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Confinement of chiral molecules in reverse micelles: FT-IR, polarimetric and VCD investigation on the state of dimethyl tartrate in sodium bis(2-ethylhexyl) sulfosuccinate reverse micelles dispersed in carbon tetrachloride

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ABSTRACT

The state of D and L-dimethyl tartrate confined within dry sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles dispersed in CCl_4 has been investigated by FT-IR spectroscopy, polarimetry, and vibrational circular dichroism (VCD). Measurements have been performed at 25 °C as a function of the solubilizate-to-surfactant molar ratio (R) at a fixed AOT concentration (0.158 M). The analysis of experimental data is consistent with the hypothesis that both enantiomers of dimethyl tartrate are mainly entrapped in the reverse micelles and located in proximity to the surfactant head-group region. The formation of this interesting self-organized chiral nanostructure involves some changes of the typical H-bonding of dimethyl tartrates in the pure solid state or as monomers dispersed in CCl_4 attributable to the establishment of specific solubilizate/surfactant head-group interactions and confinement effects.

1. Introduction

It is well known that solutions of reverse micelles can solubilize many kinds of molecules. This is because these systems are characterized by the coexistence of a multiplicity of domains: the bulk apolar solvent, the so-called palisade layer constituted by the surfactant alkyl chains, the hydrophilic region formed by the surfactant polar head groups and the internal micellar core. Hydrophobic molecules are largely dispersed in the apolar medium and micellar palisade layer, ionic and polar substances are entrapped within the hydrophilic micellar core and/or among the surfactant head groups while amphiphilic solutes are partitioned between bulk solvent and reverse micelles where they are preferentially located, opportunely oriented, between the head-group domain and the micellar palisade layer. However, the specific site of the solubilizate does not depend only from its nature but also from its size and shape as well as on the structural and dynamic properties of reverse micelles. In addition, type and surfactant concentration, nature of the counterion and apolar solvent strongly influence the hosting capability of the micellar aggregates [1–4].

Further investigations on this subject have emphasized that few small-size hydrophilic molecules distributed among several reverse micelles do not cause significant changes of micellar structural and dynamic properties. On the other hand, marked changes on the size, shape and molecular organization of micellar aggregate can be expected when a big molecule or many small-size molecules are entrapped within the reverse micelle. In the latter case, the solubilization of finite amounts of amphiphilic substances leads to mixed aggregates of oriented solubilizate/surfactant molecules; while polar and ionic substances can form a separate internal hydrophilic core or a mixed cluster composed by the solute and the surfactant head groups [5,6].

Indeed, it has been found that the solubilization of increasing amounts of vitamin E in lecithin reverse micelles causes a progressive decrease of the micellar size and the formation of mixed vitamin E/lecithin aggregates while the addition of cyanamide determines an unidimensional growth of AOT and lecithin reverse micelles and the formation in the micellar core of a mixed cluster constituted by cyanamide molecules and surfactant head groups [7,8].

It is worth to mention that the properties of molecules confined within reverse micelles are different from those of isolated

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molecules or in the pure bulk state and these properties can be opportunely modulated by changing some external parameters such as the solubilizate-to-surfactant molar ratio, temperature and nature of the system components [9].

Taking into account the steeply increasing theoretical and practical interest devoted to self-assembled nanostructures, the evaluation of the real potentialities of solutions of reverse micelles to produce and stabilize organized nanoclusters of hydrophilic substances could be of utmost importance to open the door to new and interesting technological applications of solute/surfactant/apolar solvent systems [5,8].

Moreover, from a theoretical point of view, these systems are also interesting because they give the opportunity to study solubilization and structural arrangement of finite amounts of hydrophilic solid substances within the reverse micellar core or the surfactant head-group nanodomain, size and shape control of molecular clusters in confined space and adsorption effects on the cluster properties.

In order to extend our knowledge on this field and to better understand the molecular details responsible of the solubilization power of reverse micellar systems, in the present work it has been investigated the confinement of two model chiral molecules, D and L-dimethyl tartrate as a function of the solubilizate-to-surfactant molar ratio (*R*). The study has been performed using as surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT), and CCl_4 as solvent.

The state of confined dimethyl tartrates has been investigated by FT-IR, vibrational circular dichroism (VCD) spectroscopies and polarimetry. It has been amply proved that FT-IR is well suited to gain information simultaneously on the environments of spatially separated moieties of both solubilizate and surfactant molecules and consequently on the structural arrangement of solubilizate containing reverse micelles. VCD is quite sensitive to conformational changes of chiral molecules, induced for example by different solvents. In the case of chiral molecules in direct micelles or vesicles VCD has been used for peptides [10] and proteins [11].

