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Electron Spin Echo Modulation Study of Winsor Microemulsions

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Electron spin echo studies have been carried out for a series of x-doxylstearic acid (x-DSA, where x = 5, 10, 16) spin probes in three different sets of samples of a five-component microemulsion (water, toluene, 1-butanol, sodium dodecyl sulfate (SDS), and sodium chloride) selectively deuterated in water, toluene, or 1-butanol. The sequence Winsor I, III, II was obtained by changing the salinity from 0.943×10^{-2} to 3.31×10^{-2} mole ratio, corresponding to 3% and 10% (w/w) in the nondeuterated system. Modulation effects due to interactions of the nitroxide group with water deuteriums, perdeuterated toluene, or 1-butanol have been measured as a function of x and of the brine concentration, S_M. The average probe location and probe conformation in the microemulsions as a function of x are reported. The probe conformations support the presence of oil-in-water and water-in-oil "structures" in Winsor I and Winsor II microemulsions, respectively. The comparison of the deuterium modulation depth magnitude between Winsor I microemulsions and the SDS/water/1-butanol/sodium chloride micellar system, selectively deuterated in the water or butanol, shows at a molecular level that the Winsor I microemulsions and the SDS micellar system have very similar 1-butanol distributions and the same water penetration at the interface. It is also found that toluene penetrates the SDS layer at the microemulsion interface up to 4–5 methylenes from the SDS polar headgroup. The Winsor I to Winsor III phase transition is associated with a consistent decrease of the toluene penetration into the SDS interfacial layer and probably with a variation of the SDS alkyl chains packing and/or conformation. Furthermore, the "oil" region, the "water" region, and the "interfacial" region seem to be well separated for all the microemulsions studied. The butanol is mainly located at the water side of the interface. It is also shown that the interface of bicontinuous microemulsions is little affected by S_M variation.

Introduction

A microemulsion is a stable microstructured fluid that incorporates hydrocarbons, water, surfactants, and often salt and alcohols. Microemulsion systems usually exhibit a wide variety of phase behaviors:[1-5] (1) single phase microemulsion, (2) microemulsion coexisting with excess oily or excess aqueous phase or both (Winsor phase equilibria), and (3) microemulsion coexisting with other structured phases as lyotropic liquid crystals. These phase behaviors have been extensively studied by using several techniques.[6] Most of the information of the structure and dynamics of these systems comes from light scattering, neutron scattering, X-ray scattering, fluorescence, multifield ^{13}C NMR, and Fourier transform pulse-gradient spin-echo nuclear magnetic resonance techniques.[4-13] Previous papers showed that it is possible to obtain information at a molecular level on the interface of micellar and microemulsion systems, by using continuous wave (ESR)[14-22] or pulsed (ESE or ESEM)[23-28] electron spin resonance of nitroxide spin probes. In particular, the polarity and the microviscosity of the micellar and microemulsion interface, as well as the site of solubilization of several additives and the amount of water penetration at the interface of a micelle, have been

reported.[14-28] In this paper we investigated the properties of the interfacial film of Winsor microemulsions[1,2] of the SDS/1-bu-

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TABLE I: Salinity (Salt/Brine), Expressed in Weight/Weight (S) and in Molar Ratio (S_M), for the Microemulsions Investigated

S, % (w/w)	S_M ($\times 10^2$)	S, % (w/w)	S_M ($\times 10^2$)
3.0	0.943	7.0	2.263
4.0	1.266	7.5	2.434
5.0	1.594	8.0	2.606
5.5	1.759	9.0	2.953
6.0	1.926	10.0	3.306
6.5	2.094		

tanol/toluene/H$_2$O/NaCl system. Our investigation followed an approach similar to that of Maldonado et al.[28] The weak magnetic interaction of x-doxylstearic acid spin probes with nuclear spin in its close environment has been measured by ESEM. This technique is very powerful in detecting very weak magnetic interactions,[29] especially deuterium interactions, and can provide information on the microenvironment of a paramagnetic probe. The various components of the microemulsions investigated (water, toluene, and 1-butanol) were perdeuterated to monitor modulation effects due to interaction of the nitroxide group of the doxylstearic acid probe with deuterium in the "oil", water, or elsewhere. From these measurements the location of the nitroxide spin probe in the microemulsion system, as well as the distribution and location of the "oil", water, and alcohol, at the interfacial film in each of the Winsor microemulsions has been determined. SDS micellar solutions with and without NaCl and 1-butanol, as a model of the interface of Winsor I microemulsions, have also been studied by ESEM of x-DSA probes. Quantitative results of the components at the interface, i.e., the alcohol/surfactant molar ratio, have been obtained from the analysis of the ESEM results.

