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Wetting in water–oil–nonionic amphiphile mixtures

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In a three-phase equilibrium of H_2O–oil–amphiphile mixtures, the middle amphiphile rich phase may or may not wet the water/oil interface. For nonwetting middle phases, theory predicts a nonwetting→wetting transition upon approaching either one of the two critical endpoints. With respect to an experimental confirmation of this prediction, the situation appears to be controversial. In this paper, we have, therefore, studied the wetting behavior of the middle phase as it depends on the amphiphilicity of nonionic amphiphiles. We find that in mixtures with short-chain amphiphiles, the middle phase wets the water/oil interface in the entire three-phase interval, whereas with long-chain amphiphiles it (apparently) never wets. For medium-chain amphiphiles, however, one does find a nonwetting→wetting transition. On the basis of this result, we suggest that there exist four cases for the wetting behavior as a consequence of the dependence of the relations between the three interfacial tensions on amphiphilicity. The wetting behavior can be correlated with the evolution of the three-phase bodies from a tricritical point. Upon increasing amphiphilicity, their characteristic properties pass through maxima in the range of medium-chain amphiphiles, coinciding with the transition from always wetting to never wetting.

I. INTRODUCTION

Consider ternary mixtures of water (A), an oil (B), and a nonionic amphiphile (C), with n-alkyl polyglycolethers C_iE_j as nonionic amphiphiles. Within a well-defined temperature interval ΔT, such mixtures may separate into three coexisting liquid phases, namely a lower aqueous phase (a), a middle amphiphile-rich phase (c), and an upper oil-rich phase (b).[1] The evolution of the three-phase triangle with rising temperature is shown schematically in Fig. 1. At ambient temperatures, the mixture separates into two phases with the amphiphile dissolved mainly in the lower water-rich phase (2). As one raises T, the lower phase separates at T_l at a critical endpoint into phase (a) and (c). With further rising T, phase (c) moves on an ascending trajectory around the binodal surface to the oil-rich side where it merges at T_u at a critical endpoint with phase (b). For $T > T_u$, the mixture separates into two phases with the amphiphile mainly dissolved in the upper oil-rich phase ($\bar{2}$).

Consider now the dependence of the three corresponding interfacial tensions σ_{ac}, σ_{bc}, and σ_{ab} on temperature (Fig. 2). Phases (a) and (c) separate at T_l at the critical endpoint cep_β. σ_{ac} must, therefore, rise from zero at T_l to increase monotonically with rising T. Phases (b) and (c) merge at T_u at the critical endpoint cep_α; σ_{bc} must, therefore, decrease monotonically with rising T to vanish at T_u. Thermodynamic stability requires

$$0 < \sigma_{ab} \leqslant \sigma_{ac} + \sigma_{bc}. \qquad (1.1)$$

Because σ_{ac} and σ_{bc} are monotonic functions of T with reverse temperature dependence, σ_{ab} must show a minimum close to the mean temperature

$$\bar{T} \equiv (T_l + T_u)/2 \qquad (1.2)$$

of the three-phase temperature interval

$$\Delta T \equiv T_u - T_l. \qquad (1.3)$$

The minimum of σ_{ab} close to $\bar{T}$ is thus the consequence of the nearness of two critical endpoints.

If in Eq. (1.1) the equality on the right-hand side holds, the middle phase (c) wets the a/b interface, whereas if the inequality holds, it does not. Whether or not the middle phase wets the interface can be readily demonstrated experimentally by reducing its volume (at $\bar{T}$) to a drop. If phase (c) does not wet, the drop will contract to a lens floating at the a/b interface. If it wets, it will spread across the a/b interface.

Experiment now shows that in ternary H_2O–oil–C_iE_j mixtures such with short-chain amphiphiles ($i < 4$), the middle phase (c) wets the a/b interface in the entire three-phase interval ΔT, whereas with medium- and long-chain amphiphiles ($i > 5$), it does not wet the interface at $\bar{T}$. Theory[2] now predicts that in the latter mixtures, one should find a nonwetting→wetting transition as one approaches either one of the critical endpoints, i.e., as one approaches either T_l or T_u. In an earlier paper,[3] we have, therefore, studied mixtures with various oils and long-chain amphiphiles, but were not able to detect such a transition. Robert and co-workers,[4] as well as Smith and Covatch,[5] on the other hand, have reported experiments on H_2O–n-hexadecane–C_6E_2 mixtures in which they claimed to have found a nonwetting→wetting transition well below T_u. In order to clarify this discrepancy, we have repeated the experiments with n-octane, increasing the amphiphilicity from C_4E_1 to C_8E_4.

