Water/oil microemulsions from binary ionic–nonionic surfactants

H.-F. Eicke *, W. Meier, H. Hammerich
Institut für Physikalische Chemie, Dept. Chemie, Universität Basle, CH-4056 Basle, Switzerland
Received 6 March 1996; accepted 4 June 1996

Abstract

The addition of a second surfactant to an otherwise thermodynamically stable microemulsion causes interfacial and bulk effects: the combination of AOT and C12E5 supports the formation of planar interfaces (considering the molecular geometries of the surfactants) which induces a sphere to oblate ellipsoid (~ disk) transition ensuing a lamellar liquid crystalline phase. Heats of adsorption of C12E5 (adsorbed on an H2O/AOT/i-CsH18 interface) corroborate the existence of two different interfacial states. The phase transition was inferred from combining conductometric and electro-optic Kerr effect studies.

Keywords: Binary ionic–nonionic surfactants; W/O microemulsions

1. Introduction

It is tempting to add a second surfactant to an otherwise thermodynamically stable microemulsion because it allows one to vary controllably the properties of the monolayer with respect to a given reference state, i.e. a three-component microemulsion. In order to keep to the ideal solution regime, only small amounts of additive were added. Mixtures of ionic and nonionic surfactants, however, are expected to show even at the lowest ion concentrations large deviations from Raoult's law, which hamper the application of simple approaches. In spite of this fact, interesting gross effects can be studied arising from both interfacial and bulk properties of the system. There have been a number of investigations on mixtures of ionic and nonionic surfactants, all restricted to low ionic surfactant concentrations [1]. Water/oil (w/o) microemulsions containing binary surfactants have not been studied from the colloidal point of view as far as we are aware, except the last paper (see [1]) which is concerned with the effect of ions on phase diagrams in multicomponent surfactant systems also including w/o microemulsions. This has been done recently [2], where again the condition \( \chi_{\text{ionic}} \ll 1 \) prevailed. The paper was concerned with the effect of a few isolated charges (stemming from the dissociated ionic surfactant) on the conduction mechanism in singly dispersed aqueous nanometer-sized droplets and system-spanning nano-droplet clusters. It was possible to distinguish clearly volume and interfacial charge transport in the nanodroplets and their clusters. We are now interested in investigating the opposite site case, i.e. \( \chi_{\text{nonionic}} \ll 1 \), where again interesting properties of the system are expected to be induced by the binary surfactant layer.

We wish to show that two-dimensional diluted surfactant solutions of sufficiently surface-active molecules can be studied. It is expedient in this context to adhere to some simplifying conditions because of the inherent complexity of such multi-
component systems; the total amount of surfactant in the microemulsion is kept constant. This implies that the total interface is (approximately) constant (not considering the equilibrium monomer concentration of the surfactants in the oil and water phases which, however, can be kept sufficiently low). Also, the binary mixture is formed by exchanging ionic and nonionic surfactants one by one, keeping their total number constant. To comply with the condition of a constant total interface, both surfactants should possess approximately equal interfacial molecular areas.

Concerning bulk effects, we expect variations of the interdroplet interaction potentials because the surfactants influence principally the miscibility gap of oil and water [3]. This should become apparent by a change of the critical temperature of the onset of the system spanning nanodroplet clusters. The latter might be interpreted as a preliminary state of the demixing of oil and water.

2. Experimental

2.1. Materials

AOT (sodium bis-2-ethylhexylsulfosuccinate) (>99%), isooctane (puriss), pentaethylene glycol monododecyl ether (C12E5) (>98%, GC) and deionized, doubly distilled water were used. All chemicals were obtained from Fluka (Buchs, Switzerland). If not stated otherwise, we always chose \[ x_{\text{AOT}} + x_{\text{C12E5}} = 1 \] and \[ r_w = m_{\text{H}_2\text{O}}/m_{\text{surfactant}} = 1 \] (\( m_i \) = total amount of i).

