Delta\sigma$ changes sign. This observation may be interpreted qualitatively as follows: With *j* = 0, that is, the OH group being the only hydrophilic group, the monolayer of the amphiphile at the *a/c* interface is less well ordered than the interfacial layer of the amphiphile-rich phase so that its interfacial tension against air is a little higher than that of phase (b). As one increases the attractive hydrophilic interaction between the heads and the solvent, the monolayer becomes better ordered so that the interfacial tension of the close-packed vertically oriented tails eventually becomes lower than that of phase (b).

This suggests raising temperature with an amphiphile with $\varphi < \pi/2$ at 25 °C. This should make σ_{ab} increase and, accordingly, w_σ decrease. Because the hydrophilic interaction between the heads and the solvent decreases with temperature, one, furthermore, expects the monolayer of the amphiphile at the *a/c* interface to become less ordered with rising temperature, so that w_σ may even change sign, that is, phase (b) to first shape a hemisphere ($\varphi = \pi/2$), and then an unsymmetric lens ($\varphi > \pi/2$) with further rising temperature. This is supported by experiment. For the C_8E_2 -H₂O mixture one finds at 25 °C, $\varphi < \pi/2$ (Fig. 4), at about 50 °C, $\varphi = \pi/2$, and at elevated temperatures $\varphi > \pi/2$.

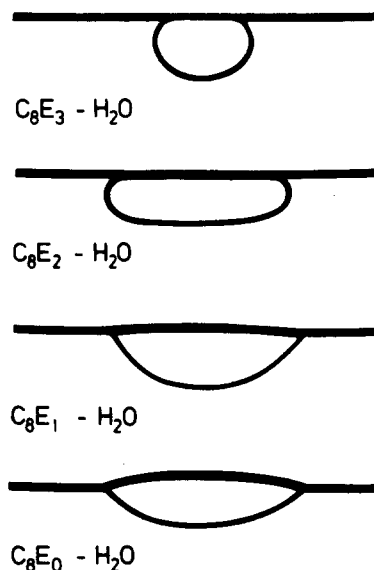


FIG. 4. Profiles of the lenses of C_8E_j (*j* = 0, 1, 2, 3) floating at the *a/c* interface at 25 °C, copied from photographs.

From these results it follows that the wetting coefficient w_σ in mixtures of nonionic amphiphiles and H_2O with an upper loop depends on the position and extension of that loop on the temperature scale, that is, on the amphiphilicity of the surfactant, as well as on the temperature of experiment. Approaching the lower critical point of the loop of medium- and long-chain amphiphiles, $w_\sigma > 0$ appears to hold and, accordingly, $\lim_{\epsilon \rightarrow 0} w_\sigma \gg +1$. With rising temperature w_σ decreases to change sign at some intermediate temperature between the lower and the upper critical temperature of the loop. Approaching the upper critical point, $w_\sigma < 0$ appears to hold and, accordingly, $\lim_{\epsilon \rightarrow 0} w_\sigma \ll -1$. This presumption is illustrated schematically on Fig. 5.

At the lower critical point of the loop, these predictions are confirmed by experiment: for sufficiently small ϵ , a tiny droplet of the upper amphiphile-rich phase shapes a globule that floats beneath the liquid/air interface, being apparently separated from air by a layer of the lower aqueous phase. As one raises temperature, the aqueous layer eventually disappears. Whether or not the amphiphile-rich spreads across the liquid/air interface at the upper critical point of the loop, is difficult to confirm because its temperature lies, in general, above the boiling temperature of the mixture.