II. THE WETTING BEHAVIOR

For further discussion, consider the approach to T_u from below. Because phases (b) and (c) merge at T_u,

nonionic
amphiphile

$T = T_u$

cep$_\alpha$

H$_2$O C oil

A C B

T

A C B

A amphiphile B

$T = T_l$

cep$_\beta$

H$_2$O oil

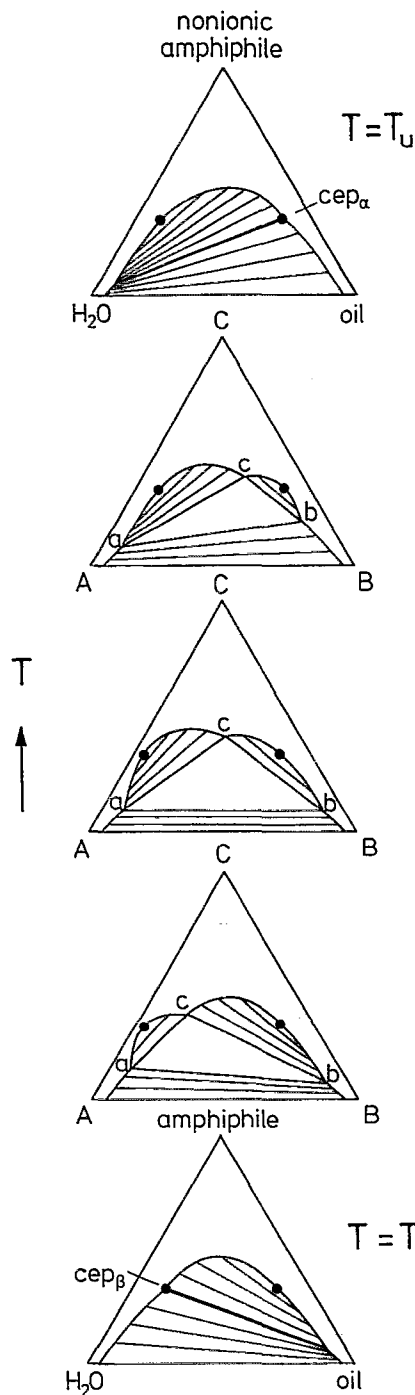FIG. 1. Evolution of the three-phase triangle in a mixture of H$_2$O–oil–non-ionic amphiphile with rising temperature (schematic).

$$\lim_{T = T_u} \sigma_{bc} = 0, \qquad (2.1a)$$

and

$$\lim_{T = T_u} \Delta\sigma = 0, \quad \text{where } \Delta\sigma \equiv \sigma_{ac} - \sigma_{ab}. \qquad (2.1b)$$

For the lens to be stable, each of the interfacial tensions must be lower than the sum of the other two. This implies, in particular, for σ_{ab} and σ_{ac},

H$_2$O - oil - nonionic amphiphile

(b)

b
c
a

θ_b θ_c (c)
θ_a

(a)

T_u

T

σ_{bc}

σ_{ab} $\sigma_{ac} + \sigma_{bc}$

σ_{ac}

T_l

0 σ

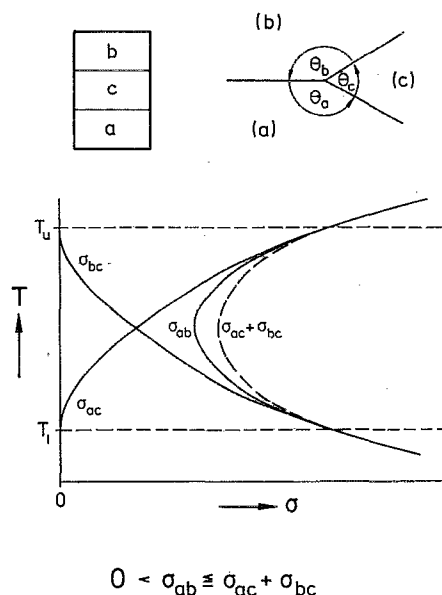$$0 < \sigma_{ab} \lesssim \sigma_{ac} + \sigma_{bc}$$