2.2. Instrumental

Two relatively simple but accurate experimental techniques were at our disposal in order to investigate singly dispersed aqueous nanodroplets and their infinite clusters. The powerful small-angle neutral scattering (SANS) method could not be applied to this system since the exchange of H2O by D2O alters the system in an uncontrollable way. This is apparent from the disappearance of the conductivity effects at \( T_c \). It is probably caused by a change of hydration in replacing H2O by D2O and thus the corresponding space requirements of the hydrated headgroups.

(i) Conductometric measurements are dependent on the concentration and mobility of the charge carriers. In the case of translational motions of the carriers, the mobility is controlled by Stokes law for (charged) spherical nanodroplets. Even for non-spherically shaped droplets a Stokian-like relation exists according to Oberbeck [4]. The particle radius is then replaced by an effective radius \( (R_{\text{eff}}) \) of a sphere producing the same resistance in a viscous medium as the nonspherical (usually ellipsoidal) particle.

The thermostated conductance cell consisted of two platinum electrodes in parallel (5 × 10 mm) and a gap width of 2 mm. Conductance was determined by an auto-balancing bridge (CDM 83; Radiometer, Copenhagen, Denmark) between 13 and 2 × 10⁻⁸ S at 73 Hz and 50 kHz.

(ii) Induced electric birefringence is a suitable method to study shape deformations of nanodroplets [5–7]. Such particles may generally possess form and intrinsic birefringences. We expect in the present context contributions from both, although the intrinsic is smaller than form birefringence for larger deviations from spherical shapes. In particular we are interested in the specific Kerr constant extrapolated to zero droplet concentration \( (\Delta n/nE^2 C_{\text{nd}})_{\text{d}} = \Delta K_{\text{sp}} C_{\text{nd}} = 0 \) to eliminate the droplet–droplet interactions. If we restrict our consideration to the case where the uniaxial ellipsoidal nanoparticles do not possess a permanent dipole moment, \( (K_{\text{sp}})_{\text{nd}} \) is given by

\[
(K_{\text{sp}})_{\text{nd}} \approx \Delta \alpha_{\text{opt}} \Delta \alpha_{\text{el}},
\]

where the first term on the right-hand side represents the optical and the second the electrical polarizability contributions. The latter is

\[
\Delta \alpha_{\text{el}} = \frac{4\pi(\epsilon_1 - \epsilon_2) - \{(\epsilon_1 - \epsilon_s)(\epsilon_2 - \epsilon_s)
\times (L_1 - L_2)/\epsilon_s]}{\{4\pi + \{|(\epsilon_1 - \epsilon_s)/\epsilon_s\} - L_1\}
\times \{4\pi + \{|(\epsilon_2 - \epsilon_s)/\epsilon_s\} - L_2\}}
\]

(2)

while the optical polarizability is obtained by replacing \( \epsilon_i \) by \( n_i^2 \); \( L_i \) are the depolarization ('form') factors of the uniaxial ellipsoid and \( \epsilon_1, \epsilon_2 \) and \( \epsilon_s \) are the dielectric constants along and perpendicular-
lar to the particle’s symmetry axis and that of the solvent, respectively.

The length of the light path in the Kerr cell was 45 mm; the plane-polarized light originated from a 5 mW He–Ne laser which was additionally polarized. The electric field (up to 3500 V cm$^{-1}$) was pulsed to avoid any excessive heating of the sample, which was carefully thermostated. The temporal changes of the light intensity emerging from the cell were detected by a photodiode and stored in a transient recorder [8].

