Tricritical Points and Wetting → Nonwetting Transitions in Nonionic Microemulsions

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Proceeding in a homologous series of oils and nonionic amphiphiles, we study the dependence of the coordinates of tricritical points and wetting → nonwetting transitions on the carbon number of the oils, and the strength of the amphiphiles. We find an inverse relation in that weakly nonpolar oils require strong amphiphiles for to be emulsified, whereas for emulsifying strongly nonpolar oils, weak amphiphiles suffice. The results are discussed qualitatively on the basis of a simple model inspired by Harkins.

Introduction

The phase behavior of ternary H_2O (A)−oil (B)−nonionic amphiphile (C) mixtures is now phenomenologically rather well understood:[1] The highest chance for finding a microemulsion in such mixtures is within that temperature interval ΔT in which the mixtures separate into three coexisting liquid phases, namely, an amphiphile-rich middle phase (c) in equilibrium with a water-rich (a) and an oil-rich (b) excess phase, the reason being that the interfacial tension σ_{ab} between the two excess phases passes a deep minimum at the mean temperature T_m of ΔT. The three-phase body evolves from a tricritical point (tcp).[2] If one starts with medium-chain *n*-alkanes and short-chain *n*-alkyl polyglycol ethers (C_iE_j), the mixtures separate into two liquid phases only. Upon gradually increasing either the carbon number k of the oil at fixed $H(i,j)$, or (i,j) at fixed k, one observes that the critical line that winds around the two-phase body will eventually break at a tricritical point (tcp) at which the mixtures separate into three coexisting liquid phases. In ternary mixtures, a tcp represents a point on the binodal surface of the two-phase body, being defined by four coordinates: T, p, and two composition variables. When searching for a tcp in a ternary mixture at atmospheric pressure it would, therefore, be purely accidental to find the tcp at either an integer k, or an integer (i,j), so that, for finding a tcp at fixed pressure, one has to proceed to quaternary mixtures by mixing either two oils of successive k or two amphiphiles of successive (i,j). At atmospheric pressure, the coordinates of a tcp are then defined by T and three composition variables. The proper procedure for locating the tcp and studying the evolution of the three phase body is, thus, to study the phase diagrams in phase tetrahedra at various T. Because this is a rather tedious procedure, we have restricted ourselves to erecting vertical sections through pseudoternary phase prisms with mixtures of oils or amphiphiles of successive integer k or (i,j), respectively. The result of such an experiment is shown in Figure 7 in ref 2, performed with mixtures of *n*-alkanes and tertiary butanol, *tert*-C_4E_0, as (very weak) amphiphile, with the tcp lying between decane and dodecane at $T_{tcp} \approx 45$ °C.

The sections through the three-phase bodies at equal masses of water and oil—having the shape of a "fish"—may be characterized by four properties, namely T_m, ΔT, the mass fraction γ_m of the amphiphile at the "tail" of the fish, and γ_0 at its "head". The fifth characteristic property, i.e., the interfacial tension σ_{ab}, has to be determined by an independent measure-ment. In this particular experiment, in which k was increased at fixed (i,j), T_m rises monotonically from T_{tcp} upon increasing k, whereas the other properties of the fish, i.e., ΔT, $\sigma_m \equiv \sigma_{ab}(T = T_m)$, and the length $\Delta\gamma = \gamma_m - \gamma_0$ of the fish, increase monotonically from zero at the tcp, with γ_0 moving to lower and γ_m to higher mass fractions. The latter fact indicates that the efficiency of the amphiphile in emulsifying water and oil decreases upon increasing k as one would expect. In a subsequent experiment,[3] we increased (i,j) at fixed k, using *n*-octane and the amphiphile series *tert*-C_4E_0, C_4E_1, C_5E_2, C_6E_3, C_8E_4, $C_{10}E_5$, $C_{12}E_6$. The H_2O−octane−*tert*-C_4E_0 mixture sepa-rates into two phases only. However, as one proceeds to the slightly more amphiphilic C_4E_1, the mixture passes a tcp. Experience tells that if one uses C_iE_j in the sequence $(i,j) \rightarrow (i + 2, j + 1)$ at fixed k, T_m varies only little. As to the other properties of the fish, one observes the following: ΔT, σ_m, and $\Delta\gamma$ again first increase from zero at the tcp, but then pass a maximum to decrease with further increasing (i,j), with γ_m moving gradually to lower mass fractions which indicates that the efficiency of the amphiphiles increases upon increasing (i,j) as one again would expect. It was these two experiments which made us suggest Figure 8 in ref 4 as a schematic representation of the evolution of three-phase bodies from tcp's.

