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Short communication

Wetting transition in a three-component surfactant system

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Résumé.— Une transition de mouillage est observée dans le système à trois composantes eau/hexadecane/C₆E₂, où C₆E₂ dénote le surfactant C₆H₁₃ (OC₂H₄)₂ OH. La transition a lieu dans la région tri-phasique à la température $T_w = 49.1 \pm 0.1^{\circ}$ C. Au dessus de T_w , la phase médiane riche en surfactant mouille l'interface séparant les phases riches en eau et en huile, alors que au-dessous de T_w elle ne le mouille pas.

Abstract. – A wetting transition in the three-component system water/hexadecane/ C_6E_2 , where C_6E_2 denotes the surfactant C_6H_{13} (OC_2H_4)₂ OH, is found to occur in the three-phase region at the temperature $T_w = 49.1 \pm 0.1^{\circ}$ C. Above T_w , the middle surfactant-rich phase wets the interface between the excess water and the excess oil phases, while below T_w it does not.

When three phases coexist at equilibrium, the middle phase can either wet or not wet the interface between the upper and the lower phases. That both cases do occur in nature is a commonplace experience, in particular in the case of two liquid phases in contact with air or with their saturated vapors, or in the similar case of a liquid on a solid substrate.

Much less obvious is the fact that a given system can exhibit both types of interfacial behavior when brought into different thermodynamic conditions, and that a transition, called a wetting transition, can occur between these two regimes. This remarkable interfacial phase transition was first observed and investigated over thirty years ago by Buff and Saltsburg in the three liquid-phase system water/heptane/aniline [1], in which the middle aniline-rich phase, which does not wet the interface between the lower water-rich and the upper heptane-rich phases, spreads at that interface when a detergent is added to the system.

More recently, it has been suggested theoretically by Ebner and Saam [2a], and by Cahn [2b], that a transition from a nonwetting regime to a wetting regime should occur in the neighborhood of a critical point, and such a transition was later observed in a mixture of cyclohexane and methanol [3a], as well as in a few other mixtures [3b]. In spite of its original success, this suggestion is based on heuristic arguments and nonrigorous calculations, and has recently been open to criticism [4]. Moreover, some systems have been found which do not undergo such a wetting transition, and remain in a nonwetting regime up to a critical point [5].

In this work, we study the wetting transition in a simple surfactant system, motivated by our expectation that some surfactant systems, if properly chosen, should exhibit wetting transitions. This expectation is based on the following argument. Firstly, there are several experimental observations [6], confirmed by theory [7], that near optimal conditions, i.e., when the water and the oil in the microemulsion middle-phase are solubilized in nearly equal proportions, the middle-phase microemulsion does not wet the water-oil interface. Next, the critical behavior of interfacial tensions in microemulsion systems obtained by light scattering techniques [8] is consistent with Cahn's argument, and consequently, if the above the theoretical suggestion is correct, a wetting transition should occur in these systems as the system moves toward a critical endpoint [9].

The third step in our argument is based on the experimental observations that if, in simple three-component surfactant systems, the chain of the surfactant molecule is fairly long, as it is, for example, in C_8E_3 , which denotes the nonionic surfactant C_8H_{17} (OC_2H_4)₃ OH, then the wetting transition may not occur, or it may occur so close to a critical endpoint as to be practically not observable [10]. On the other hand, when the surfactant molecule is short, there is experimental evidence [10] that the surfactantrich middle phase may always wet the interface between the excess phases, as it generally does for short-chained amphiphiles [11].

We therefore conjecture that the chain length of the surfactant molecule plays a pivotal role in the existence of wetting transitions in three-component surfactant systems [12], and our final step is to find the simplest possible system, i.e., a three-component system, in which the chain length of the surfactant $C_x E_y$ is intermediate between the relatively long chain of $C_8 E_3$ and the short chain of $C_4 E_1$. In contrast to five-component ionic surfactant systems such as those studied in [6], these three-component nonionic surfactant systems offer the great advantage that temperature can be chosen to be the only thermodynamic variable, with the overall composition remaining unchanged.