Experimental Section

Materials and Methods. x-DSA probes (with x = 5, 10, and 16, where x labels the position of the doxyl group along the stearic acid alkyl chain) were obtained from Molecular Probes, Eugene, OR, and used as received. Toluene, 1-butanol (1-BuOH), sodium dodecyl sulfate (SDS), and sodium chloride were obtained from Merck (purity >99%). Deuterated 1-butanol-d_{10} and toluene-d_8 (purity >99%) were obtained from Aldrich. D$_2$O (purity >99%) was obtained from Carlo Erba, Milan, Italy. H$_2$O was bidistilled and purified of any other impurities by a Milli-Q water system (Millipore). All the components have been used without further purification.

Sample Preparation. Three series of samples have been prepared as follows: (1) D$_2$O, toluene, 1-butanol, SDS, and sodium chloride (D$_2$O/Winsor phase); (2) water, toluene-d_8, 1-butanol, SDS, and sodium chloride (toluene-d_8/Winsor phase); (3) water, toluene, 1-butanol-d_{10}, SDS, and sodium chloride (1-butanol-

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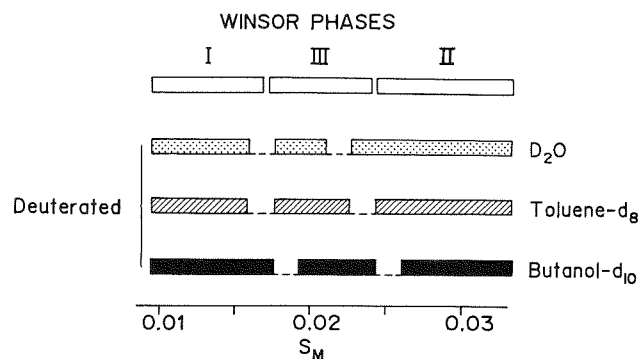

Figure 1. Winsor phase domains as a function of salinity S_M for the nondeuterated and deuterated microemulsions. The phase behavior is defined according the Winsor classification.[1]

d_{10}/Winsor phase). The alcohol/surfactant and oil/surfactant mole ratios were 7.73 and 74.21, respectively, for all the samples. The three series of samples have been prepared by changing the salinity, S_M, defined as salt/brine mole ratio, from 0.943 × 10^{-2} to 3.31 × 10^{-2}. The brine/surfactant molar ratio was in the range 368–351 depending on the salinity. These molar ratios correspond in the nondeuterated samples to a composition by weight of 46.8% (brine), 47.25% (toluene), 1.99% (SDS), and 3.96% (1-butanol) and a salinity from 3% to 10%. In Table I is given the correspondence between the salinity values in weight/weight (S) and in molar ratio (S_M); in both cases the salinity is defined as salt/brine. The samples have been stabilized at 22 ± 0.1 °C for the time necessary to attain the equilibrium (more than 1 week). When the equilibrium was attained, the phases have been separated and kept at 22 °C. No further phase separation was observed. The following SDS micellar solutions were prepared: (1) SDS/D$_2$O, (2) SDS/D$_2$O/NaCl, (3) SDS/D$_2$O/NaCl/1-BuOH, (4) SDS/D$_2$O/1-BuOH, (5) SDS/H$_2$O/1-BuOH-d_{10}, and (6) SDS/H$_2$O/1-BuOH-d_{10}/NaCl, where the SDS concentration is 0.1 M and NaCl salinity is 3% w/w. An alcohol/surfactant molar ratio in the range 1–2 has been investigated to reproduce the ESEM spectra of the Winsor I microemulsion interface. Stock solutions of the probes were prepared in chloroform. Films of the probe generated by evaporating the solvent in nitrogen atmosphere in Suprasil quartz tubes (2-mm i.d. × 3-mm o.d.) were dissolved in the microemulsion and in the micellar solution. The tubes were sealed to prevent evaporation losses. The final probe concentration was 1 × 10^{-4} M, about 1/1000 the SDS concentration in the microemulsions[10,30] or in the SDS micellar solutions. The probe addition does not perturb the equilibrium and does not change the phase diagram. Furthermore, this concentration has been demonstrated not to perturb the microemulsion structure.[31] The samples were gently mixed and equilibrated at 22 °C for at least 3 days and frozen rapidly by plunging in liquid nitrogen. Two-pulse electron spin echo spectra were recorded at a temperature of 4.2 K on a home-built spectrometer by using 20-ns exciting pulses.[32]

Results

The phase diagram was investigated by visual observation of the three sample series with water, oil, or alcohol selectively deuterated. Figure 1 shows the phase diagram of the three deuterated series versus the S_M. The phase behavior is defined according to the Winsor classification.[1,2] Winsor I, III, and II correspond respectively to two-phase, three-phase, and two-phase systems with an oil/water microemulsion in equilibrium with an excess oily phase, a bicontinuous microemulsion in equilibrium with an excess aqueous and oily phases, and a water/oil microemulsion in equilibrium with an excess aqueous phase. We recall

