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Small angle neutron scattering near the wetting transition: Discrimination of microemulsions from weakly structured mixtures

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The wetting transitions of water, *n*-alkane, and *n*-alkyl polyglycol ether (C_iE_j) systems are examined in order to locate the transition between weakly structured mixtures and microemulsions. Using small angle neutron scattering (SANS) we determine the local structure and relate it to the phase behavior and wetting transitions observed by macroscopic measurements. We measure the SANS of the mixtures across the transition along two different experimental paths. One path begins with well-structured mixtures, and the effective chain length of the surfactant combination C_6E_2/C_4E_1 is decreased by increasing the C_4E_1 fraction. The other path starts with equal amounts of water and oil mixed by the strong amphiphile C_8E_3 . The local structure of these “good” microemulsions is weakened by increasing the temperature and concomitantly the oil/water volume ratio approaching the upper critical endpoint. As in previous studies analyzing the scattering experiments quantitatively permits determination of the amphiphilicity factor which is a measure of the strength of the surfactant. We confirm predictions that the amphiphilicity factor measured at the wetting transition becomes more negative as the temperature interval between the transition and the critical endpoint decreases. © 1996 American Institute of Physics. [S0021-9606(96)50609-0]

I. INTRODUCTION

Microemulsions are thermodynamically stable mixtures of water, oil, and surfactants. Using ternary systems with surfactants of the family of the *n*-alkyl polyglycol ethers (denoted as C_iE_j) one can demonstrate that the longer chain surfactants exhibit an interfacial film separating the polar and nonpolar domains (“good” microemulsions).^{1,2} With decreasing chain length of the surfactants a decreasing degree of ordering of the amphiphiles in the interface is observed. Such less-structured fluids offer interesting potential applications as solvents of intermediate polarity for chemical reactions. As the chain length of surfactants is decreased, middle phase microemulsions become able to wet the water/oil interface.² Widom has suggested that microemulsions could be differentiated from less-structured mixtures by this feature.³ Gompper and Schick suggested that the wetting transition is connected to a change in the real-space correlation function of the microemulsions.^{4,5} The real-space correlation functions are obtained from Fourier transformation of small-angle neutron scattering (SANS) spectra.

In previous papers Langevin *et al.*^{6–8} and Schubert *et al.*^{1,2} investigated the scattering behavior of microemulsions with varying amphiphilic strengths in order to quantify the relation of amphiphilic order in the mixtures and the wetting properties. As Langevin and co-workers showed, the surfactant-rich phase (*c*) does not wet the interface between

the polar excess phase (*a*) and nonpolar excess phase (*b*), but rather forms a lens at the *a/b* interface if it is a structured microemulsion. Schubert *et al.* examined how the scattering peak vanishes when by decreasing the amphiphilicity a crossover from a nonwetting to wetting surfactant-rich phase is induced,^{1,2} so that phase (*c*) spreads at the interface between phases (*a*) and (*b*). They compared their findings with theoretical predictions by Gompper and Schick,^{4,5} analyzing the SANS spectra in terms of an amphiphilicity factor (denoted f_a) permitting to quantify the amphiphilic strength. As Gompper and Schick had predicted the transition from a wetting to a nonwetting middle phase occurred on the microemulsion (that is, on the more structured) side of a disorder line. For microemulsions approaching the critical endpoint, that is with increasing asymmetry between oil and water, Langevin and co-workers⁶ had observed that the scattering peak moved toward larger *q* values with a second peak developing around $q=0$. These findings were confirmed by Schubert *et al.*²

In this paper we extend the work of these two groups and try to answer the question whether the amphiphilicity factor at the wetting transition, induced in an asymmetric system by approaching the critical endpoint, becomes increasingly more negative as the transition is caused to occur increasingly closer to the critical endpoint. Recent theoretical work including the effect of fluctuations is predicting this to happen.⁹ One knows that one can move the wetting transition closer to the endpoint by increasing the chain length of the surfactant.⁵ Furthermore, we want to quantify more precisely

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TABLE I. The weight fractions α and γ and the volume fraction ϕ of the samples are given along with the one-phase interval of the mixtures.