Theory predicts that near-tricritical mixtures are weakly structured. This raises the question as to how to detect the transition from weakly structured mixtures to microemulsions. Experiments show that there exist a number of properties which evolve gradually upon increasing the strength of the amphiphiles, and which permit to distinguish experimentally between weakly and strongly structured mixtures. One of them is the gradual movement of the peak in small-angle scattering experiments off its position at zero wavevector in weakly structured mixtures to nonzero wavevector in more strongly structured ones.[5] In 1987, Widom[6] suggested that the progression from weakly to strongly structured mixtures may also be reflected in the wetting vs nonwetting of the oil−water interface by the middle phase, a presumption that was substantiated theoretically by Gompper and Schick.[7] In weakly structured mixtures, the middle phase (c) always wets the interface between the two excess phases (a) and (b), whereas in strongly structured mixtures, σ_m is lower than the sum of σ_{ac} and σ_{bc}, so that the system, when minimizing its interfacial free energy, tends to extrude phase (c) from the a/b interface, provided gravity permits. Hence, if the effect of gravity is reduced by reducing the mass of the middle phase

(c) at T_m until only a drop of it is left, this will contract to a lens floating at the interface between the two excess phases. Because the wetting behavior of the middle phase is experimentally rather easy to detect, we shall, in this paper, take this wetting → nonwetting (w/nw) transition as an indication for having passed the borderline between weakly structured mixtures and microemulsions.

In the first of the two experiments, in which k was increased at fixed (i,j), one cannot expect a (w/nw) transition because *tert*-C_4E_0 is a much too weak amphiphile. In the second experiment, however, in which the strength of the amphiphiles (i,j) was increased at fixed k, we did find the transition between C_4E_1 and C_5E_2[3] which demonstrates that for preparing microemulsions with strongly nonpolar oils, rather weak medium-chain amphiphiles suffice. This raises the question as to how to prepare microemulsions with weakly nonpolar oils. This problem was studied by Wormuth and Kaler[8] who used "polar" ether oils, $C_kOC_2OC_k$, and found that they had to apply the rather strong $C_{12}E_6$ to pass a tcp between $k = 2$ and $k = 3$ at about 10 °C (their Figure 4). From SAXS experiments they, furthermore, deduced that the mixtures became increasingly more structured as they increased k to 4 (their Figure 6). When supplementing their experiments by studying the wetting behavior, we found that with $k = 4$, the middle phase indeed does not wet. Hence, if one accepts the criterion suggested by Widom, one can prepare microemulsion with weakly nonpolar oil if one applies sufficiently strong amphiphiles.[9] As to the other properties of the three-phase body, they behave as in the first experiment described above, namely, ΔT and $\Delta \gamma$ increase monotonically, as does γ_m.

A (w/nw) transition requires

$$\sigma_{ab} = \sigma_{ac} + \sigma_{bc} \rightarrow \sigma_{ab} < \sigma_{ac} + \sigma_{bc} \qquad \text{at } T = T_m \quad (1)$$

Experiments show that, at fixed (i,j), $\sigma_m \equiv \sigma_{ab}(T=T_m)$ rises with increasing k.[10] Thus, if one nevertheless finds a (w/nw) transition upon increasing k, one is forced to deduce that the sum of the two interfacial tensions between the middle phase and the two excess phases must rise more strongly upon increasing k than σ_m so that, not necessarily at an integer carbon number, their sum eventually exceeds the interfacial tension between the two excess phases which makes the a/b interface become thermodynamically stable. This is, at first sight, somewhat surprising because one would intuitively expect that if γ_m increases, that is, if the efficiency of the amphiphile in emulsifying water and oil decreases upon increasing k, the chance for preparing a microemulsion should decrease too.