FIG. 2. Temperature dependence of the interfacial tensions σ_{ij} among the three liquid phases (schematic). For reasons of simplicity, we assumed the curves to be symmetric.

$$\sigma_{ab} < \sigma_{ac} + \sigma_{bc} \quad \text{and} \quad \sigma_{ac} < \sigma_{ab} + \sigma_{bc}. \qquad (2.2)$$

These two inequalities can be combined into

$$\sigma_{ac} - \sigma_{bc} < \sigma_{ab} < \sigma_{ac} + \sigma_{bc}, \qquad (2.3)$$

which permits that for $\overline{T} < T < T_u$, $\Delta\sigma$ may be either negative or positive. From the first of the two inequalities (2.2), it furthermore follows that the stability of the lens requires

$$\Sigma \equiv \Delta\sigma + \sigma_{bc} > 0 \qquad (2.4)$$

to be always positive, irrespective of the sign of $\Delta\sigma$.

With respect to the existence of a nonwetting → wetting transition, it will be shown in the experimental part of this paper that with long-chain amphiphiles ($i \gtrsim 8$), we were not

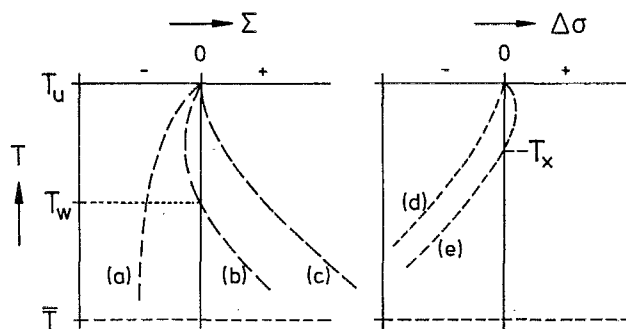$\longrightarrow \Sigma$

$\longrightarrow \Delta\sigma$

0

0

T_u $-$ $+$ $-$ $+$

T

T_w

$-T_x$

(a) (b) (c) (d)

(e)

$\overline{T}$

FIG. 3. (Left) temperature dependence of Σ [Eq. 2.4]; (right) temperature dependence of $\Delta\sigma$ [Eq. 2.1b] upon approaching T_u (schematic). For a discussion, see the text.

able to find such a transition, whereas with medium-chain amphiphiles $(4 < i < 8)$, one may observe such a transition at some temperature $T_w < T_u$.

There thus exist apparently three cases for the temperature dependence of Σ as defined by Eq. (2.4). They are shown schematically on the left-hand side of Fig. 3. In case 3(a), Σ is always negative, i.e., the middle phase wets the a/b interface in the entire interval $\overline{T} < T < T_u$. In case 3(b), Σ is positive at $\overline{T}$, but changes sign at some temperature $T_w < T_u$, i.e., one finds a nonwetting→wetting transition at T_w. In case 3(c), Σ is always positive, i.e., the middle phase never wets.

Consider now the sign of $\Delta\sigma$. In view of Fig. 2, one would intuitively expect σ_{ab} always to be higher than σ_{ac}, i.e., $\Delta\sigma$ always to be negative. Experiment, however, shows that this may not be so. At zero gravity, one has

$$\cos\Theta_c = [(\sigma_{ab})^2 - (\sigma_{ac})^2 - (\sigma_{bc})^2]/(2\sigma_{ac}\sigma_{bc}), \quad (2.5)$$

where Θ_c is defined on the upper right of Fig. 2. Because of $(\sigma_{ab})^2 - (\sigma_{ac})^2 = (\sigma_{ab} + \sigma_{ac})(-\Delta\sigma)$, it can be written as

$$[2\sigma_{ac}\sigma_{bc}/(\sigma_{ab} + \sigma_{ac})]\cos\Theta_c$$
$$= -\Delta\sigma - [(\sigma_{bc})^2/(\sigma_{ab} + \sigma_{ac})], \quad (2.6)$$

where the term in parentheses on the left, as well as the second term on the right are always positive.