In this work, we carry out this program and test our theoretical predictions by studying experimentally the wetting properties of the threecomponent system water/hexadecane/ C_6E_2 . The surfactant C_6E_2 is a good candidate for our search of a wetting transition because its chain length is intermediate between that of the surfactant C_8E_3 , for which wetting never occurs [10], and that of the surfactant C_4E_1 , for which wetting apparently always occurs [10]. Another reason for choosing C_6E_2 is that it is also available commercially at very low cost, unlike other surfactants of intermediate chain length. In accord with our expectations, we find that a wetting transition does occur at $T_w = 49.1 \pm 0.1^{\circ}$ C.

The experimental procedure shall now be briefly described. We use n-hexadecane 99+%, and C_6E_2 , 99%, both from Aldrich Chemical Co. and without further purification, and water from Barnstead Nanopure II water purification system. The samples are prepared in clean glass test tubes of 1 cm in diameter, and the compositions are such that, at room temperature, the middle surfactant-rich phase forms a small but very clearly observable lens between the upper oil-rich and the lower water-rich phases (see Fig. 1a). A typical sample in our experiments contains approximately 5 ml water, 0.2 ml hexadecane and 0.1 ml C_6E_2 , for which the oil-rich phase is fairly thin, much thinner than shown in figure 1, but the lens formed by the middle surfactant-rich phase is well separated from the oil-vapor interface above it. All three phases are transparent. To avoid any perturbation of the phase equilibrium of the system, which is very sensitive to impurities, no color enhancing dies are used.



Fig. 1.— (a) $T < T_w$: the middle S phase does not wet the interface between the W and O phases.

(b) $T \ge T_w$: the middle S phase wets the interface between the W and O phases.

S, O and W denote the surfactant-rich, oil-rich and water-rich phases, respectively.

The prepared samples are set aside for periods of several days to several weeks to allow for equilibration. They are then placed in a water bath. The temperature of the water bath, which is indicated by a calibrated mercury thermometer, is controlled manually and varies at a rate of no more than a degree per ten minutes. The wetting transition temperature T_w is recorded by direct eye observation of the spreading and contracting of the middle phase as the temperature is respectively increased above and decreased below T_w .

A typical run includes several such increases and decreases of temperature, respectively above and below T_w , to examine the reversibility of this interfacial transition, as illustrated schematically in figure 2. The transition we observe is very abrupt in that the surfactant-rich phase in seen to spread rapidly as soon as the temperature reaches T_w from below. We believe the observed spreading at $T = T_w$ is a true equilibrium phenomenon and is not induced by heat transfer from test tube walls, because the latter would have also induced spreading at any temperature, including at those below T_w .



Fig. 2.- Expansion (a) and contraction (b) of the middle surfactant-rich phase (top view).

The wetting transition temperature obtained is found to be equal to $49.1\pm0.1^{\circ}$ C. The results are reproducible for all eight samples used, for which the wetting transition is also found to be fully reversible.

Due to the fact that only a small amount of the middle phase is present in our experiments, it is necessary to verify that the phenomenon we observe is really a wetting transition rather than the disappearance of the middle phase as the three-phase system moves into a two-phase region upon increasing the temperature. This is confirmed by our observation that the amount of the middle phase does not decrease during the heating process up to the wetting transition temperature; a gradual decrease in the amount of the middle phase would be observed if the system were moving away from a three-phase region into a two-phase region.

We tried, but did not succeed, to locate the upper critical endpoint of this system; however, our investigations show that the upper critical endpoint lies at least ten degrees above the wetting transition temperature. In fact, the upper critical endpoint temperature of this system was recently found to be at 60.9° C [13], more than 10° C above the wetting transition temperature we observe.

We believe that the present surfactant system is not the only one which can exhibit both wetting and nonwetting behavior without changing the overall compositions. Work is underway to further explore this question.

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