3. Results and Discussion

Fig. 1 exhibits several interesting properties of the water, AOT/C$_{12}$E$_5$, isooctane microemulsion. The specific electric conductivity was plotted against temperature and shows well pronounced sigmoidal plots, i.e. the existence of system-spanning nanodroplet clusters. They shift towards lower temperatures with increasing amount of C$_{12}$E$_5$. All plots tend to approach an approximately common conductivity level with increasing temperature, although on closer inspection it appears that the more dilute microemulsions with respect to AOT reach a slightly higher conductivity. This observation appears to have some relevance in the discussion of electro-optical Kerr effect results (see later). Of particular interest are the slopes at the inflection points of the sigmoidal conductivity plots, i.e. at the onset of the $\sigma$-percolation. Physically they represent the temperature coefficient of the conductivity (at the onset of percolation), i.e. $(d \log \sigma/dT)_\text{onset}$. The temperature coefficient yields information on the charge transport mechanism in the system-spanning nanodroplet cluster (see Fig. 2). The plot shows that these coefficients decay in the concentration range up to about $x_{C_{12}E_5} \approx 0.1$ and approach a constant value for $x_{C_{12}E_5} > 0.1$. It might be noted in this context that electrolytes in nonpolar media show a marked concentration dependence (subject to the solvent) of the temperature coefficient, whereas aqueous electrolytes display an almost constant temperature coefficient at mean temperatures over a large concentration range [9]. This observation may be interpreted in terms of a changeover of the conduction mechanism: for $x_{C_{12}E_5} < 0.1$ the charge transport occurs via individual nanodroplets, i.e. at least partially in contact with an apolar environment, whereas for $x_{C_{12}E_5} > 0.1$ the conduction proceeds via the nanodroplet cluster in an aqueous environment (bicontinuous?). We shall return to this result later when discussing the electro-optic Kerr effect data.

Fig. 2. Temperature coefficients of specific electric conductivity at onset of percolation versus $x_{C_{12}E_5}$. System as in Fig. 1.
Fig. 3. Critical (percolation) temperature versus molar fraction of C₁₂E₅. System as in Fig. 1. Inset: analogue plot but water/C₁₂E₅/i-C₆H₁₄ microemulsion with AOT added.

water/C₁₂E₅/isooctane interface and AOT monomers in the dissolved state (see inset). The adsorption equilibrium is described by \( \mu^\text{diss}_i = \mu^\text{ads}_i \), where \( i \) is the adsorbing surfactant. Considering the temperature dependence of the chemical potential, we derive for the present purpose

\[
\frac{\partial T}{\partial x_i} = \frac{RT^2}{x_i \Delta H^\text{ads}_i},
\]

where \( \frac{\partial T}{\partial x_i} \) is the slope of the \( T_c-x_i \) plots, \( R \) the gas constant and \( \Delta H^\text{ads}_i \) the heat of adsorption of the respective surfactant. Eq. (3) allows one to derive straightfowardly concentration-dependent heats of adsorption of C₁₂E₅ and AOT at the respective water/surfactant/oil interfaces (Fig. 4).

Two peculiarities are observed. (i) Since the plots of the percolation temperature against mole fraction of C₁₂E₅ consist of two branches, one has to consider two heats of adsorption. These different heats of C₁₂E₅ are perspicuously attributed to different states of the interfaces, i.e. nanodroplets and nonspherical (disks?; see later) structures of different curvatures. In view of the high reliability of temperature measurements, the above conclusions do not appear unreasonable. (ii) The heats of adsorption of C₁₂E₅ and AOT have different signs. AOT can only be adsorbed by supplying energy to C₁₂E₅-covered interfaces (hydrophobization of the interface by C₁₂E₅ ?). The unexpectedly large values of these enthalpies of both C₁₂E₅ and AOT at infinite dilution are probably due to strong interactions between the polyethylene oxide groups of C₁₂E₅ and the sodium ion of AOT [10].

Returning again to Fig. 1, we show that we can extract important information from the lower temperature range regarding the properties of the
aqueous nanoparticles. If this portion of Fig. 1 is plotted on a larger scale, an interesting feature of the mixed surfactant systems shows up (Fig. 5): all \( \sigma-T \) plots within the concentration range \( x_{C_{12}E_5} < 0.1 \) merge into the single \( \sigma-T \) plot which corresponds to the Stokian migration of spherical nanodroplets covered solely by an AOT monolayer. The conductivities in the concentration range \( x_{C_{12}E_5} > 0.1 \), however, decay with decreasing temperature to individual \( \sigma-T \) plots. Sufficiently below the crossing over this group of \( \sigma-T \) plots show a systematic decrease of \( \sigma \) with increasing \( x_{C_{12}E_5} \).