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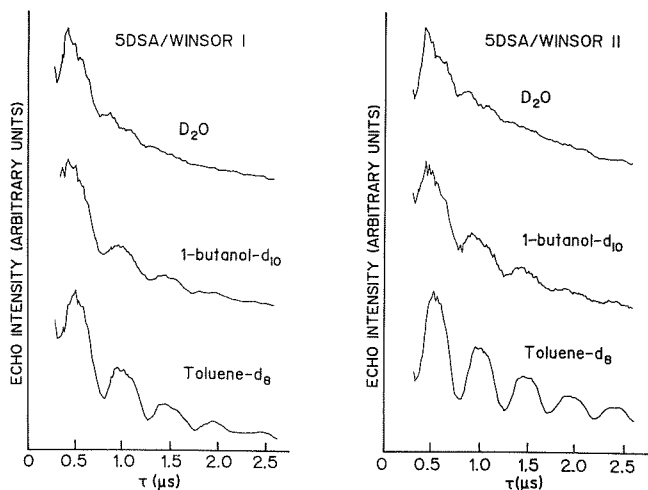
Figure 2. Two-pulse electron spin echo decay envelopes for 5-doxylstearic acid spin probe in Winsor I and Winsor II microemulsions with deuterated water, 1-butanol, or toluene. The baselines have been offset vertically to avoid overlap.
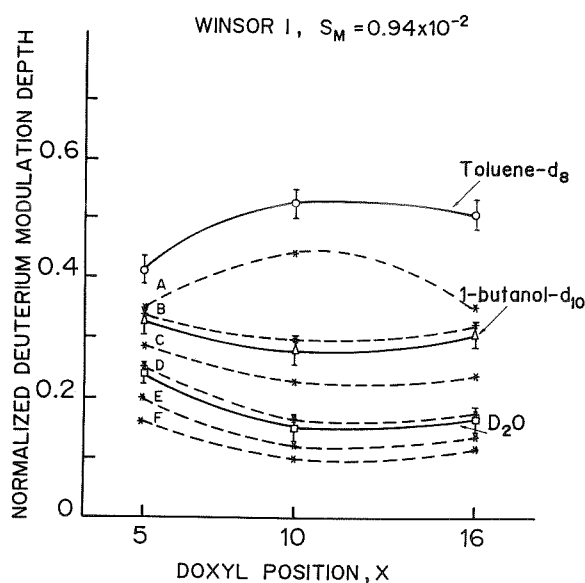

Figure 4. Dependence of normalized deuterium modulation depths on the doxyl group position (x) in the stearic acid alkyl chain for Winsor III microemulsions with deuterated water, 1-butanol, or toluene.

Figure 3. Dependence of normalized deuterium modulation depths on the doxyl group position (x) in the stearic acid alkyl chain for Winsor I microemulsions with deuterated water, 1-butanol, or toluene, and SDS micellar solutions with salt and butanol added. (A) $SDS/H_2O/BuOH$-d_{10}; (B) $SDS/H_2O/1$-$BuOH$-$d_{10}/NaCl$; (C) $SDS/D_2O/1$-$BuOH$; (D) $SDS/D_2O/1$-$BuOH/NaCl$; (E) SDS/D_2O; (F) $SDS/D_2O/NaCl$. See also Experimental Section.

Figure 5. Dependence of normalized deuterium modulation depths on the doxyl group position (x) in the stearic acid alkyl chain for Winsor II microemulsions with deuterated water, 1-butanol, or toluene.

