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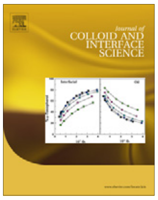

FT-IR and ^{1}H NMR studies of the state of solubilized water in water-in-oil microemulsions stabilized by mixtures of single- and double-tailed cationic surfactants

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ABSTRACT

The structure of solubilized water in water-in-*n*-heptane aggregates stabilized by mixtures of single- and double-tail quaternary ammonium surfactants, namely didodecyldimethylammonium chloride/dodecyltrimethylammonium chloride (DDAC/DTAC) or didodecyldimethylammonium bromide/dodecyltrimethylammonium bromide (DDAB/DTAB) was studied by two noninvasive techniques, ^{1}H NMR and FT-IR. In the former, the chemical shift data, δ_{obs}, were used to calculate the so-called deuterium/protium fractionation factor, φ_M, of the aggregate-solubilized water and were found to be unity. In the FT-IR study, upon increasing water/surfactant molar ratio, *W*, the frequency, ν_{OD}, of the HOD species decreases, while its full width at half height and its area increase. The results obtained from both techniques indicate that the water appears to be present as a single nano-phase and the structure varies continuously as a result of increasing *W*. In addition, the effect of changing the counter-ion (Br^- or Cl^-) on ^{1}H NMR and FT-IR results was investigated. In spite of the known difference in the dissociation of these counter-ions from micellar aggregates, this was found not to affect the state of solubilized water. This report gives further insight into the contradictory scientific debates on the structure of water in the polar nano-cores of microemulsions.

1. Introduction

Certain surfactants aggregate in organic solvents of low polarity and dielectric constant, for example, hydrocarbons and chlorohydrocarbons, forming reverse or inverse micelles. One of their most important properties is that they solubilize water well above its solubilization limit in the organic solvent. Such solubilization of water results in the formation of an aqueous nanodroplet surrounded by a monolayer of surfactant molecules. The molar ratio [water]/[surfactant], *W*, is usually used to designate the aggregates present in solution, either as reverse micelle, RM, or water-in-oil microemulsion, W/O μE. In RMs, the amount of solubilized water is ⩽ the amount necessary to hydrate the surfactant head-group. Solubilization of water over and above this *W* threshold results in the formation of a W/O μE [1,2]. Knowledge of the state of solubilized water is important because this bears on the applications of these species, for example, in solubilization, catalysis of chemical reactions [3,4] and in size and polydispersity of nanoparticles synthesized in the microemulsion [5].

The characteristics of this water have been investigated by using different techniques [6–10]; the results have been explained by models that pictures the water as present in "layers" of different structures. For example, In the two-layer model [11,12], water is present in two layers, the first contains water molecules that interact strongly with the surfactant head-group, this is hydration or bound water, with different physical properties (organization, mobility, microviscosity, conductivity, etc.) from those of bulk water [13–15]. The second type has physical properties similar to those in bulk water and hence called (bulk-like). In the three-layer model [16], the water located at the interface is considered to be of two types, trapped water located between the chains of the surfactant and water that solvates the head-groups [17]; a four-layer model has also been advanced [18–20]. The suggested four types of water as follows: W_{bound} (water molecules tightly bound to the surfactant head-group); $W_{intermediate}$ (distorted H-bonded water species); bulk-like water, $W_{bulk\text{-}like}$; interfacial water, $W_{interfacial}$, (lies between hydrophobic interfacial tails, which is unfavorable environment for water). This can be water in-transit during the breakdown and fusion of the droplet, which is a well-known phenomenon in microemulsion.

Depending on the type of surfactants, some researchers have determined the number of water molecules required for the hydration of the surfactant head-group to be in the range of 3–6 molecules [21,22]. In a previous work, we have shown that for

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water-in-oil (*W*/*O*) microemulsions of spherical droplets with minimum droplet attractive interaction, the system conductivity depends on the droplets size, and hence *W*, where it shows an increase below a certain droplet size after which a monotonic decrease in conductivity observed [23]. This increase at low *W* is referred to the incomplete hydration of the surfactants head-groups and counter-ions, while the decrease at large *W* is referred to the dominant of the droplet diffusion on the conductivity behavior [23].

Most studies on the structure of the water solubilized in reverse aggregates were based in two noninvasive techniques, ^{1}H NMR and FT-IR [24–26]. Using ^{1}H NMR, the deuterium isotope effect on the chemical shift of solubilized H_2O–D_2O mixtures at constant *W* was investigated, which has been used to calculate the deuterium/protium "fractionation factor," φ_M, whose value determine the structure of water within the aqueous nanodroplet [27]. Using FT-IR, the dependence of the properties of ν_{OD} of solubilized HOD on *W* was studied, and peak deconvolution was carried out in order to determine the types of water present.

Herein, we focus on studying the structure of water solubilized by reverse aggregates of mixtures of DDAX/DTAX ($X = Br^-$ or Cl^-) in *n*-heptane, and its dependence on the nature of the counter-ion by two noninvasive techniques, ^{1}H NMR and FT-IR. The water structure of *W*/*O* microemulsion stabilized in such cationic mixtures with different counter-ions (namely Br^- and Cl^-) in pure *n*-heptane was not studied before. The results of both techniques indicate that reverse aggregate-solubilized water does not seem to coexist in layers of different structures; its properties change continuously as a function of increasing *W*. In other words, there is a gradual change in the structure rather than a sharp one from surface to bulk properties.