As long as $0 < \Theta_c < \pi/2$, it follows from Eq. (2.6) that for

$$\cos\Theta_c > 0, \quad \Delta\sigma < -(\sigma_{bc})^2/(\sigma_{ab} + \sigma_{ac}) < 0. \quad (2.7)$$

Experiment now shows that Θ_c may become larger than $\pi/2$. This, however, does not prove $\Delta\sigma > 0$, because in the case of $\Delta\sigma = 0$, one has from Eq. (2.6)

$$\cos\Theta_c = -\sigma_{bc}/2\sigma_{ac} < 0$$

which shows that Θ_c may exceed $\pi/2$ for $\Delta\sigma \lesssim 0$.

The experimental difficulties in determining both the interfacial tensions and the angles do not allow precisely a conclusive decision whether or not $\Delta\sigma$ may actually become positive in some cases. Very close to T_u, however, one may make use of the relation

$$0 = \sigma_{ac} + \sigma_{ab}\cos\Theta_a + \sigma_{bc}\cos\Theta_c. \quad (2.8)$$

Because the densities of the two upper near-critical phases (b) and (c) approach each other, whereas the density difference between both of them and the lower aqueous phase (a) remains finite, the effect of gravity enforces a practically planar surface of the lower phase, so that $\Theta_a \approx \pi$ and Eq. (2.8) may be approximated by Young's equation

$$\cos\Theta_c \approx -\Delta\sigma/\sigma_{bc}. \quad (2.9)$$

Because with long-chain amphiphiles one observes $\cos\Theta_c$ to be distinctly negative near T_u (see Fig. 5), we cannot exclude that in Fig. 2 σ_{ac} may overshoot σ_{ab} slightly upon approaching T_u, i.e.,

$$\sigma_{ab} < \sigma_{ac} < \sigma_{ab} + \sigma_{bc}, \quad \text{for } T_x < T < T_u. \quad (2.10)$$

In that case, there would exist two cases for the temperature dependence of $\Delta\sigma$ as shown schematically on the right of Fig. 3. In case 3(d), $\Delta\sigma$ is always negative, whereas in case 3(e), it changes sign at some temperature $T_x < T_u$.

From these considerations, we deduce that there may exist four cases in the wetting behavior of the middle phase. These are shown schematically in Fig. 4 in which we have plotted both Σ and $\Delta\sigma$ vs T, observing that Eqs. (2.3) and (2.4) require that always $\Sigma > \Delta\sigma$.

Case (i). For weak amphiphiles $(i \lesssim 4)$, both Σ and $\Delta\sigma$ are always negative. The middle phase wets the a/b interface in the entire interval $\overline{T} < T < T_u$.

With increasing amphiphilicity, both Σ and $\Delta\sigma$ increase gradually, with zero at $T = T_u$ as the pivot point.

Case (ii). $\Delta\sigma$ remains negative, but Σ becomes positive at $\overline{T} < T_w < T_u$. The middle phase does not wet at $T = \overline{T}$, but shows a nonwetting→wetting transition at $T = T_w$.

Case (iii). $\Delta\sigma$ remains negative, but Σ is now always positive. The middle phase never wets. This, however, does not exclude that Θ_c may become slightly larger than $\pi/2$ for $T \to T_u$.

Case (iv). $\Delta\sigma$ becomes positive at $T_x < T_u$. The middle phase never wets, but Θ_c becomes considerably larger than $\pi/2$ for $T \to T_u$ before it approaches $\pi/2$ at $T = T_u$.

Equivalent considerations hold if T_l is approached from above.