From these experiments we deduce the following: if (i,j) is increased at fixed k, the strength (i,j) of the amphiphile must exceed a certain limit for the mixture to pass a tcp, and then, upon further increasing (i,j), a (w/nw) transition. If, on the other hand, the carbon number k of the oils is increased at fixed (i,j), k must exceed a certain limit for the mixture to pass a tcp, and then, upon further increasing k, a (w/nw) transition. In other words, with respect to the coordinates of the tcp's and those of the (w/nw) transitions there appears to exist an inverse relation between the carbon number k of the oil and the strength (i,j) of the amphiphile.

Weakly nonpolar oils require strong amphiphiles for to be emulsified, whereas for emulsifying strongly nonpolar oils, weak amphiphiles suffice. In this paper we shall study this relation in some more detail by determining the coordinates of the tcp's and those of the (w/nw) transitions as they depend on i, j, and k, by increasing both (i,j) and k in a homologous series.
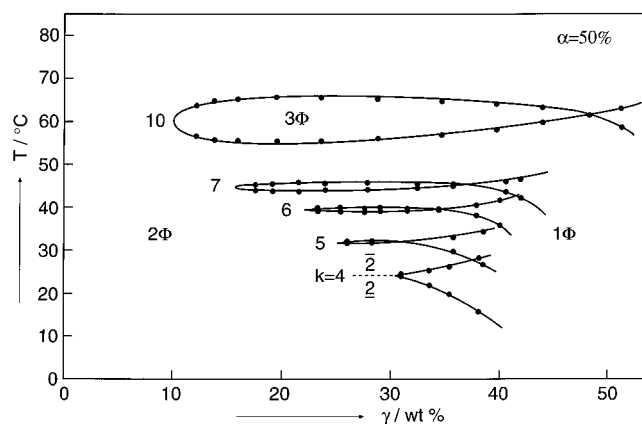

Figure 1. Vertical sections through the phase prisms of H_2O-alkylbenzene (k)$-C_5E_3$ mixtures at equal masses of water and oil. The tricritical point (tcp) is passed between $k = 4$ (butylbenzene) and $k = 5$ (pentylbenzene). In all mixtures with $k \geq 5$, the middle phase wets the water/oil interface.

Experiments

Because the series of *n*-alkanes does not permit to lower their carbon number below $k = 6$, because of the low boiling points of short-chain alkanes, we have chosen the series of alkylbenzenes (phenylalkanes), $(C_6H_5)(CH_2)_kH$, increasing the carbon number k of the alkane group from $k = 0$ (benzene) to $k = 12$ (dodecylbenzene), and increasing the strength (i,j) of the amphiphiles from short-chain to long-chain C_iE_j. The hydrocarbons were purchased from Aldrich and Fluka and used as delivered. The wetting behavior (at $T = T_m$) was observed as described previously.[11] In an earlier experiment,[12] we had already searched for a tcp with alkylbenzenes and C_4E_2 and found the tcp to lie between $k = 6$ (hexylbenzene) and $k = 7$ (heptylbenzene) at about 50 °C. As an example, Figure 1 shows the results for alkylbenzenes and C_5E_3. At equal masses of water and oil (!), the mixture with $k = 4$ (butylbenzene) separates into two phases only, whereas with $k = 5$ (pentylbenzene) one finds three phases. From this we deduce that the tcp lies between $k = 4$ and $k = 5$. Because tcp's will, in general, not lie at equal masses of water and oil, we cannot exclude that the tcp actually lies a little below $k = 4$ on the water-rich side of the binodal surface. This, however, is of little relevance for our further considerations. Upon increasing k, T_m, ΔT, and γ_m increase, while γ_0 decreases. In all mixtures the middle phase wets the water/oil interface.

The detailed results of the experiments are presented in the tables in the Appendix. At this point we shall restrict ourselves to a summing up (Figure 2): (i) With short-chain amphiphiles (left field), i.e., from C_4E_j to C_5E_j, one finds tcp's only, but no (w/nw) transitions. As one proceeds in the series C_4E_1, C_4E_2, C_5E_2, to C_5E_3, the carbon number k of the alkylbenzenes required for passing the tcp drops monotonically from 8 to 5. In those mixtures which have passed the tcp, all middle phases wet, irrespective of k.