If this presumption was correct, binary H_2O -nonionic amphiphile mixtures would offer an opportunity for studying the transition from nonwetting to partial wetting of the liquid/air interface by the upper amphiphile-rich phase near the lower critical temperature, and the transition from partial wetting to complete wetting near the upper critical temperature of their (upper) closed miscibility gap, whereas hitherto such a transition from $w_\sigma \gg +1$ to $w_\sigma \ll -1$ could only be found in ternary mixtures as, e.g., in hexane-methanol-dodecane mixtures at constant T .³

III. MIXTURES OF WATER, OIL, AND NONIONIC AMPHIPHILES (MICROEMULSIONS)

Liquid mixtures of H_2O (A), nonpolar solvents (B), and nonionic amphiphiles (C) may separate into three liquid phases within a well-defined temperature interval

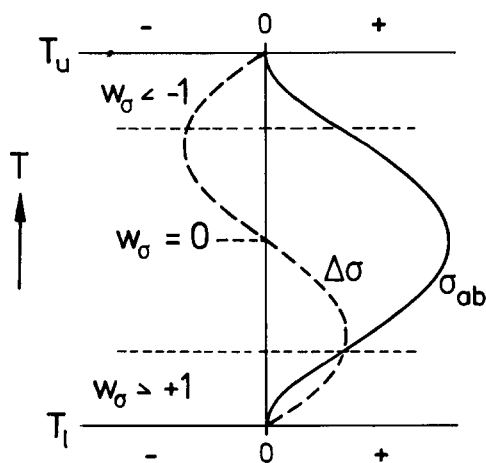


FIG. 5. Wetting in mixtures of nonionic amphiphiles and water vs temperature (schematic). For discussion see text.

$\Delta T = T_u - T_l$, namely a lower aqueous phase (a), a middle amphiphile-rich phase (c) and an upper oil-rich phase (b).⁶ Below and above this temperature interval, the mixtures separate into two liquid phases only, namely a lower aqueous phase and an upper oil-rich phase. The three-phase triangle (a)-(b)-(c) appears at T_l by separation of the lower aqueous phase into phase (a) and (c) at the endpoint cep_β of the critical line that enters the phase prism at the lower critical temperature of the upper loop of the binary (A)-(C) mixture. With rising temperature, the amphiphile-rich phase (c) moves on an ascending trajectory around the surface of the body of heterogeneous phases to the oil-rich side,

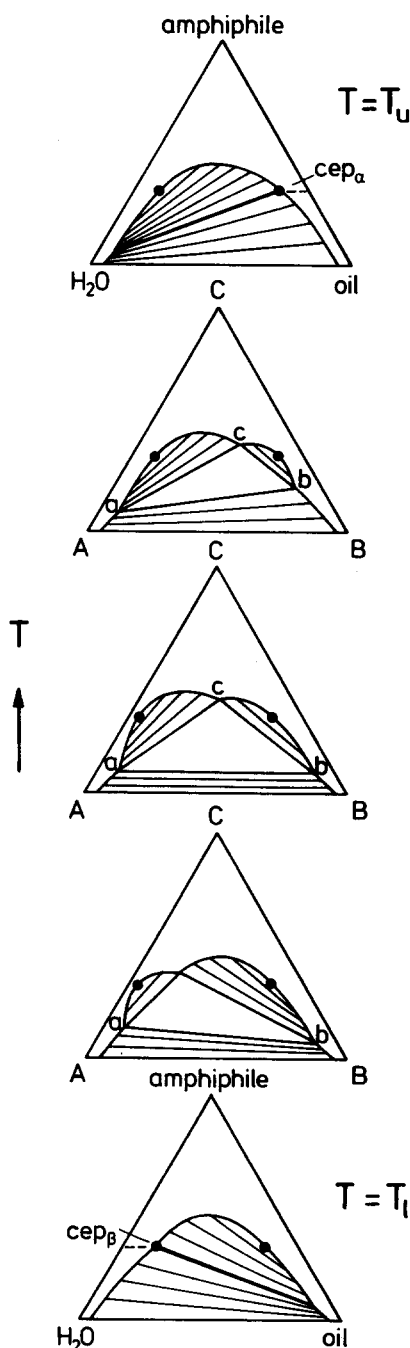


FIG. 6. Evolution of the three-phase triangle in a mixture of H_2O -oil-nonionic amphiphile with rising temperature (schematic).

where it merges with phase (b) at T_u at the endpoint cep_α of the critical line that enters the phase prism at the upper critical temperature of the miscibility gap of the binary (B)–(C) mixture. Figure 6 shows schematical isothermal sections through the phase prism demonstrating the evolution of the three-phase triangle with rising temperature.