III. EXPERIMENT

The mixtures were filled into an optical quartz cuvette of 1 mm thickness, and placed in a water thermostat with glass walls. Thermal equilibrium was established by shaking the cuvettes within the water bath by means of a specially constructed holder. After equilibrium was reached, the middle phase was removed carefully by means of a pipette until only a tiny drop of it was left. The drop was observed through a horizontally mounted stereo microscope by
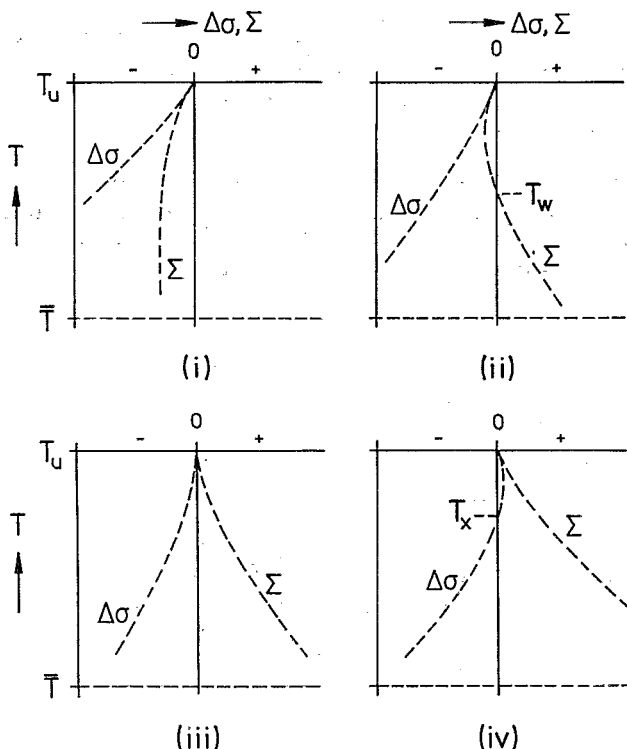

FIG. 4. Temperature dependence of Σ and $\Delta\sigma$ as it changes with increasing amphiphilicity (schematic). For a discussion, see the text.
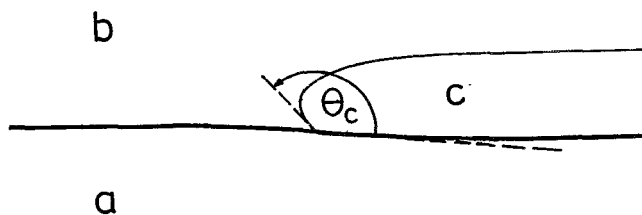
FIG. 5. H_2O–octane–C_8E_4: profile of a lens of the middle phase (c) at 1.2 °C below T_u (copied from a photograph).
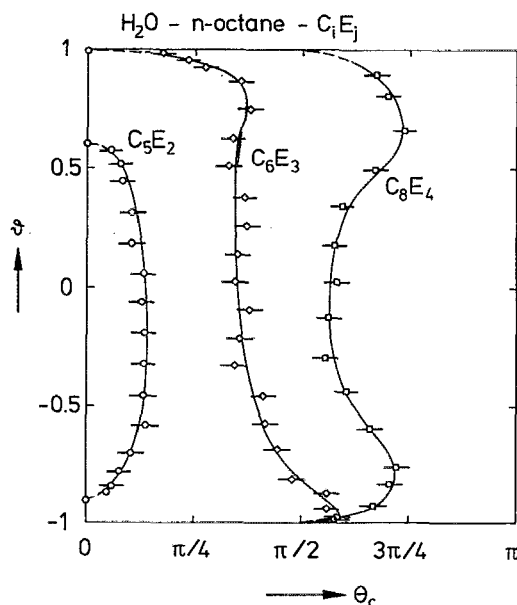

FIG. 6. H_2O–octane–C_iE_j: temperature dependence of the contact angle Θ_c (see Fig. 2) as it changes with increasing amphiphilicity. For a discussion, see the text.

means of a color video camera (SONY DXC-102 P), connected to a color video monitor (SONY PVM-2010 QM). The contact angle Θ_c was determined graphically from photographs taken from the monitor by means of a video graphic printer (SONY UP-811). Because these photographs are difficult to reproduce, we have copied a representative example as drawing in Fig. 5 showing the projection of a lens of the H_2O–octane–C_8E_4 mixture at $T = 46.97$ °C, i.e., 1.23 °C below T_u, with Θ_c distinctly larger than $\pi/2$.

We then studied the mixtures H_2O–n-octane–C_iE_j with C_4E_1, C_5E_2, C_6E_3, and C_8E_4. Figure 6 shows the contact angle Θ_c vs ϑ, where

$$\vartheta \equiv 2(T - \overline{T})/\Delta T, \quad -1 < \vartheta < +1. \quad (3.1)$$

The inevitable errors in determining Θ_c are indicated by the horizontal bars. The corresponding data for the four mixtures are summarized in Table I.

The result can be interpreted as follows:

C_4E_1 (not shown in Fig. 6) is a short-chain amphiphile corresponding to case (i) in Fig. 4. The middle wets the a/b interface in the entire three-phase temperature interval, i.e., $\Theta_c = 0$ for $T_l < T < T_u$.