System	α	γ	δ	ϕ_a	ϕ_b	ϕ_c	ϕ_d	1-phase/°C
D ₂ O- <i>n</i> -decane-C ₄ E ₁ -C ₆ E ₂	0.3969	0.3913	1	0.3032	0.3138	0	0.3830	11.64–13.71
D ₂ O- <i>n</i> -decane-C ₄ E ₁ -C ₈ E ₃	0.3964	0.5082	0.500	0.2432	0.2513	0.2590	0.2465	18.35–20.07
D ₂ O- <i>n</i> -decane-C ₄ E ₁ -C ₆ E ₂	0.3980	0.5268	0.401	0.2328	0.2420	0.3207	0.2045	20.87–22.02
D ₂ O- <i>n</i> -decane-C ₄ E ₁ -C ₆ E ₂	0.3966	0.5535	0.247	0.2212	0.2201	0.4262	0.1325	24.65–25.91
D ₂ O- <i>n</i> -decane-C ₄ E ₁ -C ₆ E ₂	0.3967	0.5839	0	0.2031	0.2102	0.5867	0	32.92–34.70
D ₂ O- <i>n</i> -octane-C ₈ E ₃	0.3883	0.1990	0	0.4042	0.4042	0.1916	0	13.55–15.36
D ₂ O- <i>n</i> -octane-C ₈ E ₃	0.4867	0.1919	0	0.3242	0.4839	0.1919	0	15.40–17.11
D ₂ O- <i>n</i> -octane-C ₈ E ₃	0.5956	0.1996	0	0.2479	0.5739	0.1782	0	17.23–18.75
D ₂ O- <i>n</i> -octane-C ₈ E ₃	0.7165	0.1697	0	0.1719	0.6835	0.1446	0	18.76–19.86
D ₂ O- <i>n</i> -octane-C ₈ E ₃	0.8497	0.1152	0	0.0914	0.8163	0.0923	0	19.49–20.50

at which numerical value of the amphiphilicity factor for symmetric microemulsions the wetting transition is approached by weakening the surfactant.

We chose to examine two systems, which permit the crossing of wetting transitions along the two different experimental paths. We first studied symmetric microemulsions ($\phi = 0.5$) in the systems D₂O-*n*-decane-C₄E₁-C₆E₂ as a function of C₄E₁ content. In this family the middle phase wets the water/oil interface for pure C₄E₁. Increasing the C₆E₂ fraction leads to the wetting transition (at $\delta = 0.4$) (see below for the definitions of δ and ϕ). Next scattering patterns for ternary water-*n*-octane-C₈E₃ mixtures with varying ϕ were measured in order to determine to what extent local structure persists as the wetting transition is induced by approaching the critical endpoint.

II. SCATTERING THEORY

Teubner and Strey¹⁰ suggested to describe small-angle scattering curves by

$$I(q) = (a_2 + c_1 q^2 + c_2 q^4)^{-1} + b, \quad (1)$$

where the parameters stem from the coefficients of an order parameter expansion, and b is an incoherent background. As has been demonstrated before^{1,2,10} and as will be seen below Eq. (1) is indeed a versatile description of scattering peaks in microemulsions and their weakly structured counterparts. The parameters a_2 , c_1 , and c_2 may be grouped together to formulate an amphiphilicity factor

$$f_a = c_1 / (4a_2 c_2)^{1/2} \quad (2)$$

that has been used a number of times to quantify the amphiphilic strength of the surfactant.^{1,2} The factor f_a is typically close to -1 for good microemulsions, is equal to 0 at the Lifshitz line, is equal to $+1$ at the disorder line, and is even more positive near the tricritical point. A graph illustrating the relative locations of the regions and points is given in Ref. 1. We only note here that at the Lifshitz line the peak moves to zero q . The correlation length

$$\xi = \left[\frac{1}{2} \left(\frac{a_2}{c_2} \right)^{1/2} + \frac{c_1}{4c_2} \right]^{-1/2} \quad (3)$$

and the periodicity

$$\frac{d}{2\pi} = \left[\frac{1}{2} \left(\frac{a_2}{c_2} \right)^{1/2} - \frac{c_1}{4c_2} \right]^{-1/2} \quad (4)$$

may also be expressed in terms of the order parameter coefficients a_2 , c_1 , and c_2 . More details are discussed in Refs. 1, 2, and 5. The maximum of the scattering peak is related to the correlation length and periodicity by¹⁰

$$q_{\max} = \left[\left(\frac{2\pi}{d} \right)^2 - \frac{1}{\xi^2} \right]^{1/2}. \quad (5)$$