2. Experimental

(−)-(2*S*,3*S*)-Dimethyl tartrate (dimethyl-D-tartrate or DDT) and (+)-(2*R*,3*R*)-dimethyl tartrate (dimethyl-L-tartrate or DLT) were Fluka products (optical purity >99%) and used without further purification. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT, Sigma, 99%, racemic mixture) was dried under vacuum for several days before use. To remove residual traces of water, solutions of AOT in CCl_4 (Riedel-de Haën, 99.8%) were gently stirred for several days in the presence of activated type 4A molecular sieves (Fluka, beads of 4 Å pore size). Solutions at various solubilizate-to-surfactant molar ratios (*R*) were prepared by adding the appropriate amounts of AOT/CCl_4 solutions to a weighed quantity of DDT or DLT.

While D and L-dimethyl tartrate have low solubility in CCl_4 (0.040 M for both enantiomers at 25 °C), the highest *R* value which can be reached in 0.158 M AOT/CCl_4 solutions in the presence of solubilizate crystals is $R = 1.9$ for DDT and $R = 1.4$ for DLT. This evidence of a different behavior of D and L enantiomers is somewhat at odds with all other findings of this work: in particular no difference has been seen by chiroptical techniques.

On the other hand, in absence of solubilizate crystals, dimethyl tartrates can be solubilized up to $R = 4$ in 0.158 M AOT/CCl_4 solutions at 25 °C giving samples sufficiently stable to allow their FT-IR and VCD investigation. This interesting supersaturation effect indicates that confinement of hydrophilic substances within reverse micelles effectively influences the homogeneous nucleation process inhibiting the crystal growth and precipitation of thermodynamically unstable samples.

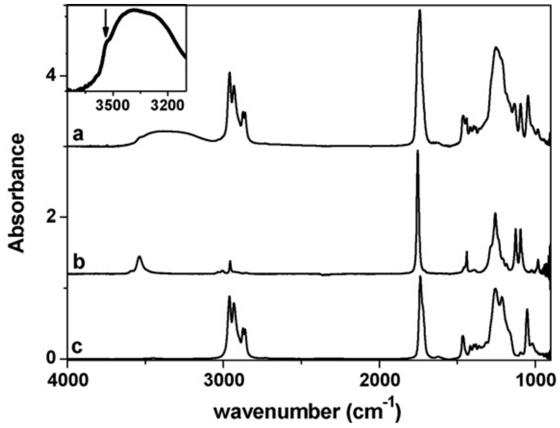

Fig. 1. Infrared spectra of (a) DDT/AOT/CCl_4 ([AOT] = 0.158 M, $R = 1.0$; (b) DDT/CCl_4 ([DDT] = 0.04M); (c) AOT/CCl_4 ([AOT] = 0.158 M) systems in the 900–4000 cm^{-1} frequency range. The inset shows the enlarged OH band of DDT in AOT/CCl_4 solution.

FT-IR spectra of all liquid samples were recorded with solvent compensation in the spectral region 900–4000 cm^{-1} using a PerkinElmer (Spectrum BX) spectrometer and a cell with CaF_2 windows. The FT-IR spectra of solid D and L-dimethyl tartrate were recorded using a pressed disk of the compound mixed with KBr powder. All measurements were collected at 25 °C with a spectral resolution of 2 cm^{-1}.

VCD spectra in the mid-IR region were taken in 0.05 and 0.2 mm path length BaF_2 cells using a JASCO FVS4000 FTIR instrument equipped with an MCT detector; 4000 scans were taken, with 4 cm^{-1} resolution. The spectra were recorded for both enantiomers, and mirror image appearance was obtained for them.

Optical rotation measurements have been performed at 25 °C on a JASCO P-1010 polarimeter at sodium D line and using a 1 dm optical path cell.

3. Results and discussion

A typical spectrum of dimethyl-D-tartrate/AOT/CCl_4 system in the frequency range 900–4000 cm^{-1} is shown in Fig. 1. For comparison, the spectra of dimethyl-D-tartrate/CCl_4 and AOT/CCl_4 systems are also shown. All the observed bands can be attributed to the functional groups of dimethyl-D-tartrate (DDT) and AOT and their assignments, made according to the literature, are collected

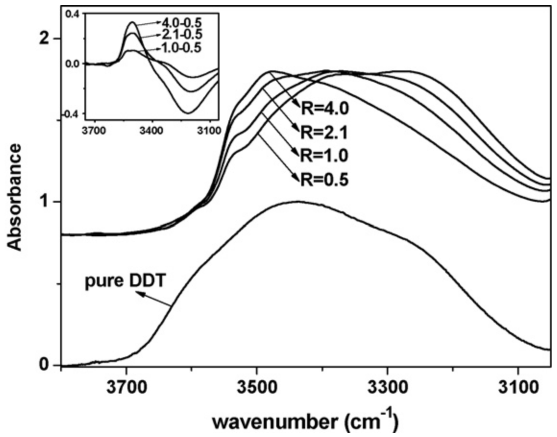

Fig. 2. Comparison between the normalized OH stretching bands of solid DDT and those of DDT/AOT/CCl_4 system at various *R* values. The inset shows the difference spectra obtained by subtracting spectrum at $R = 0.5$ to that of the other DDT/AOT/CCl_4 samples.