that the salinity ranges of the nondeuterated samples for the Winsor I, III, and II phase equilibria[9,10,33] are 3–5.3%, 5.4–7.4%, and 7.5–10% (w/w), or in mole ratio 0.94×10^{-2}–1.69×10^{-2}, 1.73×10^{-2}–2.40×10^{-2}, and 2.43×10^{-2}–3.31×10^{-2}. These phase transitions have been accurately defined as the phase transition regions have been extensively studied.[30,34,35] Since in this paper we were not interested in an accurate characterization of the phase transition regions, the minimum step in salinity between two different samples was about 0.2×10^{-2}. In the limit of resolution of the salinity variation, the Winsor I to Winsor III phase transition for deuterated water or toluene samples is in the same salinity (S_M) range of the nondeuterated system ($1.59 \times$
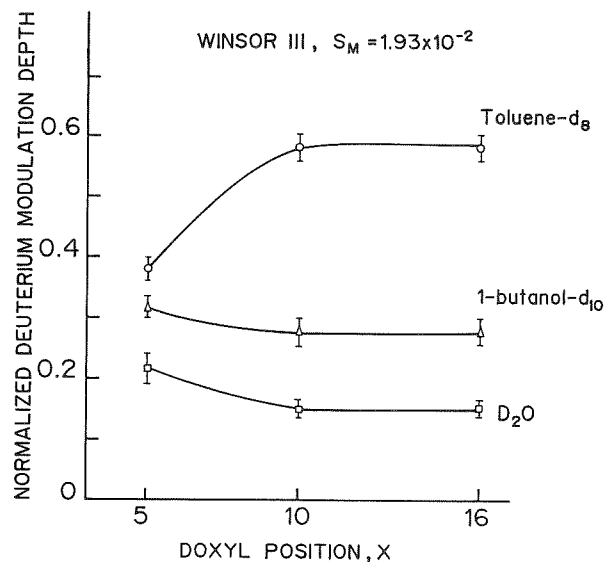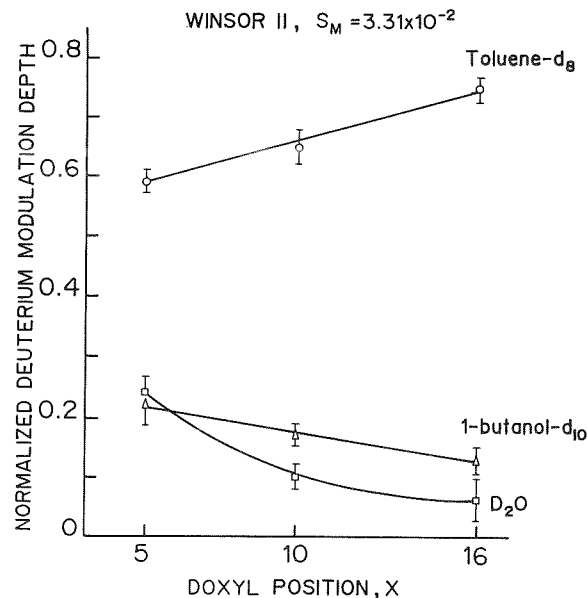
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10^{-2}–1.76×10^{-2}). In the presence of deuterated alcohol the transition is shifted to higher salinity (1.76×10^{-2}–1.93×10^{-2}). The Winsor III to Winsor II phase transition for deuterated toluene is in the same salinity range of the nondeuterated system (2.26×10^{-2}–2.43×10^{-2}), while it is shifted to a lower (2.09×10^{-2}–2.26×10^{-2}) or higher (2.43×10^{-2}–2.61×10^{-2}) salinity range in the presence of deuterated water or deuterated 1-butanol, respectively. The sample deuteration does not dramatically change the phase diagram; in fact, Winsor I, III, and II phase equilibria versus the salinity increase are observed in the same order as in nondeuterated samples. However, as a small variation of the phase equilibria boundaries has been observed, a structural investigation is in progress to test whether structural parameters or simply physical constants are responsible for the phase diagram changes.

Figure 2 shows typical two-pulse ESE spectra of 5-DSA in the Winsor I and Winsor II microemulsions with different deuterated components. The echo decay curves show detectable modulation with a period of 0.5 μs corresponding to the deuterium Larmor frequency. Similar ESEM patterns have been obtained with the other probes for all the samples studied. Some ESEM spectra showed an additional weak proton modulation with period of 0.08
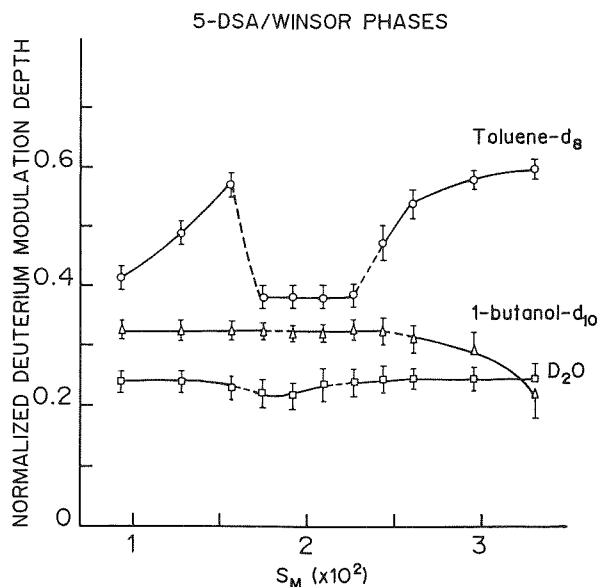
Figure 6. Dependence of the normalized deuterium modulation depth for 5-DSA probe as a function of S_M for microemulsions with deuterated water, 1-butanol, or toluene.

Figure 7. Dependence of the normalized deuterium modulation depth for 10-DSA and 16-DSA probes as a function of S_M for microemulsions with deuterated water, 1-butanol, or toluene.