III. EXPERIMENT

A. Materials

N-octane and *n*-decane were purchased from Merck, Darmstadt (Germany) with a purity $>99\%$. D₂O (degree of deuteration $>99.9\%$) was from Cambridge Isotope Laboratory (Cambridge, MA). The solvents were used without further purification. 2-Butoxy ethanol (H-(CH₂)₄-(OCH₂CH₂)₁-OH; C₄E₁) and diethyleneglycol monohexylether (C₆E₂) were purchased from Fluka (Neu Ulm, Germany) with a purity $>98\%$. The cloud points at critical composition of the binary systems water-C_{*i*}E_{*j*} were checked and found to correspond to purified surfactants within a few tenth of a degree.^{11,12} Using the known densities (in g/cm³) at 20 °C for D₂O (1.105), *n*-octane (0.703), *n*-decane (0.730), C₄E₁ (0.903), C₆E₂ (0.932), and C₈E₃ (0.948) volume fractions were calculated. The mass fraction α of the oil in the mixture of water (A) and oil (B) is denoted by $\alpha = m_b / (m_a + m_b)$, where m_i is the mass component i . The overall concentration γ of surfactant (C) is calculated from $\gamma = m_c / (m_a + m_b + m_c)$. The mass fraction δ of the second surfactant (D) in the mixture of the two $\delta = m_d / (m_c + m_d)$. The oil/water volume ratio ϕ is defined by $\phi = \phi_b / (\phi_a + \phi_b)$, where ϕ_i is the volume fraction of component i .

B. Phase diagram determination and sample preparation

A detailed description of phase diagram determinations can be found in Ref. 1. Here, it suffices to note that the samples were located in the so-called fishtail, that is at a slightly higher surfactant concentration (by about 1%) than the composition of the middle phase. This allows for a one-

phase interval sufficiently wide to assure safe experimentation. In a water bath the phases were observed as function of temperature and the one-phase interval was determined (see Table I). From the phase behavior of such systems it can be judged that these sample are indistinguishably close to the middle phase microemulsions one finds for the temperature corresponding to the middle of the one-phase interval given. There the SANS spectra were taken. Sample preparation was carried out as described in previous papers.^{1,2} All samples were studied in bulk contrast with water deuterated (D_2O). All other compounds were hydrogenated.

C. SANS experiment

As previously,^{6,8} the scattering experiments were carried out on the PAXE spectrometer at Saclay, France. The q range covered ranged from $0.1 < q/\text{nm}^{-1} < 3.1$. The mean neutron wavelength was $\lambda = 0.6$ nm. The wavelength spread was $\Delta\lambda/\lambda = 10\%$. The collimation path was chosen such that the sample-to-detector distance was approximately equal to the sample-to-source distance. The data were taken at two sample-to-detector distances, 1.15 and 5.05 m. All samples were measured in 1 mm Hellma QS cells with Teflon stoppers. Care was taken that the measurements were made on homogeneous samples.

D. Data treatment

The scattered intensity was recorded on a two-dimensional detector. Measurement of the incoherent scattering of H_2O with sufficiently good statistics was used to calibrate the sensitivity of the individual cells. The raw data were normalized by the monitor value, radially averaged and corrected for the detector sensitivity, using standard software existing at Saclay. Conversion of these relative intensities into absolute units [differential cross section, referred to as $I(q)$] was done by measuring the intensity of the primary beam using an attenuator and a graphite sample as described by Cotton.¹³ In all cases the scattering of an empty cell was subtracted and the transmission of the samples properly taken into account. Data sets from the two sample-to-detector distances were independently placed on absolute scale and were in good agreement (always less than 5% difference for a given sample). The data taken at the two distances were then superimposed and used this way for the analysis. The measurements were extended to sufficiently large q in order to obtain good estimates for the incoherent background scattering, precise knowledge of which is important for quantitative analysis of the scattering curves.