C_5E_2 is a medium-chain amphiphile corresponding to case (ii) in Fig. 4. The middle phase does not wet at $\overline{T}$, but shows nonwetting → wetting transitions at $T_l < T_{wl} < \overline{T}$ and $\overline{T} < T_{wu} < T_u$.

C_6E_3 appears to lie on the borderline between cases (ii) and (iii). Θ_c ($T = \overline{T}$) is considerably larger than for C_5E_2. Upon approaching T_u, it passes a maximum before it drops to zero at $T = T_{wu}$ (case ii). Upon approaching T_l, however, Θ_c slightly exceeds $\pi/2$ before it appears to drop to $\pi/2$ at $T = T_l$ [case (iii)].

C_8E_4 is a long-chain amphiphile corresponding to case (iv) in Fig. 4. The middle phase apparently never wets the a/b interface. Θ_c is larger then $\pi/2$ at $T = \overline{T}$ and passes

maxima before it approaches $\pi/2$ for $T \rightarrow T_l$, and $T \rightarrow T_u$, respectively.

We emphasize, however, that we cannot exclude that in those experiments in which Θ_c appears to approach $\pi/2$ at T_u or T_l, respectively, it may actually drop to zero very close to $\vartheta = \pm 1$, although we have not found any indication that could support such a conclusion. If for long-chain amphiphiles nonwetting → wetting transitions actually exist very close to T_l and T_u, respectively, they must occur at temperatures that lie within the very narrow thermal fluctuations of the thermostat.

In this context, we recall that the nonwetting of the polar/nonpolar interface by an amphiphile-rich phase is not a particular property of water/oil interfaces, but can be traced from the binary H_2O–C_iE_j mixture through the adjacent two-phase region (both with air as the "nonpolar" phase) into the three-phase triangle (Fig. 11 in Ref. 1).

We furthermore note that in mixtures with oils of higher carbon numbers than octane, the observation of the contact angles, in particular, close to T_l becomes difficult because of the wetting of the glass walls by the aqueous phase.

TABLE I. H_2O–n-octane–C_iE_j.

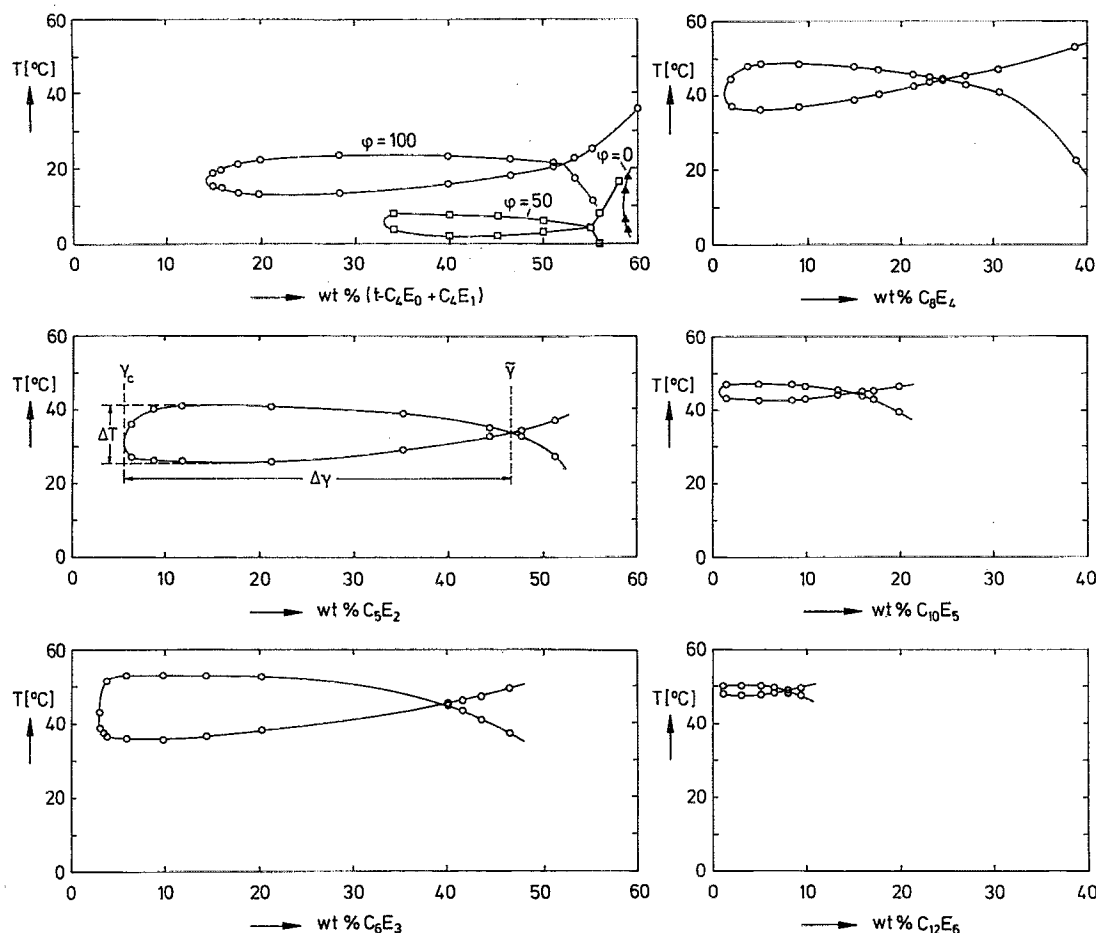| C_iE_j	T_l (°C)	T_u (°C)	$\overline{T}$ (°C)	ΔT	$\Delta\gamma$ (wt.%)	σ_{ab} (mN m^{-1})
C_4E_1	12.9	23.9	18.4	11.0	37.5	0.38
C_5E_2	25.8	41.3	33.6	15.5	40.8	0.36
C_6E_3	35.5	52.1	43.8	16.6	36.6	0.15
C_8E_4	35.5	48.2	41.8	12.7	22.7	0.04