μs. Figures 3–5 show the variation of the normalized deuterium modulation depths, computed as previously described,[23–29] as a function of the doxyl position, x, and of the deuterated microemulsion components, for the Winsor I, III, and II microemulsions, with $S_M = 0.94 \times 10^{-2}$, 1.93×10^{-2}, and 3.31×10^{-2}, respectively. Similar trends have been obtained for the other samples investigated, and they are typical of Winsor I, III, and II microemulsions. For comparison the modulation depth profiles for several SDS micellar solutions are depicted in Figure 3 as well. The alcohol/surfactant molar ratio is 1.5 for all the micellar solutions reported in Figure 3. A 1-butanol/SDS molar ratio from 1 to 2 has been investigated. However, since the modulation depth is about constant in this concentration range (see also ref 23), the alcohol concentration at the micellar interface cannot be deduced with a greater accuracy. In addition, the modulation depth values for the system $SDS/H_2O/1\text{-}BuOH\text{-}d_{10}$ are the same as those reported in ref 36 for the system $SDS/H_2O/1\text{-}BuOH\text{-}d_9$, where a 0.2 M alcohol concentration was used. Finally, Figures 6 and 7 show the deuterium modulation depths as a function of the salinity S_M and of the deuterated components of the microemulsions studied.

Discussion

Electron spin echo (ESE) spectroscopy is a pulse version of electron spin resonance (ESR) and enables the detection of very weak electron–nuclear dipolar hyperfine interactions. These interactions can be detected up to about 5–6 Å from the unpaired electron and can be analyzed in terms of the number and distance of the magnetic nuclei interacting with the unpaired electron.[29,37] This technique has been successfully employed to study the micellar interface of ionic and nonionic surfactants, mixtures between cationic and anionic surfactants, and the effect of added aliphatic alcohol, urea, and crown ethers to micellar solutions.[23,27,38] In such complex systems it is not felt reasonable to interpret the deuterium modulation in terms of average distances and numbers of interacting nuclei. Therefore, for these systems an average strength of interaction is defined, as measured by the depth of the modulation, between a paramagnetic probe and deuterium located in specific positions in the colloidal system (surfactant alkyl chain, polar headgroup of the surfactant, water solvent, or elsewhere). A typical example is reported in a recent paper where

three different deuterium locations have been used in the study of a micellar system:[38] (i) micelle deuterated in the surfactant polar headgroup; (ii) micelle deuterated in the core region (surfactant alkyl chain); (iii) nondeuterated surfactant in deuterated water. The comparison of the deuterium modulation depth in these systems allows determination of the probe location and conformation in the micelle and the amount of water penetration into the micelle surface. In liquid solutions the anisotropic hyperfine interactions, which are responsible for the modulation appearance of dipolar interactions, are averaged out by rapid molecular tumbling, and consequently modulation can only be observed in rapidly frozen solutions. It has already been established[23–27,38–41] that upon fast freezing micellar structure is retained. Several specific experiments indicate that upon fast freezing the structure is retained in microemulsion as well. Jahn and Strey[42] showed by freeze fracture electron microscopy that the structure of several microemulsion systems is retained; their results are in agreement with observations obtained by other techniques.[43–45]

x-Doxylstearic acids are sparingly water soluble and are comicellized with the surfactant molecules.[46] Previous studies showed that the carboxyl group of these spin probe molecules is located at the polar micellar surface leaving the hydrophobic chain, containing the doxyl group, to seek a location in the micelle according to the hydrophobic–hydrophilic and steric forces acting in the system.[23–27,47] Two limiting probe conformations are possible for the x-doxylstearic acid spin probes solubilized in micelles: an all-trans conformation and a bent or U-folded conformation.[47] When the probe presents an all-trans conformation, increasing x moves the doxyl group further away from the surface of the micelle. Therefore, if the water solvent is deuterated, one expects a decrease in the normalized deuterium modulation depth. On the other hand, a decrease of the deuterium modulation depth from $x = 5$ to 10 and an increase at $x \approx 12$ and 16 indicates that the doxyl probe bends near $x \approx 10$ and 12, thus having a U-shape introduced by few gauche links. The

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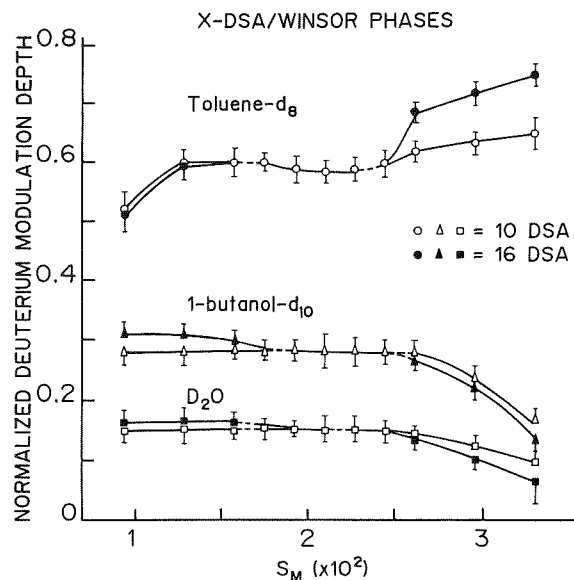
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conformation of the x-DSA probe solubilized in several anionic, cationic, and nonionic micellar systems has been reported to be always bent or U-folded.[23-28,47-49] A different behavior is found in reverse micelle and vesicles. Hiff and Kevan[50] showed that the normalized deuterium modulation depth of x-DSA in several phosphatidylcholine vesicles decreases monotonically as x increases from 5 to 16. Similar results were reported for isooctane/ AOT/water reverse micelles.[51] This indicates that the probe conformation can be correlated to the presence of direct or inverted aggregates in solution and therefore can indicate the kind of aggregate in solution.