(ii) With medium-chain amphiphiles (central field) of the type C_6E_j, all mixtures separate into three phases within the experimental window; that is, the tcp's must lie below 0 °C. Instead, one now finds a systematic dependence of the (w/nw) transition on k. As one proceeds in the series C_6E_3, C_6E_4, to C_6E_5, the carbon number of the oil required for passing the (w/nw) transition, drops monotonically from 10 to 7.

(iii) With amphiphiles of carbon number $i \geq 8$ (right field), all mixtures separate into three phases, with all middle phases
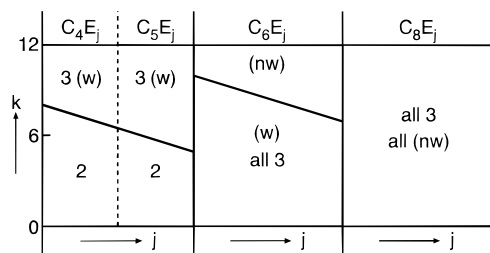
Figure 2. Summing up the results (for details see Appendix). Left field: from C_4E_1 to C_5E_3, the carbon number k of the alkylbenzenes required for passing the tcp drops monotonically from 8 to 5. Above the tcp's, all middle phases wet the water/oil interface. Central field: from C_6E_3 to C_6E_5, the carbon number k required for passing the (w/nw) transition drops monotonically from 10 to 7. Right field: With C_8E_j, all mixtures have passed both the tcp and the (w/nw) transition.

nonwetting; that is, both the tcp's and the (w/nw) transitions must lie below 0 °C.

The coordinates of the mixtures studied in refs 2 and 3 lie beyond the left field in the upper left, and those studied in ref 8 beyond the right field in the far lower right.

At first sight, the results confirm the above presumption: as one increases the strength (i,j) of the amphiphiles, the carbon number k of the oils required for passing a tcp as well as a (w/nw) transition drops. From the fact that with *n*-octane, C_5E_2 suffices to pass the (w/nw) transition (see above), whereas with decylbenzene, one has to proceed to C_6E_3, we furthermore deduce that it is not merely the carbon number of the oil that determines the coordinates of the (w/nw) transitions, but its structure as well, i.e., steric obstructions, in this case due to the slightly polar benzene ring.

The inverse relation between the carbon number k of the oil and the strength (i,j) of the amphiphile appears to apply also to the formation of lyotropic mesophases within the homogeneous phase at amphiphile concentrations $\gamma > \gamma_m$, i.e., behind the "tail" of the fish. Consider again Figure 4 in ref 8, in which the carbon number of a weakly nonpolar oils is increased in the presence of a strong amphiphile. Whereas the mixtures with $k < 4$ do not show such a mesophase (LC), the one with $k = 4$ does. It, hence, appears as if the tendency for forming (macroscopic detectable) mesophases does not depend on the strength of the amphiphile alone, but on the nonpolarity of the oil as well, in that k must again exceed a certain limit. In these mixtures with weakly nonpolar oils, the formation of mesophases appears to coincide with the (w/nw) transition. This, however, does not apply to strongly nonpolar oils. Consider Figure 2 in this paper, and increase (i,j) at fixed $k = 7$. With C_5E_j, the mixture has passed its tcp, but is still "this side" of the (w/nw) transition. As one proceeds to C_6E_j, one has to increase j to 5 (see table) to make the mixture pass the (w/nw) transition, but with no anisotropic mesophases becoming detectable (by visual observation through crossed polarizers). These appear not until the strength of the amphiphile has been increased further to C_8E_4. These results are in accord with those found by Schubert et al.[13] by SANS experiments, namely, that as one increases the strength of the amphiphile in mixtures with *n*-alkanes, one first passes the tcp, then the (w/nw) transition, to finally find lamellar mesophases (their Figure 1). We again emphazise that the same sequence is found in oil-free water−amphiphile mixtures. Upon increasing (i,j), one first finds a bicritical point at which the homogeneous mixtures separate into a water-rich and an amphiphile-rich phase, then a (w/nw) transition at the interface between these two phases, and, finally, lyotropic mesophases at high amphiphile concentrations which gradually move to lower concentrations with further increasing (i,j). In ternary

mixtures, the "distances" between these transitions appear to depend on the strength of the amphiphiles as well as on the nature of the oils in that they appear to shrink with decreasing nonpolarity.