This conductance pattern controlled by the nonionic surfactant concentration is striking. We interpret the smooth conductivity plot (below 300 K) for \( x_{C_{12}E_5} < 0.1 \) by a Stokian transport of uniformly charged spherical nanodroplets. The experimental conductivity can quantitatively be reproduced by the available set of experimental data for nanodroplet concentration, mobility, viscosity and degree of dissociation. This finding hints at an independence of particle shape (and volume) by adding small amounts of nonionic surfactants. Larger concentrations of nonionics \( (x_{C_{12}E_5} > 0.1) \), however, show that the isothermal conductivity decreases with increasing amount of \( C_{12}E_5 \). We conclude accordingly that the nanoparticles are now of a nonspherical shape, which also implies a change of volume since the total amount of surfactant which determines the o/w interface is kept constant. As already mentioned (see Experimental), Stokes law may also be applied in this case and one derives from the ratio of the conductivities of nonspherical and spherical particles (whose size is only determined by the amount of solubilized water) the inverse ratio of the respective radii of these nanoparticles, i.e. \( R_0/R_{\text{eff}} \). The effective radius of the particle (see Experimental) derived from translational motions should agree with the hydrodynamic radius obtained from the rotational diffusion coefficient which can be determined by electrooptic Kerr effect measurements.

From molecular geometry and curvature energy considerations [11] in the case of mixing of surfactants in saturated interfaces, one may conclude ad hoc that a mixture of AOT (which resembles structurally an inverted truncated cone [12] and \( C_{12}E_5 \) (which is of cylindrical or better conical shape with the long axis along the hydrocarbon backbone) tends to form a planar configuration with increasing amount of \( C_{12}E_5 \). We therefore claim the hypothesis that oblate-ellipsoidal (\( \approx \) disk-like) particles are the thermodynamically preferred species. The existence of nonspherical particles is further supported by the observation that for \( x_{C_{12}E_5} > 0.4 \) a lamellar liquid crystalline phase is formed between about 273 and 335 K [above \( x_{C_{12}E_5} \approx 0.4 \) in a water/AOT/\( C_{12}E_5 \) isoctane w/o microemulsion, a lamellar liquid crystalline phase is formed between \( \sim 0 \) and \( > 60^\circ \text{C} \) (experimental observation by Y. Hauger)]. This mixing of surfactants will qualitatively increase the 'fappiness' of the interface by introducing more 'holes' into the monolayer. A quantitative discussion according to the approach of Safran et al. [13] concerning different phases (i.e. spherical, cylindrical or disk-like) appears inappropriate. In this respect, the situation seems considerably more involved compared with two more recent studies where also such structural transitions were investigated [14, 15]. Both papers are, however, essentially concerned with reversed micellar systems. The added water could only be varied in the range of maximum water of hydration and thus it did not form an independent thermodynamic phase (hence no microemulsions were formed). Also, no mixing of surfactants was carried out. In the first paper a nonionic (PDMS) surfactant in cyclohexane was studied which seems to show a sphere–disk transition. The other paper also describes such a shape
transition of reversed aggregates in oil by using divalent metal ion derivatives of AOT. Again, only the water of hydration could be varied. In both cases the considerable advantage was the application of SANS in carrying out these investigations which yielded strong evidence in favor of such transitions. This, however, is the drawback of our system, which changes in an uncontrollable way (see comments under 'Experimental') in replacing \( \text{H}_2\text{O} \) by \( \text{D}_2\text{O} \) and thus did not allow us to use this technique [the system was kindly investigated for us by SANS by D. Steytler (School of Chemical Sciences, University of East Anglia); it turned out, however, that \( \text{D}_2\text{O}/\text{AOT},\text{C}_{12}\text{E}_5/\text{i-C}_8\text{H}_{18} \) is not comparable with \( \text{H}_2\text{O}/\text{AOT},\text{C}_{12}\text{E}_5/\text{i-C}_8\text{H}_{18} \)]. Hence our particular efforts to analyze carefully conductivity and Kerr effect measurements which, however, yields only indirect information regarding this transition.