IV. RESULTS

A. Phase diagrams and wetting transitions

In Table I the one-phase intervals for the system D_2O - n -decane- C_4E_1 - C_6E_2 ($\phi = 0.50$) are given. As can be seen, with increasing amount of C_4E_1 the effective chain length of the surfactant mixture decreases, resulting in a less effective surfactant mixture (e.g., for $\delta = 1$ a surfactant fraction of $\gamma = 0.391$ is required to solubilize equal amounts of

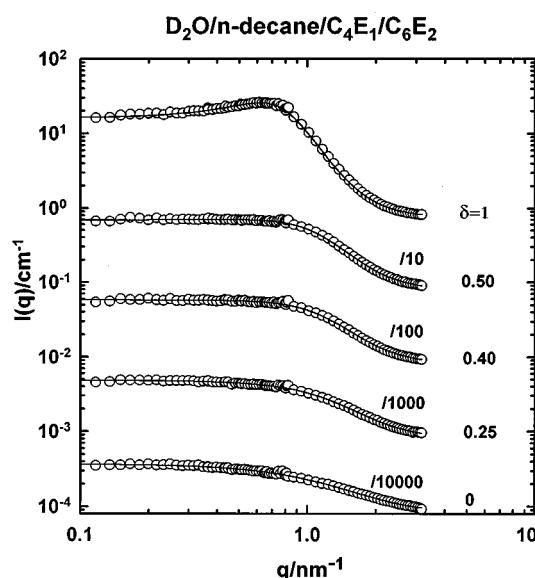


FIG. 1. The scattering curves for water- n -decane- C_4E_1 - C_6E_2 along with fits of Eq. (1) are shown. Decreasing the ratio δ of C_6E_2 in the mixture of C_4E_1 and C_6E_2 weakens the surfactant and induces the wetting transition. The fit parameters are given in Table II. As can be seen there the amphiphilicity factor changes sign close to the point of the wetting transition.

water and oil, whereas for $\delta = 0$ one needs $\gamma = 0.584$). Also, with decreasing effective chain length of the surfactant mixture the one-phase region is shifted to higher temperatures. Both effects contribute to the occurrence of a wetting transition for this system located at $\delta = 0.40 (\pm 0.05)$. For lower δ one observes a wetting and for higher δ a nonwetting middle phase.

The system D_2O - n -octane- C_8E_3 is suited to examine the effect of the oil/water ratio on the wetting properties of the middle phase. Increasing oil content ϕ leads to a reduction of required surfactant volume fraction accompanied by the characteristic shift in temperature toward the upper critical endpoint temperature $T_u = 19.5$ °C (see Table I). The wetting transition in this system occurs for $\phi = 0.85 (\pm 0.05)$, for $T_u - T = 0.2 (\pm 0.1)$ K.

B. The system water- n -decane- C_4E_1 - C_6E_2 , effect of surfactant chain length

In Fig. 1 the bulk contrast scattering spectra of the D_2O - n -decane- C_4E_1 - C_6E_2 systems are shown on absolute scale. All spectra are presented on a double-log scale and are displaced from each other by integer numbers of orders of magnitude as indicated. The solid lines through the data points represent the fits using the Teubner-Strey formula [Eq. (1)]. The fit curves describe the spectra quantitatively, with the fit parameters are summarized in Table II. Previously obtained SANS data¹ showed an amphiphilicity factor for the $\delta = 1$ sample (there it was denoted I6K 10) of $f_a = -0.63$ in very good agreement with the present observation of $f_a = -0.62$ (see Table II). Decreasing the effective chain length of the surfactant mixture leads to a decrease of the coherent scattering intensity. Increasing surfactant con-

TABLE II. The fit parameters for the D_2O - n -decane- C_4E_1 - C_6E_2 system, a_2 (in cm), c_1 (in $cm\ nm^2$), c_2 (in $cm\ nm^4$) and the incoherent background b (in cm^{-1}). Also given are the correlation length ξ and the periodicity d [from Eqs. (3) and (4)]. The location of the maximum q_{max} [from Eq. (5)] and the amphiphilicity factor f_a [from Eq. (2)].

