

Note

Micelles and reverse micelles in the nickel bis(2-ethylhexyl) sulfosuccinate/water/isooctane microemulsion

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Abstract

The ternary system $\text{Ni}^{2+}(\text{AOT})_2$ (nickel 2-bis[2-ethylhexyl] sulfosuccinate)/water/isooctane presents w/o and o/w microemulsions with a Winsor progression ($\bar{2}\Phi - 3\Phi - \underline{2}\Phi$), without the addition of salt; the “fish diagram” was obtained for $\alpha = 0.5$ and $\gamma = 0.02\text{--}0.22$. Using static and dynamic light scattering the micellar size, the ratio of water to surfactant, and the density of micelles for this system were estimated. In addition, the mean interfacial curvature as a function of temperature was obtained.

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Sodium [bis-2-ethylhexyl] sulfosuccinate ($\text{Na}(\text{AOT})$)/water(w)/oil(o) systems form w/o microemulsions at low surfactant concentration and low temperature; at high temperature, they form o/w microemulsions. These ternary systems usually do not exhibit a three-phase region where microemulsion coexists with water-rich and oil-rich phases at intermediate temperatures. However, the addition of salt as a fourth component induces the formation of a three-phase body at intermediate temperatures [1,2]. The key to understanding this behavior emerges from the recognition that the temperature is the most fundamental field variable controlling the phase behavior of microemulsions [1]. Around the so-called hydrophile–lipophile balance temperature in the “fish diagram,” the affinity of the surfactant toward water and oil is the same. Here, the oil–water interface consisting of a monolayer of surfactant molecules has on the average zero mean curvature [3,4]; a bicontinuous structure is formed in the three phase-body, 3Φ , and in the one-phase microemulsion, 1Φ . When the surfactant concentration increases other phases appear [5]. The roles of surfactant tails and of the

added salts are reasonably well understood in many of these systems; however, the reported phase diagrams differ considerably with respect to the extensions and shapes of the phases. This is because small amounts of residual impurities have a large effect [6–8]. In the last decade, there has been an increasing interest in ternary mixtures of M^{2+} [bis 2-ethylhexyl] sulfosuccinates, $(\text{M}^{2+}(\text{AOT})_2)/\text{w/o}$ [9–14]. Recently, our group presented a survey for three metallic systems, $\text{M}^{2+}(\text{AOT})_2/\text{w/isooctane}$, where $\text{M} = \text{Ni}, \text{Co},$ and Cu , in a wide region of the phase diagram prism [15]. At low surfactant concentration, these metallic systems present a Winsor progression ($\bar{2}\Phi - 3\Phi - \underline{2}\Phi$) without the addition of salt. Here, we present the results of light scattering (LS) for a microemulsion when $\text{M} = \text{Ni}$. This allows to get relevant information about the micellar size and about the mean interfacial curvature for this system.

The most important quantity that controls all structuring processes in a microemulsion is the curvature free energy, described by the Helfrich equation [16]. To deal with this issue, most studies have focused on nonionic alkyloligoglycol ethers surfactants [17] where the mean interfacial curvature, $\langle H \rangle = 1/R_m$ (R_m is the micelle radius) can be tuned by just changing the temperature. In these systems, $\langle H \rangle$ changes

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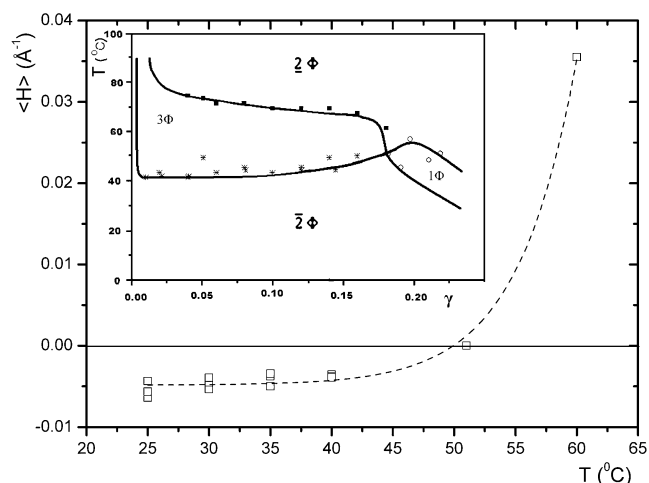