Static and dynamic Kerr effect measurements were consulted for additional pieces of evidence. We discovered that \( (K_{sp})_{\text{nd} \rightarrow 0} \) passes through zero with very small additions of \( \text{C}_{12}\text{E}_5 \) (\( x_{\text{C}_{12}\text{E}_5} \approx 0.05 \)) where the nanodroplets are still of spherical shape, as discussed above. With larger amounts of \( \text{C}_{12}\text{E}_5 \) the specific Kerr constant increases parabolically (Fig. 6). This would be in line with growing nonspherical nanoparticles [see Eq. (2)]. In previous electro-optic Kerr effect studies of water/AOT/isooctane microemulsions, the specific Kerr constant passed through zero with increasing amount of solubilized water [5]. It was found that \( (K_{sp})_{\text{nd} \rightarrow 0} = 0 \) at \( w_0[= \text{mol H}_2\text{O/mol surfactant} \approx r_w] = 32.7 \). In the present experiment we chose \( r_w = 1 \) (\( w_0 = 25 \))=constant, but varied \( x_{\text{C}_{12}\text{E}_5} \).

From a comparison of the results of both experiments, we conclude that the addition of \( x_{\text{C}_{12}\text{E}_5} \approx 0.05 \) to the water/AOT/isooctane microemulsion is equivalent to increasing the nanodroplet volume by a factor of 1.3, although QLS measurements confirmed no increase in the nanodroplet volume. The most sensitive test, however, is the identical specific conductivities of the nanodroplets even after the exchange of about 10% AOT against \( \text{C}_{12}\text{E}_5 \). We hence have to conclude that the apparent increase in the electrical polarization is due to the presence of \( \text{C}_{12}\text{E}_5 \). A possible clue in favor of such an explanation might be the recently reported increase in the electrical conductivity [16] after solubilization of polyethylene oxide in aqueous nanodroplets. Pentaethylene glycol monoalkyl ether nonionics contain polar headgroups which are chemically identical with POE. These apparently reduce the potential energy barrier of the interfacial counterion mobility (for details of the proposed mechanism, see Ref. [2]).

In dynamic Kerr effect measurements we found again the above-discussed break of the graph on plotting the rotational relaxation time against \( x_{\text{C}_{12}\text{E}_5} \) (Fig. 7). This break is located very close to the previously determined figure of \( x_{\text{C}_{12}\text{E}_5} \approx 0.1 \). If we follow the arguments put forward above and assume an oblate ellipsoid as the most probable particle shape, we may obtain an average value of its characteristic diameter by expanding the frictional coefficient for rotation of oblate ellipsoids of revolution (\( p = a/b < 1 \)).

![Fig. 6. Specific Kerr constant versus \( x_{\text{C}_{12}\text{E}_5} \). System as in Fig. 1.](image)

![Fig. 7. Rotational relaxation time from dynamic Kerr effect measurements versus \( x_{\text{C}_{12}\text{E}_5} \). System as in Fig. 1.](image)
Starting from the general expression of the reciprocal rotational relaxation time \([17]\), i.e.
\[
\tau_{\text{rot}}^{-1} = (k_B T/8 \eta_0 V) r(p),
\]
where
\[
r(p) = 1.5 p^2 (1 - p^2)^{-1} [1 + (1 - 2 p^2)(1 - p^2)^{-0.5} p^{-1} \arctan(1 - p^2) 0.5 p^{-1}],
\]
\(
\eta_0 \) is the viscosity of the dispersion medium and \(V\) is the volume of the dispersed particle, we obtain for \(p \ll 1\)
\[
\tau_{\text{rot}}^{-1} \approx 9 k_B T/16 \eta_0 d^3, \quad d/2 = b,
\]
where \(d\) is the largest diameter of the oblate ellipsoid. In this approximation, \(\tau_{\text{rot}}\) does not depend on the ratio of \(a\) and \(b\).