FIG. 7. Transition from weakly to strongly structured H_2O–octane–C_iE_j mixtures by stepwise increasing the amphiphilicity of C_iE_j from t-C_4E_0 (top left) to $C_{12}E_6$ (bottom right). For a detailed discussion, see the text.

IV. TRANSITION FROM WEAKLY TO STRONGLY STRUCTURED SOLUTIONS

On the basis of the above results, we propose the following sequence for the evolution of a strongly structured H_2O–oil–C_iE_j mixture (microemulsion) for fixed oil with increasing amphiphilicity of C_iE_j: We start with tertiary butanol (t-C_4E_0). H_2O–octane–t-C_4E_0 mixtures do not separate into three phases, but shows instead a $2 \to \bar{2}$ transition with rising temperature. Consequently, the (connected) critical line changes from the oil-rich side to the water-rich side of the phase prism at some temperature $\tilde{T}$ (Fig. 7, top left, $\varphi = 0$ wt.%). This critical line can be looked upon as an elastic spring. As one increases the amphiphilicity by adding C_4E_1, the "bending tension" of the critical line increases, i.e., the tangent at its inflection point at $\tilde{T}$ becomes increasingly horizontal until it eventually breaks at a tricritical point (tcp).[6] At this point, the homogeneous solution separates into the three coexisting phases (a), (b), and (c). The characteristic properties of the three-phase body, i.e., its three-phase temperature interval ΔT, the height h of the isosceles three-phase triangle (at $\bar{T}$), and the interfacial tension σ_{ab} [measured by means of a spinning-drop apparatus at the a–b side

of the isosceles triangle at $\bar{T}$ (Fig. 1)] rise from zero to increase rapidly with increasing mass fraction φ (in wt.%) of C_4E_1 in the mixture of the two amphiphiles, with the middle phase (c) wetting the a/b interface. Because the exact determination of the height h of the isosceles triangle at $\bar{T}$ requires some effort, we took the difference

$$\Delta\gamma \equiv \tilde{\gamma} - \gamma_c \lesssim h \qquad (4.1)$$

as a measure for h. Here γ_c and $\tilde{\gamma}$ stand for the mass fraction of the amphiphile (in wt.%) at the "head" and the "tail" of the "fish," respectively (measured at equal volumes of water and oil). At first $\tilde{\gamma}$ decreases only little, whereas γ_c decreases rapidly as can be seen from the fish measured with equal masses of t-C_4E_0 and C_4E_1 ($\varphi = 50$ wt.%). Finally, the three-phase body for pure C_4E_1 is reached ($\varphi = 100$ wt.%), its data being given in Table I.