Sample, δ	a_2	c_1	c_2	b	ξ (nm)	d (nm)	q_{max} (nm^{-1})	f_a
1	0.067	-0.130	0.1692	.76	2.91	8.87	0.620	-0.62
0.500	0.165	-0.035	0.0989	.80	1.34	7.33	0.422	-0.14
0.401	0.202	0	0.0899	.82	1.16	7.26	0.077	0
0.247	0.249	0.090	0.0664	.85	0.87	7.92		0.34
0	0.351	0.290	0.0409	.82	0.56			1.21

entrainment leads to a decrease in the length scale d , and the contrast supplied by the D_2O . The incoherent background determines the scattering intensity at high q . On approaching the wetting transition (located at $\delta=0.40$), the scattering peak moves continuously toward $q=0$, as is evident from Table II, and the amphiphilicity factor f_a changes sign there. This indicates that the transition occurs very near the Lifshitz line. The correlation length ξ and d [calculated from Eq. (3) and (4)] decrease systematically as function of the chain length of the surfactant. However, as the disorder line, (where d becomes infinite), is approached d does indeed begin to increase (see d for $\delta=0.25$ in Table II).

C. The system water- n -octane- C_8E_3 , effect of oil content

We studied the scattering behavior of this system because the wetting transition can be approached by varying the water-to-oil ratio for a given ternary system. Compared to the water- n -hexadecane- C_6E_2 system studied previously,^{1,6,7} C_8E_3 is a stronger amphiphile. This is seen by the minimum amount of surfactant γ needed to solubilize equal amounts of water and oil (see Table I). For the system C_6E_2 $\gamma=0.391$, for the system C_8E_3 $\gamma=0.199$. The scattering spectra are fitted using [Eq. (1)]. Critical scattering is seen to occur approaching the critical endpoint. In Fig. 2, again on a double log scale, the $\phi=0.90$ sample is given on absolute scale. The neighboring compositions are displaced again by a factor of 10. With increasing oil content (from bottom to top in Fig. 2) one finds a weakening of the characteristic peak, while at the same time the scattered intensity at low q increases. The fit parameters are summarized in Table III. f_a decreases, but is still larger and negative at the macroscopically observable wetting transition, which is found at $\phi=0.85$. The peak at large q (clearly seen for $\phi=0.50, 0.60, 0.70$ in Fig. 2) disappears for larger ϕ , but a shoulder remains, an indication of persisting structure. This feature is different from the water- n -hexadecane- C_6E_2 system (compare to Fig. 5 in Ref. 1). At $q=0$ the intensity rises for increasing ϕ (seen for $\phi=0.80, 0.90$) accompanied by f_a becoming of smaller magnitude, but still remaining negative.

Looking very closely for $\phi=0.50$ the fit in Fig. 2 shows a slight deviation for $q=2q_{max}$. This has been noted before,² and is a consequence of the relatively sharp peak exhibiting to some degree second order scattering. As the peak becomes

broader the fit in this q range becomes perfect ($\phi=0.60, 0.70, \dots$).

V. DISCUSSION

The amphiphilic strength of the surfactants in ternary (or pseudoternary) mixtures water, n -alkanes, and n -alkyl polyglycol ethers (C_iE_j) depends on the chain length of the surfactant, the composition of the mixtures, chain length of the hydrocarbon and temperature. As discussed by Schubert *et al.*,² it is possible to shrink the three phase body with decreasing amphiphilicity for aqueous systems starting from C_6E_2 by adding C_4E_1 . For sufficiently weak surfactants or surfactant mixtures a transition in the wetting behavior is observed, before the three-phase body disappears at a tricritical point. The middle phase (c) for the system D_2O - n -octane- C_4E_1 , for instance, wets the a/b interface, whereas using C_6E_2 , instead of C_4E_1 , phase (c) does not wet.¹ The change in these systems was interpreted as a transition from weakly to more structured mixtures.^{5,14-16} An-