Since phases (a) and (c) separate at cep_β , the interfacial tension σ_{ac} must rise from zero at T_l to monotonically increase with rising temperature, as shown schematically in Fig. 7. Phases (b) and (c), on the other hand, merge at cep_α .

Consequently, the interfacial tension σ_{bc} must decrease monotonically with rising temperature to vanish at T_u . Because the sum of two monotonical functions with reverse temperature dependence must show a minimum at some temperature between T_l and T_u , the interfacial tension

$$\sigma_{ab} \leq \sigma_{ac} + \sigma_{bc},$$

must show a minimum near the mean temperature \bar{T} of the three-phase body. Actually, experiment shows that for medium- and long-chain amphiphiles

$$\sigma_{ab} < \sigma_{ac} + \sigma_{bc} \quad (14)$$

which implies that the amphiphile-rich middle phase does not spread across the a/b interface but shapes a lens floating at that interface.⁷

In these mixtures one has, in general, $\rho_a \gtrsim \rho_c \gtrsim \rho_b$. In view of our definition of the wetting coefficient [Eq. (1)] one, accordingly, has to distinguish between approaching the lower critical endpoint, that is, approaching T_l from above, and approaching the upper critical endpoint, that is, approaching T_u from below. In the first case we consider as wetting coefficient $T \rightarrow T_l$ from above:

$$w_\sigma = (\sigma_{cb} - \sigma_{ab}) / \sigma_{ac}, \quad (15)$$

whereas in the second case we consider $T \rightarrow T_u$ from below:

$$w_\sigma = (\sigma_{ac} - \sigma_{ab}) / \sigma_{bc}, \quad (16)$$

where in view of Fig. 7 in both equations $\Delta\sigma < 0$. One thus expects either case (1) or (2), that is, either $\lim w_\sigma = 0$, or $\lim w_\sigma < -1$. Near the mean temperature \bar{T} , that is, at $\sigma_{ac} = \sigma_{bc}$, one has

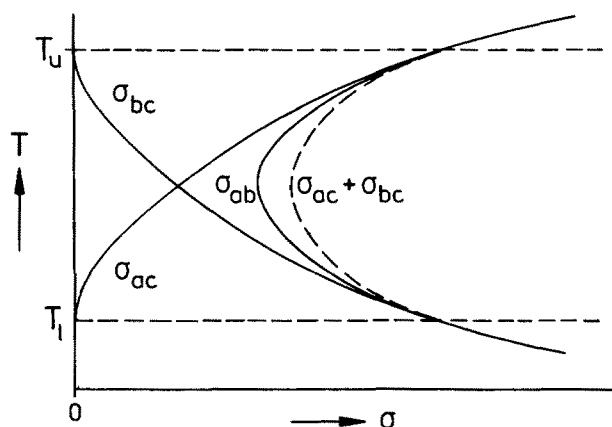


FIG. 7. Interfacial tensions between the three phases vs temperature (schematic). For reasons of simplicity we assumed the curves to be symmetric which is, in general, not the case.

$$w_\sigma = 1 - (\sigma_{ab} / \sigma_{ac}) = 1 - (\sigma_{ab} / \sigma_{bc}) < 0,$$

experiment, Eq. (14), showing that for medium- and long-chain amphiphiles

$$1 < (\sigma_{ab} / \sigma_{ac}) < 2. \quad (17)$$

Because the densities of the three phases differ only little, one may neglect the effect of gravity. In that case phase (c) shapes a lens at the a/b interface, the contact angles being given by the relation (Fig. 8)

$$\sin \alpha / \sigma_{bc} = \sin \beta / \sigma_{ac} = \sin \gamma / \sigma_{ab} \quad \text{with } \alpha + \beta + \gamma = 2\pi. \quad (18)$$