Discussion

These results demonstrate that, when modeling microemulsions, both the strength of the amphiphile and the nonpolarity of the oil should be considered as important parameters.

Consider first the dependence of the tcp on i, j, and k (left field in Figure 2). This dependence can be qualitatively understood on the basis of the phenomenological model suggested by us in ref 12: the separation of a ternary mixture into three coexisting liquid phases arises from the interaction of the lower B−C miscibility gap, and the upper A−C loop with the "central" A−B miscibility gap. If the upper critical temperature, T_α, of the B−C gap, and the lower critical temperature, T_β, of the A−C loop are too far apart, the critical line that enters the prism at T_α winds around the binodal surface of the A−B gap to terminate at T_β. T_α drops with increasing i, but rises with increasing j and k. T_β, on the other hand, shows the same dependence on i and j, but does, evidently, not depend on k. Hence, if one increases k at fixed (i,j) (vertical path in the left field of Figure 2), this will make T_α rise, thereby increasing the "bending tension" of the "connected" critical line until the latter eventually breaks at a tcp. If one, on the other hand, increases j at fixed k (horizontal path), this makes both T_α and T_β rise with, as experiments show, T_α rising more strongly than T_β which again increases the bending tension of the critical line. For a more detailed discussion, one evidently also has to consider the effect of i, j, and k on the trajectories of the critical lines, in particular, on the oil-rich side of the phase prism. However, for a qualitative explanation of the dependence of the coordinates of the tcp's on i, j, and k, their effects on T_α and T_β suffice.

Consider now the dependence of the (w/nw) transition on i, j, and k (central field in Figure 2): in ref 1 we suggested to view amphiphiles as "chemical dipoles" with their heads and tails as opposite "charges" which differ from electric dipoles in that their charges can be varied independently of each other, and that opposite charges repel each other.[14] Another important difference lies in the fact that with chemical dipoles the polar charges decrease with rising temperature because of the weakening of the hydrogen bonds between the headgroups and water. If offered an interface between a polar and a nonpolar fluid bulk phase, the hydrocarbon tail of the amphiphile is expelled by water, whereas its hydrophilic headgroup is attracted by water. As a consequence, the amphiphile molecules accumulate at the interface between the two bulk phases, with their tails anchored in the nonpolar phase and the heads in the polar phase. This reduces the interfacial tension between the two bulk phases, in analogy to electric dipoles which, in a sigmoidal potential, accumulate at the surface of steepest gradient, thereby reducing the energy density at that surface. Evidently, the driving force for the accumulation of amphiphiles should increase with increasing "dipole moment", i.e., increasing (i,j), and increasing "polarity gradient" between the two bulk phases, i.e., increasing k. Accordingly, the reduction of the interfacial tension should increase with increasing (i,j) at fixed k.

If this analogy was an approach to reality, one would expect that chemical dipoles with unsymmetric charges will, depending
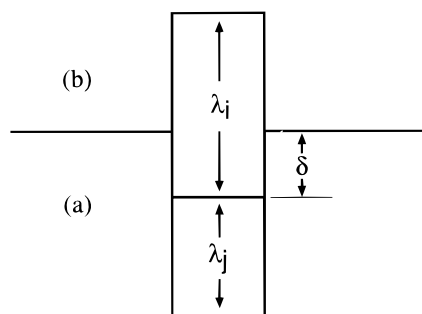
Figure 3. Modeling a saturated unimolecular layer of amphiphiles at a water (a)/oil (b) interface, with the vertical "log" representing an amphiphilic molecule. For further discussion see text.