Fig. 1. Mean curvature vs temperature for o/w (2Φ) and w/o (2Φ) microemulsions in the $\text{Ni}^{2+}(\text{AOT})_2/\text{water}/\text{isooctane}$ ternary system vs γ , at $\alpha = 0.5$. The line is a guide to the eye. Inset: “fish diagram” T vs γ with phases 2Φ , 3Φ , 2Φ , and 1Φ .

gradually and nearly linearly with temperature from positive (2Φ) to negative (2Φ), passing through zero for a bicontinuous microemulsion [3]. Qualitatively, two effects support the observed curving tendency of the surfactant film with increasing temperature, hydration of the head groups decreases and oil penetration into the surfactant tails increases. Both effects therefore explain the inversion from o/w to w/o structures.

Our experimental procedures were the same as in our previous work [15]. We used the mass fraction notation to determine concentration in the phase diagram prism [1,15]. Light scattering (LS) experiments were performed in a conventional homemade setup [18], where counts per second and correlation functions were obtained by a multiple-tau correlator. The coherence area was optimized when dynamic LS was done and static light conditions were optimized until pure (0.02 nm) filtered isooctane gave a horizontal line between 30° and 150° .

The inset of Fig. 1 presents a fish diagram obtained for the system under study. The hydrophile–lipophile balance temperature is ~ 324 K. The Winsor progression in this system does not need salt addition. Different stock surfactant

preparations gave the same kind of phase diagram, although there are important variations in the temperature at which the phase changes did occur; however, the sequence of events is exactly the same. Two factors that could be partially responsible for this behavior are (AOT) $^-$ decomposition due to hydrolysis and the possibility that the phases in the diagram of Fig. 1 could be metastable phases. We discussed this problem elsewhere [15].

The LS of microemulsions was measured as a function of the scattering vector, q , at different temperatures and γ values ($\alpha = 0.5$). Light intensity was found to be independent of the scattering angle. In all cases, dynamic LS measurements showed a linear relation between decay rate and q^2 (correlation ≈ 0.97 – 0.99), revealing a diffusive decay. Intensity correlation functions were treated with a constrained regularization method (CONTIN), applying the Siegert relation, to get a continuous distribution of relaxation times that enables the calculation of micellar diffusion coefficients from the peaks of these distributions ($\sigma = 6.4\%$). At low concentrations ($\gamma \leq 0.05$), micellar interaction and hydrodynamic correlations should be low enough to approximate the diffusion coefficient to the Stokes–Einstein diffusion coefficient, D_0 . From here, R_m and $\langle H \rangle$ can be estimated using the Stokes–Einstein equation and using the phase volumes, some physicochemical quantities can be calculated, such as the water pool radius, R_{WP} , $W = [w]/[S]$, the number of micelles N_{mc} , and the micellar volume fraction Φ ; see Table 1. In the case of w/o microemulsions, our calculated values for W are quite close to the estimated values W_{est} using the known relation in Na(AOT) systems $W_{est} \sim R_{WP} (\text{\AA})/1.7$ [9,19]. In the case of o/w microemulsions, LS data are quite difficult to obtain because the microemulsion phase is close to the boiling point. Fig. 1 shows, as far as we know for the first time, the nonlinear variation of $\langle H \rangle$ vs T . The high-temperature point was obtained from a zero-concentration extrapolation to avoid interaction contribution. Here, in contrast to the nonionic systems, the curvature is negative at low T and changes sign close to the hydrophile–lipophile balance temperature to become positive at high T [3]. Here, double-charged ion condensation certainly will modify the electrostatic contribution on bending moduli as temperature increases [20]. This could explain the nonlinear relation between $\langle H \rangle$ and T .