2. Experimental

2.1. Materials

All chemicals were purchased from Merck or Aldrich and are of high purity (>99%). The DDAC surfactant was purchased from Wako (Japan, 99%). DTAC was purchased from Fluka, and DTAB was purchased from Sigma. DDAB was synthesized as described elsewhere [28] by the reaction of *N*,*N*-dimethyldodecylamine with the *n*-dodecylbromide in ethanol:

$$C_{12}H_{25}N(CH_3)_2 + C_{12}H_{25}Br \rightarrow (C_{12}H_{25})_2(CH_3)_2N^+Br^-$$

The product was purified by crystallization from ethanol and several washing with cold diethyl ether. The surfactant was dried at 50 °C, under reduced pressure, over P_4O_{10} until constant weight. Its purity was >99.5%, as determined by gas chromatography (Bruker 3900). Elemental analysis (as non-hygroscopic perchlorates) gave satisfactory results, ICP-MS (Varian 820-MS).

2.2. Solubilization limits and microemulsion preparation

The water/*n*-heptane microemulsions stabilized by DDAC/DTAC or DDAB/DTAB were prepared as follows: appropriate amounts of water were added to the surfactants and oil mixture to produce μEs. The water solubilization limits (minimum and maximum) of the microemulsion were determined by visual inspection n after leaving the samples overnight in waterbath at 25 °C. Based on the solubilization limits, the *W* values were selected to be in the range 22–30 for DDAB/DTAB system and 36–42 for that of DDAC/DTAC.

Microemulsions contain the following solubilizates: (pure) H_2O, for recording the background of the FT-IR experiment; 4% D_2O in H_2O, for measuring the effect of *W* on ν_{OD}; 75% D_2O in H_2O, (pure) H_2O and (pure) D_2O for the determination of the effect of *W* on δ_{obs} and the determination of φ_M. Effort has been made to ensure that these microemulsions contain the same amounts of surfactant and solvent, and equivalent amounts of (pure) H_2O, (pure) D_2O, or a mixture of H_2O and D_2O, respectively. Typical difference in weight between a pair of matched microemulsions was $\leqslant$0.1%. This matching procedure has been followed in the preparation of each sample prepared thereafter.

2.3. Characterization

2.3.1. FT-IR spectroscopy

The surfactant solution was at concentration of 0.20 M. The cell was ZnSe (0.05 mm), and the exact path length was found to be 0.055 mm as calculated by fringe method [29].

FT-IR spectra were recorded with a JASCO FT-IR-6300 spectrophotometer. The ν_{OD} band is superimposed on a finite background, which could be approximated with the spectrum of 100% H_2O in the ν_{OD} spectral region. Therefore, the reference sample at each *W* was a matched microemulsion sample of the same *W* for the studied sample, but the aqueous H_2O/D_2O mixture replaced by pure H_2O. Band deconvolution was carried out using the commercial software Origin.6, Microcal software Inc.

2.3.2. ^{1}H NMR spectroscopy

The surfactant solution was of concentration of 0.20 M. A Bruker Avance-600 NMR spectrometer was used. The spectra were recorded at 25.0 °C. The "water" employed in the determination of the effects of *W* on chemical shift δ_{obs} was a mixture of H_2O–D_2O, 25: 75%, by volume. The spectrometer probe temperature was periodically monitored; values of δ_{obs} (after 10 min in the sample compartment for thermal equilibration, measured relative to internal tetramethylsilane, TMS) were within the digital resolution limit.

2.3.3. Dynamic light scattering

The particle size of the water nanodroplets of a microemulsion was determined by using a dynamic light scattering instrument Model no: ZEN3500 from Malvern Instruments Ltd. The light source used was a 532 nm, 50 mW green laser; the μE samples were double filtered through 0.22-μm Millipore microfilter; the cylindrical measurement cell was washed with μE solution. Measurements were taken at 25°, and the intensity data were processed by using the appropriate software (DTS 5/nanoapplications). Essentially, the instrument measured the diffusion coefficient (*D*) of the dispersed droplets and evaluated the hydrodynamic radius (r_h) in terms of the Stokes–Einstein equation:

$$r_h = \frac{kT}{6\pi\eta D} \tag{1}$$

where η, *k*, and *T* are the viscosity of the medium, the Boltzman constant, and the absolute temperature, respectively.

3. Results and discussion

3.1. Solubilization limits and the role of counter-ion

The difference between the solubilization limits at 25 °C of the studied DDAB/DTAB and DDAC/DTAC microemulsions was clearly identified. Before stating such difference, it is useful to introduce here the so-called packing parameter, *p*, which is the ratio of the area available per the surfactant hydrophobic part to that available per the hydrophilic part ($p = v/al$ [30] where *v* is the volume of the hydrophobic tail of the amphiphile, *a* is the area available for its hydrophilic head-group and *l* the length of its tail). Partially