It is now possible to derive \(d\) from the rotational relaxation time and the remaining axis of the oblate ellipsoid ('thickness' of the 'disk') from the condition that the total surfactant concentration and the total amount of solubilized water are constant.

We take \(R_{\text{eff}}, \sigma\) and \(d\) as the primary experimental results (within the frame of our above assumptions). From the latter we derive \(R_{\text{eff,Kerr}} \approx (\pi d^2 h/4)^{1/3}\), values of which are given in Table 1 as a function of the molar fraction of \(C_{12}E_5\). These values are sufficient to determine the effective hydrodynamic radii of the nanometer-sized particles, \(R_{\text{Kerr}}\). In order to compare these radii with the 'effective' particle radii evaluated from conductivity measurements (see Table 1), one has to consider the possible mean orientation of the migrating particles. Two limiting cases of orientation exist, i.e. the oblate ellipsoids moving broadside-on or edgewise. Thus the effective particle radius is bounded by two limits,
\[
0.566d/2 < R_{\text{eff}} < 0.85d/2\ [18].
\]
A reasonable coincidence is obtained between the results of both experiments if the migrating particles are allowed an average deviation of about 30% with respect to the 'broadside-on' limiting case, i.e. \(0.6R_{\text{Kerr}}\) (cf. columns 1 and 4 in Table 1). In line with these findings, we propose a sphere–oblate ellipsoid (≈ disk)-induced phase transition occurring at \(x_{C_{12}E_5} \approx 0.1\).

Revisiting the above discussion concerning the high-temperature region of the \(\sigma-T\) plots, where we suggested that the conductivity for larger additions of \(C_{12}E_5\) seems to adopt larger values (corresponding to the just mentioned 'disk-like' particles), while the lower concentration region of \(C_{12}E_5\) (where spherical droplets prevail) produces a smaller conductivity, could now be explained by the different composition and thus properties of the monolayer. AOT monolayers containing larger amounts of \(C_{12}E_5\) may tend to fuse when in the percolated state, thus providing a continuous aqueous electrolytic path, in contrast to the AOT-covered nanodroplets to which only small amounts of \(C_{12}E_5\) were added. This is strongly supported by the break of the temperature coefficients of the conductivity at \(x_{C_{12}E_5} \approx 0.1\) as discussed above.

4. Conclusion

A careful and detailed analysis of a multicomponent apolar surfactant system was carried out by conductometric and electro-optic Kerr effect investigations. SANS techniques could not be applied to study the system since the addition of \(D_2O\) changed the system. Interesting and mutual supporting data were derived which were tentatively used to describe the most characteristic feature of the system, i.e. a sphere–oblate ellipsoid (≈ disk)-induced phase transition of nanometer-sized aqueous particles covered by a mixture of ionic and nonionic surfactants.

### Table 1

<table>
<thead>
<tr>
<th>(R_{\text{eff}}, \sigma) (nm)</th>
<th>(R_{\text{eff,Kerr}}) (nm)</th>
<th>(h/R_{\text{eff}}) ((p = a/b))</th>
<th>(R_{\text{eff}} \approx 0.6R_{\text{Kerr}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.9</td>
<td>12.3</td>
<td>0.53</td>
<td>7.4</td>
</tr>
<tr>
<td>8.0</td>
<td>15.0</td>
<td>0.38</td>
<td>9.0</td>
</tr>
<tr>
<td>8.8</td>
<td>16.3</td>
<td>0.35</td>
<td>9.7</td>
</tr>
</tbody>
</table>

\(x_{C_{12}E_5} \approx 0.13, 0.17, 0.22\)

Acknowledgments

The authors are grateful to Y. Hauger for help with the experiments. This work was supported by the Swiss National Science Foundation.
References