Figures 3-5 show the trend of the normalized deuterium modulation depth for the Winsor I, III, and II microemulsions as a function of the doxyl position along the stearic acid chain and different deuterated regions of the microemulsions. The analysis of Figure 3 (Winsor I microemulsion) shows that the deuterium modulation is weak when the deuterium is located in the water, while it is quite large when the deuterium is located in the toluene. Intermediate values are found with 1-butanol-d_{10}. The shape of the curves of the deuterium modulation depth as a function of x-doxyl position indicates that the doxylstearic acids are bent in the Winsor I microemulsion as they are in direct micelles. This is in agreement with the presence of oil-in-water aggregates as demonstrated by different techniques.[7,8,30,33-35] It is interesting to compare the normalized deuterium modulation depth obtained for deuteriums located in different regions of the microemulsion with the modulation obtained for SDS micellar systems with or without NaCl and 1-butanol added which represents a reference system of oil-in-water droplets.

In Figure 3 are reported the results obtained with a 0.1 M SDS micellar solution in the presence of different additives and as a function of the doxyl position. The first consideration is that the addition of 3% NaCl to SDS 0.1 M micellar solutions leads to a decrease of the deuterium modulation depth, indicating a decrease of the water penetration at the micellar surface. This result can be easily explained by considering that the addition of sodium chloride decreases the area per surfactant polar headgroup[52,53] of about 12 Å^2. The above and previous ESR results[19] show that the decrease in the area per polar headgroup is associated with the expulsion of water molecules from the micelle interface with a decrease of the polarity of the interface itself.

It has been reported that the addition of different types of alcohols including 1-propanol, 2-propanol, 1-butanol, 1-pentanol, and 1-octanol[23,48,49] to SDS micelles produces an increase of the water penetration at the micelle interface by intercalating in the headgroup region of the micelle and by opening up the headgroup region to stronger water interactions which depends on the alcohol concentration. This is clearly shown from the increase of the deuterium modulation depth in passing from the system SDS/D$_2$O to SDS/D$_2$O/1-BuOH. It is interesting that the addition of NaCl to the SDS/D$_2$O/1-BuOH system produces a decrease of the deuterium modulation depth to values very close to that of the microemulsion system. This supports that the interface of the D$_2$O/Winsor I microemulsion is very similar to that of the SDS/D$_2$O/NaCl/1-BuOH system.

A further proof of this is obtained from the deuterium modulation analysis arising from deuterated butanol. Kevan and co-workers[48,49] found that for the system SDS/H$_2$O/1-BuOH-d_9 the deuterium modulation depth as a function of the doxyl position in x-doxylstearic acid spin probes reaches a maximum around x = 10 and 12, meaning that 1-BuOH intercalates in the headgroup region of the micellar surface. The addition of sodium chloride (see Figure 3) leads to a different trend of the modulation depth

as a function of the doxyl position with a minimum around x = 10. Since the 10-DSA probe is located deeper[47-49] inside the micelle interface than the 5- and 16-DSA probes, we deduce that 1-BuOH moves toward the water phase upon the addition of NaCl. Furthermore, the values of the deuterium modulation depth obtained for SDS/H$_2$O/1-BuOH-d_{10}/NaCl are close to the values obtained for the 1-BuOH-d_{10}/Winsor I microemulsion as the values for SDS/D$_2$O/1-BuOH/NaCl are close to the values for D$_2$O/Winsor I microemulsions. This indicates that the interfacial distributions of 1-BuOH and water in the Winsor I microemulsion and in the micellar system, used to reproduce the microemulsion interface, are very similar.

The symmetrically inverse shapes of the curves reported in Figure 3 for the deuterated toluene versus the deuterated 1-butanol or D$_2$O are also consistent with the different deuterated regions of the microemulsion being separated as expected for a droplet model with a smooth interface in which toluene is located in the core and 1-BuOH at the water side of the interface.[47] Furthermore, in analogy to previous studies,[38,47] the above result suggests that little or no mixing is present at the interface between toluene and 1-butanol; i.e., the interfacial butanol is mainly partitioned in the water side of the microemulsion aggregate. In summary, from the analysis of the trend of the normalized deuterium modulation depth for the Winsor I microemulsion the following was deduced: (i) the x-DSA probe has a bent conformation, which is characteristic of this probe solubilized in a "direct" micelle and supports the presence of a direct aggregate in the microemulsion; (ii) the interface of the Winsor I microemulsion is very similar to the interface of a SDS micelle in the presence of NaCl and 1-BuOH. The above picture of a Winsor I microemulsion agrees with that of the pseudophase model,[9,10,54,55] i.e., separated "core", interface, and dispersed phases, composed of oil (with 4% 1-BuOH), alcohol, and surfactant in molar ratio about 1 and brine (with 2% 1-BuOH), respectively. Also, it agrees with a previous study in which SDS added in very small amount to a H$_2$O/ NaCl/1-BuOH/toluene two-phase system (aqueous and oily phase) recalls toluene from the oily phase to give a dispersion of oil droplets stabilized by an alcohol and surfactant interfacial film in aqueous medium (with some butanol).[11]