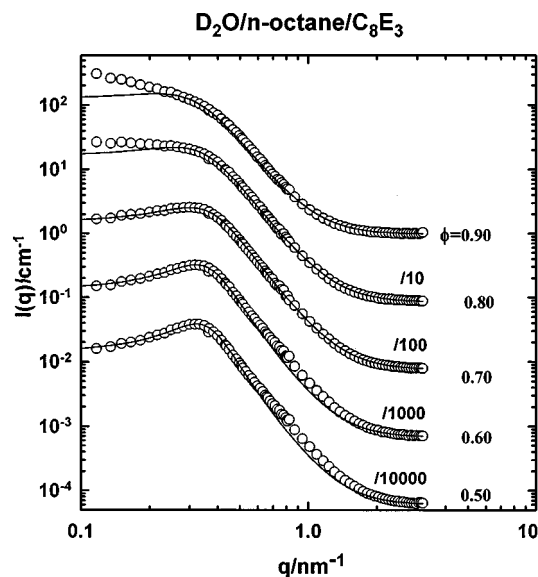


FIG. 2. The scattering curves for water- n -octane C_8E_3 along with fits of Eq. (1) are shown. The wetting transition is passed by changing the volume fraction of oil with increasing temperature the middle-phase approaching the upper critical temperature of the three-phase body, and inevitably wets the a/b interface.

TABLE III. The fit parameters for the D_2O - n -octane- C_8E_3 system (units as for Table II) along with the correlation length ξ and the periodicity d [from Eqs. (3) and (4)]. The location of the maximum q_{\max} [from Eq. (5)] and the amphiphilicity factor f_a [from Eq. (2)].

Sample, ϕ	a_2	c_1	c_2	b	ξ (nm)	d (nm)	q_{\max} (nm $^{-1}$)	f_a
0.5	0.0071	-0.087	0.4201	0.60	8.70	18.38	0.322	-0.80
0.6	0.0075	-0.086	0.4199	0.68	8.00	18.29	0.320	-0.77
0.7	0.0067	-0.061	0.3389	0.76	6.29	18.50	0.300	-0.65
0.8	0.0063	-0.053	0.4050	0.83	5.81	20.38	0.256	-0.53
0.9	0.0082	-0.065	0.7251	0.98	5.70	22.85	0.212	-0.43

other way of inducing the wetting transition, already investigated by Langevin *et al.*⁶ and later by Schubert *et al.*,¹ is to change the oil/water ratio approaching one of the critical endpoints. The wetting transition can be made to approach the endpoint even more closely by increasing the chain length of the surfactant. It has been predicted by Schmid and Schick⁹ that as one does so, the value of the amphiphilicity factor at the wetting transition will become increasingly negative. In the following we will analyze the experimental scattering curves in terms of the appropriate scattering function [Eq. (1)] and extract the amphiphilicity factors.

A. Effect of surfactant chain length

Changing the surfactant chain length induces systematic changes in amphiphilicity (see Table II). In the water- n -alkane- C_4E_1 - C_6E_2 system a shorter effective chain length of the surfactant mixture leads to three phase bodies at higher temperatures and larger surfactant concentrations (cf. Table I). The scattering behavior changes according to the effectively weaker surfactant and increased surfactant concentration. The spectra become less pronounced (see Fig. 1). The amphiphilicity factor f_a varies significantly, changing sign (see Table II) at the wetting transition (located at $\delta=0.40$). This indicates that the wetting transition occurs near the Lifshitz line, where the microemulsion is weakly structured. Concomitantly, we observe that on approaching the wetting transition, the scattering peak does move continuously towards $q=0$ as expected from theory.⁴

B. Effect of oil/water volume fraction

For the D_2O - n -octane- C_8E_3 system, as for all systems of this type, the oil content taken up by the middle phase microemulsion is a strong function of temperature (see Table I). In other words, the volume fraction of water domains in the microemulsions decreases as one approaches the critical endpoint. As mentioned above, the wetting transition is located at $\phi=0.85$. The scattering spectra reveal the accompanying changes in microstructure (see Fig. 2). From Table III one finds that the magnitude of f_a decreases with increasing ϕ towards the critical endpoint, located close to the $\phi=0.9$ sample, the ϕ of which is a little larger than that of the macroscopically observable wetting transition at $\phi=0.85$. ξ decreases and d increases slightly, a similar trend as already observed by Schubert *et al.*^{1,2} From theory⁵ one might have expected a much stronger movement of d because one is moving towards the disorder line, however, d increases only