If $\lim_{\epsilon \rightarrow 0} w_\sigma = 0$ (case 1), one would observe $\gamma \rightarrow \pi/2$, and for

$$T \rightarrow T_l: \beta \rightarrow \pi, \text{ and } \alpha \rightarrow \pi/2, \quad (19)$$

$$T \rightarrow T_u: \alpha \rightarrow \pi, \text{ and } \beta \rightarrow \pi/2. \quad (20)$$

If, however, $\lim_{\epsilon \rightarrow 0} w_\sigma \leq -1$ (case 2), one would observe $\gamma \rightarrow 0$, that is, phase (c) to spread across the a/b interface.

Experiment shows that for all medium- and long-chain amphiphiles hitherto studied, $\lim w_\sigma = 0$ (case 1) appears to hold as shown schematically on Fig. 9. For medium- and long-chain nonionic amphiphiles we, therefore, presume the wetting coefficient w_σ in a three-phase body to approach zero at the lower and upper critical tie line as shown schematically in Fig. 10. We can, of course, not exclude a nonwetting-wetting transition very close to the critical endpoints, that is, a $w_\sigma \approx 0$ to $w_\sigma \leq -1$ transition as discussed, e.g., by Widom.⁸ Such a transition, however, seem to be unlikely because the interfacial tension between the two near-critical phases appears to vanish more rapidly than the density difference. As a consequence, the lenses attain the shape of flat pancakes for $\epsilon \rightarrow 0$. We recall at this point that in mixtures with surface active substances as one of the components, the density difference between two near-critical phases is, in general, not proportional to the difference between their interfacial tensions against a noncritical phase.

Robert and Jeng⁹ have recently reported a nonwetting-wetting transition in a H_2O – n -hexadecane– C_6E_2 mixture at 49.1°C , that is, about ten degrees below T_u (61°C). The authors chose an water/oil ratio of about 25, and a C_6E_2 concentration of about 2 wt. %, thus a mean composition in the water-rich corner of the Gibbs triangle. If in this corner the mean composition does not lie very close to the upper critical tie-line (see Fig. 6, top), the amphiphile-rich phase may disappear well below T_u . It is, furthermore, not clear from their paper whether or not they equilibrated the mix-

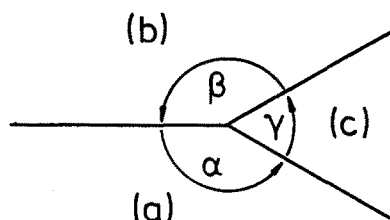


FIG. 8. Contact angles between three liquid phases. See Eq. (18).

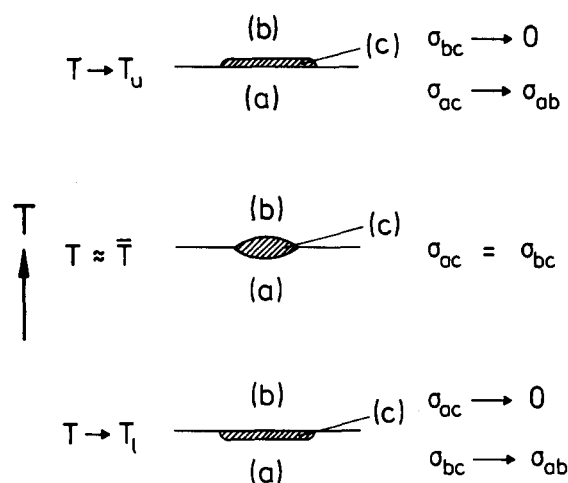


FIG. 9. Change of shape of the lens of the amphiphile-rich phase (c) with rising temperature (schematic).