Table 1

Table of results of w/o (low T) and o/w microemulsions (high T)

T (°C)	γ , w/o	$D \times 10^{11}$ ($\text{m}^2 \text{s}^{-1}$)	R_m (Å)	R_W (Å)	W	W_{est}	N_m	Φ
25	0.021	2.94	175	165	100.5	97	7.87×10^{15}	0.060
30	0.021	3.12	177	167	101.8	98	7.57×10^{15}	0.060
25	0.038	3.13	165	154	93.9	91	2.17×10^{16}	0.072
25	0.040	2.91	177	167	101.5	98	1.87×10^{16}	0.129
30	0.040	2.52	220	209	127.5	123	9.46×10^{15}	0.124
25	0.050	2.81	184	173	105.6	102	5.90×10^{16}	0.382
T (°C)	γ , o/w	$D \times 10^{11}$ ($\text{m}^2 \text{s}^{-1}$)	R_m (Å)	R_{OP} (Å)	a_m (Å 2)		N_m	Φ
60	0.040	13.6	41	31	109		1.23×10^{18}	0.16
60	$\gamma \rightarrow 0$	20.0	28	18				

Using the phase volumes, we estimated the head area of the surfactant in the micelle $a_{Ni(AOT)_2} \approx 109 \text{ \AA}^2$. This value is larger than the value 76 \AA^2 from the Na(AOT)/decane/(0.6% NaCl) water system at $\gamma = 0.12$ and $\alpha = 0.50$ obtained by small-angle neutron scattering in the 1Φ phase [4], and to the value 73 \AA^2 obtained from the Na(AOT)/heptane/highly concentrated brine system [21].

Our calculations are based on geometric models where the water or the oil pool volume $= (4/3)\pi R^3$, with an area $= 4\pi R^2 = a_{AOT}N_{AOT}$. Here, the pool radius is $R = R_m - l_{AOT}$, l_{AOT} is the length of the surfactant tail, and a_{AOT} is the area of the $(AOT)^-$ polar head. In w/o micelles, the number of water molecules, N_W , in the water pool volume, V_{WP} , of radius R_{WP} is $N_W = (V_{WP}/\nu_w) - N_c - \pi R_{WP}^2/a_{AOT}$. Here, we took into account the nickel ion volume and the volume of N_c coordinated water molecules. N_{AOT} is the number of surfactant molecules at the pool surface, and ν_w is the molecular volume of water [12]. The number of micelles is $N_m = V_m^w/N_W\nu_w$, $W = N_W/N_{AOT}$, and the volume fraction of micelles is $\Phi = (4/3)\pi N_m R_m^3/V_{ph}$. Here, V_m^w is the volume of the micellar phase (added water less the water-rich phase), and V_{ph} is the phase volume. To get estimates we used the following values for $\nu_w \approx 30 \text{ \AA}^3$, $l \approx 10.5 \text{ \AA}$, and $a_{AOT} \approx 55 \text{ \AA}^2$ [12]. In the o/w micelles, the volume in the oil pool is $V_{OP} = N_o\nu_o$, where N_o is the number of oil molecules in the pool and ν_o is the volume of the oil molecule. Using $N_m = V_m^o/V_{OP}$, $\Phi = (4/3)\pi N_m R_m^3/V_{ph}$, $N_o = V_{OP}/\nu_o$, $N_{AOT} = N_{AOT}/N_m$, where V_m^o is the micellar oil volume (added oil less the oil-rich phase), N_{AOT} is the number of added $(AOT)^-$, and N_m^{AOT} is the number of AOT moieties in the micelle. The area of the surfactant head can

be evaluated with $a_{AOT} = 2\pi R_m^2/N_m^{AOT}$. For our estimates, we used $\nu_o \approx 308 \text{ \AA}^3$ [21].

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