slightly. Also these findings are in agreement with Schubert *et al.*¹ Calculating q_{\max} from Eq. (5) one finds that the scattering peak moves to smaller q exhibiting a less pronounced peak in approaching the wetting transition, in agreement with theory.⁵ The scattering intensity increases at $q=0$ in approaching the critical endpoint, accompanied by f_a less negative. However, f_a at the wetting transition in this system is more negative than at the wetting transition in the shorter chain surfactant system D_2O - n -hexadecane- C_6E_2 previously studied.¹ These findings are agreement with the theoretical predictions by Schmid and Schick.⁹

C. Wetting transitions and amphiphilicity factors

In the previous papers^{1,2} a number of wetting transitions were investigated with the observation that an amphiphilicity factor of $f_a=-0.33$ at the wetting transition was consistent with all systems studied. Thus, wetting transitions were located on the microemulsion side of the Lifshitz line (where $c_1=0$ and $f_a=0$), which is, as predicted by theory, on the microemulsion side of a disorder line (at which d goes to infinity). Theory predicts⁵ the scattering peak to move in to $q=0$ in approaching the wetting transition. This feature is clearly seen in Fig. 1 and the parameters in Table II for the water- n -decane- C_4E_1 - C_6E_2 system. One can also see that at the wetting transition in this system we have $f_a=0$, that is, it occurs near the Lifshitz line.

Previously, studying water- n -hexadecane- C_6E_2 , Langevin *et al.* observed⁶ that the peak first moved towards higher q values and then developed at around $q=0$. Here, we find for the water- n -octane- C_8E_3 system that the wetting transition is clearly located on the microemulsion side of the Lifshitz line, and all samples still show a scattering peak at nonzero q . Separately from this structural scattering, the critical scattering develops near $q=0$ upon approaching T_u (see Fig. 2 and Table III). Actually, in approaching the Lifshitz line the scattering peak moves somewhat toward smaller q (see Table III), but it was not observed to reach $q=0$.

We therefore conclude that depending on the type of wetting transition, at symmetry by weakening the surfactant or by approaching a critical endpoint, the amphiphilicity factors range between 0 and -0.5, and do not occur at a values closely centered around -0.33 as it seemed from the systems hitherto studied.¹ Still the conclusion holds that the wetting transition occurs on the microemulsion side of the disorder

line (for which $f_a = +1$), in agreement with the theoretical prediction.⁵

D. Critical scattering

Analyzing the water-*n*-octane- C_8E_3 one observes a critical contribution at low q for the larger ϕ (see Fig. 2). The critical scattering contribution arises from the divergence of the Ornstein-Zernike correlation length ξ_{OZ} as T_u is approached. Our experiments were not designed to quantify critical scattering. We only note that subtracting a critical component from the scattering curves would result in an even more negative amphiphilicity factor, as Schubert *et al.* showed on a different system.¹ Due to the location of the peaks at rather low q for the present system, light scattering might be the more appropriate tool to provide the power law for the Ornstein-Zernike relation.

VI. CONCLUSIONS

For the two systems examined, the quantitative analysis of small angle neutron scattering spectra permits to extract an amphiphilicity factor. Gompper and Schick⁴ predicted for symmetric systems that the scattering peak should move toward zero wave vector as the wetting transition is approached due to a change in the local microscopic structure. Examining the water-*n*-decane- C_4E_1 - C_6E_2 system revealed that the scattering peak moved to zero q , and the Lifshitz line was crossed close to the wetting transition (see Table II). These results are in agreement with Gompper and Schick's predictions.^{4,5}

In the water-*n*-octane- C_8E_3 system a wetting transition was induced by increasing the temperature which leads to an increasing oil/water volume ratio ϕ of the middle phase. The scattering spectra showed the persistence of local structure

through the wetting transition (see Fig. 2 and Table III). Here, critical scattering and scattering from the microstructure are superimposed. The scattering peak was found to move to smaller q , but remained non-zero at the wetting transition. From the quantitative analysis we conclude that the closer the wetting transition is to the critical endpoint, the more structured is the microemulsion at the wetting transition, an effect predicted by Schmid and Schick.⁹

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