ture after each change of temperature. Experience shows that diffusion is much too slow for attaining equilibrium so that such mixtures have to be stirred at each temperature of experiment. By doing so we were able to detect a lens up to about 55 °C. At higher temperatures it becomes increasingly difficult to detect because phase (c) wets glass better than the other two phases do so that phase (c) tends to form a ring along the glass walls rather than a lens in the center. This suggested studying the wetting approaching the lower temperature T_l (20 °C). Here the lens can be readily observed down to temperatures very close to T_l , with α and γ approaching $\pi/2$. Replacing hexadecane by decane makes the three-phase temperature interval drop to 5–23 °C. In this mixture the lens can be readily observed even when approaching T_u , with β and γ approaching $\pi/2$.

We then repeated our earlier experiments with C_4E_1 . With decane as oil, the mean temperature \bar{T} of the three-phase body lies at about 40 °C. In this mixture the amphiphile-rich phase (c) appears to spread across the a/b interface in the entire temperature interval between T_l and T_u . With octane as oil, however, \bar{T} drops to about 20 °C. In this mixture, phase (c) shapes a lens close to the mean temperature. Whether or not phase (c) spreads across the a/b interface close to the critical endpoints, is difficult to observe because even at the mean temperature, the lens is very flat indicating w_σ to be close to -1 .

If one applies very weak surfactants such as short-chain alcohols, phase (c) spreads across the a/b interface even at ambient temperatures.¹⁰ These findings indicate that with short-chain amphiphiles, the wetting behavior may change from case (ii) at ambient temperatures to case (i) at elevated temperatures which again could be understood by assuming the rather weak hydrophilic interaction between one or two $O(CH_2)_2$ groups and H_2O to decrease rapidly with rising temperature.

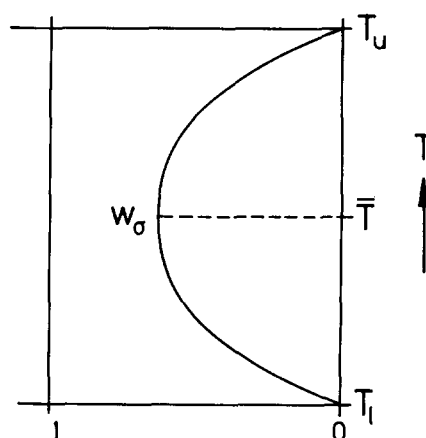


FIG. 10. Wetting coefficient in a three-phase body (with medium- and long-chain amphiphiles) vs temperature (schematic).

IV. CONCLUSION

In the three-phase temperature interval of ternary H_2O –oil–nonionic amphiphile mixtures with medium- and long-chain amphiphiles, a drop of the (middle) amphiphile-rich phase does not spread across the H_2O –oil interface but shapes a lens. This behavior is not a particular property of microemulsions but exhibits itself already in oil-free binary H_2O –amphiphile mixtures in which the (upper) amphiphile-rich phase does not spread across the H_2O –air interface. The wetting behavior differs insofar as in the binary mixtures one may observe a nonwetting–wetting transition as one approaches the upper critical point of the upper closed miscibility gap, whereas in the ternary mixtures the lens apparently continues to exist as one approaches either one of the two critical endpoints.

¹J. W. Cahn, *J. Chem. Phys.* **66**, 3667 (1977).

²See for comparison Fig. 8.10. (also due to J. W. Cahn) in J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford 1982), p. 229.

³M. Kahlweit, G. Busse, D. Haase, and J. Jen, *Phys. Rev. A* **38**, 1395 (1988).

⁴See, e.g., N. Nagarajan, W. W. Webb, and B. Widom, *J. Chem. Phys.* **77**, 5771 (1982).

⁵E. G. Carter and D. C. Jones, *Trans. Faraday Soc.* **30**, 1027 (1934).

⁶See, e.g., S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1988), Vol. 12, p. 1.

⁷See Fig. 4 in M. Kahlweit, R. Strey, D. Haase, and P. Firman, *Langmuir* **4**, 785 (1988).

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