The modulation depth profile for D$_2$O and 1-BuOH-d_{10} in Winsor III microemulsion (see Figure 4) is very similar to that of Winsor I microemulsions, indicating that the probe experiences the same environment on the water side of the interface, whereas for toluene-d_8/Winsor III microemulsions the variation between x = 5 and x = 10 or 16 is higher than that of Winsor I microemulsions. Furthermore, the deuterium modulation depth for 10-DSA and 16-DSA in Winsor III microemulsions has the same value, supporting that the probe in these microemulsions is less bent than in Winsor I. As with Winsor I, the different profiles for the deuterated toluene versus deuterated 1-BuOH and D$_2$O agree with the different deuterated regions of the microemulsion being separated.

A different behavior is found in Winsor II microemulsions (see Figure 5). In this microemulsion the deuterium modulation depth increases monotonically when toluene is deuterated while the reverse occurs when 1-butanol or water is deuterated. This trend is in agreement with an extended probe conformation and suggests that the different deuterated regions are well-separated, as found for Winsor I and III microemulsions. Furthermore, the probe conformation agrees with the presence of water in oil "structures", as demonstrated by different techniques.[4-13]

Another consideration that emerges from the analysis of the deuterium modulation depth is that all the x-DSA probes "see" deuterium in all the deuterated regions and for all the Winsor microemulsions investigated (see Figures 6 and 7). However, the magnitude of the D modulation is a function of the doxyl position and of the salt concentration. We recall that the magnitude of

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the deuterium modulation depth depends on the number of the interacting nuclei and their distance from the spin probe. An increase in the modulation depth can be interpreted as a movement of the probe toward the region with a relatively higher concentration of deuterated species or an increased penetration of deuterated species toward the probe region. A careful analysis of the modulation depth is necessary to discriminate between these two possibilities.

The analysis of the deuterium modulation depth for the Winsor I and Winsor III microemulsions gave two important results: (i) The D modulation of the 5-DSA is independent of the salinity when water or butanol is deuterated. When toluene is deuterated, a strong increase of the D modulation is present as a function of the salt concentration in the Winsor I microemulsion, followed by a decrease of the modulation magnitude in the Winsor III microemulsion. (ii) The D modulation magnitude of Winsor I microemulsions is in the order 5-DSA $\ll$ 16-DSA $\leq$ 10-DSA when the deuterated region is toluene while the reverse occurs when the deuterated region is water or butanol. This result shows that 5-DSA is located closer to the interface than 10-DSA and 16-DSA are. As already mentioned, the D modulation magnitude, arising from D_2O or 1-BuOH, of Winsor I microemulsions is very similar to that of the SDS micellar system in the presence of alcohol and sodium chloride, meaning that the 5-DSA probe has a similar location in SDS micelles and Winsor I microemulsions. This location has been reported to be close to the SDS polar headgroups at the α or β methylene.[19,48,49] The invariance of the D modulation of 5-DSA as a function of S_M with deuterated water or deuterated butanol demonstrates that the salt addition does not change the probe location at the microemulsion interface. The high deuterium modulation depth value found for toluene-d_8 ($>$0.4) shows that the SDS layer is consistently penetrated by toluene at the interface. If we consider that ESEM can measure realistic modulation signals up to 5–6 Å and that the nitroxide group of the probe is located close to the polar headgroup of SDS, we conclude that toluene penetrates (in Winsor I microemulsion) up to 4–5 methylenes from the surfactant polar headgroup. This also provides support at a molecular level of previous light scattering results in which it is suggested that the SDS chain can penetrate into the oil of the droplet in Winsor microemulsions.[30]

Furthermore, the strong increase of the toluene-d_8 modulation depth found in Winsor I microemulsion as S_M increases shows that toluene has moved toward the microemulsion interface. Since this variation is not coupled to a redistribution of alcohol or water molecules (1-BuOH-d_{10} and D_2O modulation depths are constant), we must conclude that the increase in S_M also produces a change in the SDS alkyl chain conformation to allow toluene to penetrate the SDS layer. This is probably related to an increase of the gauche and even bent conformation of the SDS alkyl chain and or to a different alkyl chain packing. A similar behavior has been reported for micellar solutions when the sodium counterion is exchanged with lithium or tetramethylammonium.[48,49,56]