on whether the polar charge or the nonpolar charge of the amphiphile is the higher one, not accumulate at the surface of steepest gradient but either on the more polar or the more nonpolar side, respectively, which should reduce the interfacial tension to a lesser extent than in the symmetric case. For reaching the maximum reduction at a given temperature, one then has to vary either i or j in the proper direction, or, if (i,j) are given, to vary temperature in order to adjust the polar charge j in the proper direction. This could explain qualitatively why for a given k, the dipole moment (i,j), or, for a given (i,j), the gradient, expressed in terms of k, must exceed a certain level for the interfacial tension σ_{ab} to be become lower than the sum of the two others. The problem is, evidently, how to quantify the model, that is, how to define the "dipole moment" of an amphiphile, and the "polarity gradient" between the two liquids. Because we did not succeed in suggesting a satisfactory quantitative treatment, we shall restrict ourselves to a much simpler model inspired by Harkins.[15] In discussing the accumulation of amphiphiles at a water/air interface, he made the following comparison: "The logs which are seen floating upon the surface of the water of a river or lake are in a nonsymmetrical field of force. They orient themselves with their longitudinal axis horizontal. If, however, each log is weighted with a mass of iron of the proper weight, it may still float, but the longitudinal axis becomes vertical, the iron sinks below the surface, and the wood projects above it. The vertical type of orientation is due to the fact that the weighted end of each log is more highly attracted by the earth than the unweighted end. It may be assumed that the polar end of an (amphiphilic) molecule is more highly attracted by the (polar) liquid than the nonpolar end."

We shall now apply this model to a saturated unimolecular layer of amphiphiles at a water/oil interface: consider a planar interface between a lower polar phase (a), and an upper nonpolar phase (b), with $\rho_a > \rho_b$ denoting their densities (Figure 3). Let the logs, representing the amphiphilic molecules, be of constant cross section, and let i stand for the nonpolar tail, and j for the polar headgroup, with λ_i and λ_j denoting their length, and $\rho_i < \rho_j$ their densities. Let, furthermore $(\lambda_j + \delta)$ be the length of that part of the log that is immersed in phase (a). Equilibrating the mass of the logs with their buoyancy, we obtain

$$\delta = [\lambda_i(\rho_i - \rho_b) + \lambda_j(\rho_j - \rho_a)]/(\rho_a - \rho_b) \qquad (2)$$

For preventing the logs to be completely immersed in either phase (a) or (b), one has as additional condition

$$-\lambda_j < \delta < \lambda_i \qquad (3)$$

Of the 24 possible cases, of which most can be excluded for physical reasons, let us consider the case $\rho_j > \rho_a > \rho_b > \rho_i$ as

being of particular interest. For this case it follows from eq 2

$$\delta \underset{>}{\overset{<}{=}} 0 \quad \text{for} \quad \lambda_i/\lambda_j \underset{<}{\overset{>}{=}} (\rho_j - \rho_a)/(\rho_b - \rho_i) \qquad (4)$$

in which the ρ's must now be viewed as measures for the interaction energies, i.e., the numerator on the right-hand side as measure for the attractive forces between water and each ethylene oxide group in the headgroup (including the OH group), and the denominator as measure for the repulsive forces between water and each CH_2 group (including the CH_3 group) in the oil and the tail, respectively, of which those between water and the tail groups should be a little weaker due to the adjacent headgroup. Then, if at a fixed temperature, i.e., at fixed interaction energies, the ratio λ_i/λ_j, that is, the ratio between the carbon number of the tail and the number of ethylene oxid groups in the headgroup, is too large, part of the headgroup will be immersed in the upper oil-rich phase ($\delta < 0$), whereas, if it is too small, part of the tail will be immersed in the lower aqueous phase ($\delta > 0$). If one now assumes that the interfacial layer reaches its maximum effect in reducing σ_{ab} at a certain δ, e.g., $\delta = 0$, this could explain the temperature dependence of the efficiency of the amphiphiles. Because, in particular, the hydrogen bonds between the ethylene oxid groups and water become weaker with rising temperature, each temperature requires a certain ratio λ_i/λ_j for σ_{ab} to reach its minimum, in accord with the fact that, at fixed k, T_m varies only little, if one proceeds in the sequence $(i,j) \rightarrow (i+2, j+1)$. In view of the "electrostatic analogy" one would, furthermore, expect the absolute value of $\sigma_m \equiv \sigma_{ab}$ ($T=T_m$) to decrease with increasing absolute values of λ_i and λ_j, that is, with increasing number of nearest-neighbor interactions. For estimating the dependence of σ_m on i, j, and k, this suggests to proceed on the basis of an extended lattice model.[16]

Inequality (3) requires

$$(\rho_j - \rho_a)/(\rho_a - \rho_i) < \lambda_i/\lambda_j < (\rho_j - \rho_b)/(\rho_b - \rho_i) \qquad (5)$$

If λ_i/λ_j reaches the left value, then $\delta = \lambda_i$; i.e., the tail becomes completely immersed in phase (a), whereas, if it reaches the right value, then $\delta = -\lambda_j$; i.e., the head becomes completely immersed in phase (b).