If one continues increasing the effective amphiphilicity by adding C_5E_2 to C_4E_1, both ΔT and $\Delta\gamma$ increase further, whereas σ_{ab} passes its maximum. After having passed the three-phase body for pure C_5E_2 (Fig. 7, center left), one adds C_6E_3. This makes $\tilde{\gamma}$ decrease more rapidly than γ_c, so that now $\Delta\gamma$ passes its maximum, whereas ΔT increases slightly further. Near pure C_6E_3 (Fig. 7, bottom left), ΔT,
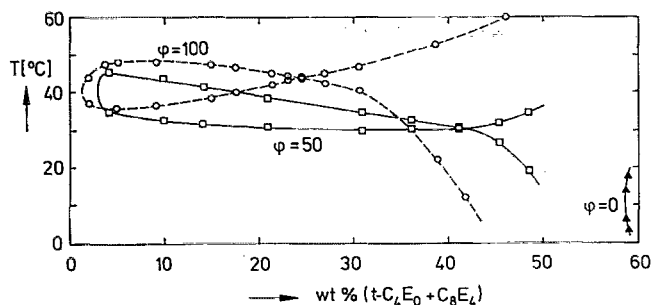
FIG. 8. Evolution of the three-phase body upon adding C_8E_4 to a H_2O–octane–t-C_4E_0 mixture. For a discussion, see the text.

too, passes its maximum so that from then on all the three quantities decrease upon further increasing amphiphilicity as shown on the right of Fig. 7, with σ_{ab} decreasing from C_8E_4 to $C_{12}E_6$ by about one order of magnitude.

A similar dependence of ΔT, $\Delta\gamma$, and σ_{ab} is observed as one increases the effective amphiphilicity by adding C_8E_4 directly to t-C_4E_0, i.e., omitting the intermediate medium-chain amphiphiles. Figure 8 shows the section for pure t-C_4E_0 (being identical with that on the upper left of Fig. 7, $\varphi = 0$ wt.%), the one for equal masses of t-C_4E_0 and C_8E_4 ($\varphi = 50$ wt.%), and that for pure C_8E_4 (being identical with that on the upper right of Fig. 7). Again one observes the extensions of the three-phase body to pass through a maximum upon increasing amphiphilicity. In this case, however, the quaternary mixture deviates rather strongly from a pseudoternary mixture as one deduces from the inclination of the fish. The reverse is, evidently, observed if one starts with a long-chain amphiphile and adds a short-chain amphiphile in order to reach a tcp. The (small) three-phase body of the strongly structured solution will not shrink monotonically, but first grow and pass through a maximum before it finally collapses into the tcp.

V. CONCLUSION

Ternary H_2O–oil–nonionic amphiphile mixtures with weak short-chain amphiphiles separate in two liquid phases. As the amphiphilicity is increased gradually, the mixture will separate into three phases at a tcp. The three characteristic properties of the three-phase body ΔT, $\Delta\gamma$ ($\hat{=}h$), as well as σ_{ab} rise from zero to increase rapidly. As one passes through the range of medium-chain amphiphiles, the three properties pass through maxima to decrease upon further increasing amphiphilicity. The maxima appear to coincide with the transition from wetting to nonwetting middle phases. While with short-chain amphiphiles, the amphiphile-rich middle phase always wets the water/oil interface, one finds nonwetting→wetting transitions with medium-chain amphiphiles, but (apparently) always nonwetting with long-chain amphiphiles. In view of Widoms[2] suggestion that the transition from weakly to strongly structured solutions be identified with the wetting→nonwetting transition, this suggests that this transition may be identified alternatively with that region in which the three properties pass their maxima. With respect to the theoretical description of the phase behavior, we accordingly expect that the initial stages can be described by the scaling laws for (weakly structured) near-tricritical mixtures, whereas in describing the later stages, the strong adsorption of the amphiphiles at the water/oil interface has to be considered.[7] The transition from the first to the second description lies in that range in which the properties of the three-phase bodies pass through their maxima.

ACKNOWLEDGMENTS

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[2] See, e.g., B. Widom, Langmuir 3, 12 (1987).
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