The decrease of the toluene D modulation present for 5-DSA in passing from the Winsor I to the Winsor III phase is consistent with a decrease of the toluene concentration close to the SDS polar headgroup and probably is associated with a change of the conformation of the SDS alkyl chain, supporting theoretical models based on geometrical assumptions,[57,58] in which an extended conformation of the SDS alkyl chain is considered. The comparison of the 5-DSA/toluene-d_8 modulation with 10-DSA/toluene-d_8 or 16-DSA/toluene-d_8 modulations shows that the same trend is present for Winsor I microemulsions, while no increase as a function of S_M in the modulation is present for Winsor III microemulsions. This supports that the phase transition (Winsor I to Winsor III) is associated with a different toluene distribution (and therefore SDS alkyl chain conformation and/or packing) at the interface of the Winsor I and Winsor III microemulsions.

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However, this effect does not interest all the "SDS monolayer" at the interface. A rough calculation, based on the fact that ESEM can detect modulations up to a distance of about 5–6 Å and considering that the probe has an all-trans conformation up to $x \approx 9$ and 10, shows that the toluene distribution in Winsor I (with NaCl $\approx$ 5%) and Winsor III microemulsions is very similar from the eighth–ninth carbon atom of the SDS alkyl chain, but it is quite different close to the SDS headgroups. Previous X-ray and neutron scattering investigations[12,13] indicate that the area per surfactant polar headgroup is about 60 Å^2, the thickness of the polar headgroups is 5 Å, and the hydrocarbon chain thickness is about 10 Å. These results suggest that the SDS hydrocarbon chain is consistently penetrated by toluene.

Finally, the analysis of the modulation depth measured for 5-DSA in the Winsor II microemulsion supports that the increase in S_M is associated with an increase of the toluene penetration of the SDS layer (increase of the toluene D modulation and no variation of the water modulation as S_M increases) and to a decrease of butanol concentration at the interface. Unfortunately, it is not possible to determine the extent of 1-butanol concentration decrease along the microemulsion interface, since 10-DSA and 16-DSA show an increase in the deuterium modulation arising from the toluene-d_8 associated with a decrease of water and butanol modulation. This can be due either to a decrease of water and butanol and to an increase of toluene at the microemulsion interface or simply to the shift of the probe toward the oil phase. Another conclusion arising from the analysis of the ESEM results of Winsor II microemulsions is that the interfacial 1-butanol, as already reported for the Winsor I microemulsions, is mainly partitioned at the water side of the microemulsion interface.

Furthermore, the invariance of the normalized modulation depths in the Winsor III microemulsions as a function of S_M provides evidence at a molecular level that the interface of these microemulsions is little affected by S_M variation.

Conclusions

The results obtained from the analysis of the electron spin echo modulation depth of doxylstearic acid spin probes, due to doxyl probe interaction with deuteriums in selectively deuterated microemulsion components (toluene, water, or 1-butanol), show that the doxyl probes solubilize in the microemulsions with the doxyl group at the oil/water interface of the microemulsion. The trend of the deuterium modulation depth for x-DSA shows that little or no mixing is present between toluene and 1-butanol or water and that the stearic acid chain of the probe has a bent or U-folded conformation in Winsor I microemulsions. An all-trans conformation is present in Winsor II microemulsions. These conformations indicate the presence in the microemulsion of direct (oil in water) or reversed (water in oil) "structures". Furthermore, the deuterium modulation magnitude of x-DSA in the Winsor I microemulsion supports that the distribution of toluene, butanol, and water at the microemulsion interface is very similar to that of a SDS micelle in the presence of NaCl and 1-butanol with a 1-butanol/SDS molar ratio between 1 and 2. This supports the view that oil-in-water microemulsions can be considered as "oil" swollen micelles.

Modulation effects of x-DSA in Winsor I and as a function of sodium chloride concentration (S_M) are in agreement with an increase of toluene penetration of the SDS alkyl chains as S_M increases. It is found that toluene penetrates the SDS alkyl chain up to 4–5 methylenes from the SDS polar headgroup. The phase transition Winsor I to Winsor III is related to a decrease of the toluene concentration in the SDS alkyl chains probably associated with a change of the alkyl chains conformation and/or packing. This effect is present at least up to the eighth–ninth carbon atom on the SDS chain.

The decrease of the deuterium modulation depth of the 5-DSA probe in the 1-butanol-d_{10}/Winsor II system, due to S_M increase, seems to support that the alcohol concentration decreases at the microemulsion interface as the salinity increases. However, the decrease in the deuterium modulation could be due to a possible probe movement at the microemulsion interface toward the oil

phase. This possibility cannot be excluded for Winsor II microemulsions.

Another conclusion from the ESEM analysis is that the "oil" region of the microemulsions seems to be well separated from the "water" region with little or no mixing between toluene and butanol.

Furthermore, the invariance of the normalized modulation depths in the Winsor III microemulsions as a function of S_M provides evidence at a molecular level that the interface of these microemulsions is little affected by S_M variation.