Consider, finally, the curvature of the interfacial layer: as δ changes its sign from >0 to <0, the position of the amphiphile molecules with respect to the a/b interface changes from "hydrophilic" to "hydrophobic". Because in the hydrophilic case the headgroups prefer water molecules as neighbors rather than other headgroups, this could result in a tendency of the headgroup layer to expand parallel to the interface due to the intrusion of water molecules between them, that is, to bend convex toward phase (a). In the hydrophobic case, however, water molecules are extruded from the headgroup layer which could result in a tendency of the layer to contract parallel to the interface, that is, to bend concave toward phase (a). This would be in accord with Bancroft's rule:[17] "a hydrophile colloid will tend to make water the dispersing phase while a hydrophobe will tend to make water the disperse phase".

Although this model is, admittedly, rather crude, it can at least qualitatively explain some of the features observed in experiment. It, in particular, points out the possibility that the position of the interfacial layer with respect to the water/oil interface may not be fixed, but may change gradually from the oil-rich to the water-rich side of that interface upon raising temperature. This could explain why because of $\partial\sigma/\partial T = \partial S/\partial A$ in a closed two-phase system with a planar interface, the

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Table 1[a]

	C4E1				C4E2				C5E2				C5E3			
k	Φ	w/nw	T_m	γ_m	Φ	w/nw	T_m	γ_m	Φ	w/nw	T_m	γ_m	Φ	w/nw	T_m	γ_m
12	3	w	41	59					3	w	36	50	>			
10	3	w	28	55					3	w	30	44	3	w	60	49
9					3	w	73	54								
8	3	w	11	48	3	w	64	52					3	w	48	
7	2		3	46	3	w	56	48	3	w	16	35	3	w	45	37
6					2		46	46	3	w	11	32	3	w	39	35
5									2		3	32	3	w	32	31
4													2		24	30

[a] C8E3 ($k \geq 9$), C8E4 ($k \geq 4$), C8E5 ($k \geq 2$): all 3 Φ, and nw. All other k: <.

Table 2[a]

	C6E3				C6E4				C6E5			
k	Φ	w/nw	T_m	γ_m	Φ	w/nw	T_m	γ_m	Φ	w/nw	T_m	γ_m
10	3	nw	37	35	3	nw	59	38				
9	3	w	29		3	nw	51	33				
8	3	w	25	29	3	w	46	31	3	nw	62	33
7									3	nw	60	
6			3			w	40	26	3	w	55	26
5												
4	3	w	9	23					3	w	43	24
3	3	w	3	22	3	w	23	23				
2	<											
1					3	w	6	23	3	w	20	23
0	3				<					w	12	24

[a] C8E3 ($k \geq 9$), C8E4 ($k \geq 4$), C8E5 ($k \geq 2$): all 3 Φ, and nw. All other k: <.

interfacial excess entropy $\partial S/\partial A$ too changes sign at the minimum of σ_{ab}.

Appendix

In Tables 1 and 2 we have summarized the results in more detail. Each table gives the results for one of the C_iE_j, proceeding from C4E1 to C8E5. The first column gives the carbon numbers k of the alkylbenzenes, proceeding from $k = 0$ (benzene) to $k = 12$ (dodecylbenzene). The second column (Φ) tells whether the mixture separates into two (2) or three (3) phases within the experimental window. The third tells whether the middle phase (c) wets (w) or nonwets (nw) the a/b interface. The fourth column gives the mean temperature T_m of the three-phase body in °C, the last column the mass fraction γ_m of the amphiphile at the tail of the fish at equal masses of water and oil in wt %.

In the case of a separation into two phases only, T_m and γ_m refer to the position of the waist observed in the binodal surface of the two-phase body (see Figure 2, $k = 4$). The sign < indicates that the three-phase bodies lie below 0 °C, the sign >, that they lie above 80 °C.

References and Notes

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