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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.

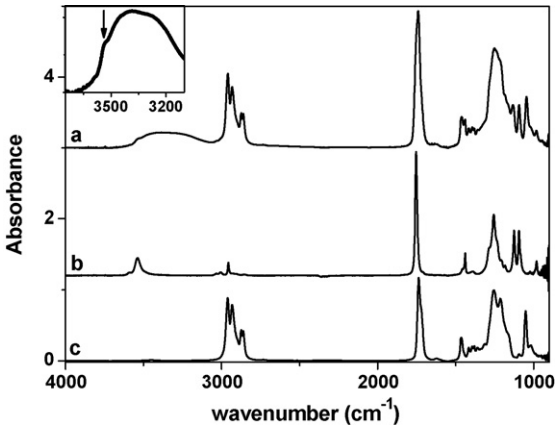

Fig. 1. Infrared spectra of (a) DDT/AOT/CCl_4 ([AOT] = 0.158 M, R = 1.0; (b) DDT/CCl_4 ([DDT] = 0.04M); (c) AOT/CCl_4 ([AOT] = 0.158 M) systems in the 900–4000 cm^{-1} frequency range. The inset shows the enlarged OH band of DDT in AOT/CCl_4 solution.

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

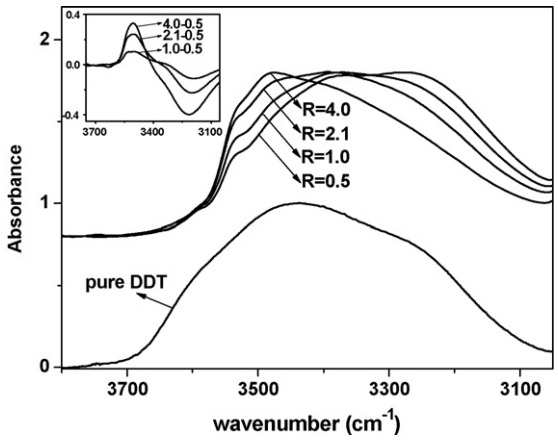

Fig. 2. Comparison between the normalized OH stretching bands of solid DDT and those of DDT/AOT/CCl_4 system at various R values. The inset shows the difference spectra obtained by subtracting spectrum at R = 0.5 to that of the other DDT/AOT/CCl_4 samples.

Table 1
Infrared frequencies of the functional groups of dimethyl-D-tartrate and AOT in the 1000–4000 cm^{-1} frequency range and their assignments

DDT in CCl_4	Solid DDT	DDT in DDT/AOT/CCl_4	AOT in DDT/AOT/CCl_4	Assignment
3539, 3592 sh				ν(OH) intramolecularly H-bonded
	3600–3000	3600–3000		ν(OH) intra and intermolecularly H-bonded
3006			2961	$\nu_{as}(CH_3)$
			2932	$\nu_{as}(CH_2)$
2956				$\nu(C^*H)$
			2874	$\nu_s(CH_3)$
			2861	$\nu_s(CH_2)$
1754	1748	1752	1736	ν(CO)
			1130–1310	$\nu_{as}(SO_3^-)$ + stretch of ester linkage
			1050	$\nu_s(SO_3^-)$

in Table 1 together with the band assignments of dimethyl-D-tartrate in the pure solid state [8,12]. Similar data concerning dimethyl-L-tartrate (DLT) have not been reported because they are indistinguishable from those of DDT.

From the spectra of Fig. 1 it can be seen that the DDT and AOT bands are more or less affected when both are present in the solution, unveiling direct interaction between DDT and reverse micelles. The most significant bands, which will be analyzed here in detail, are those due to the stretchings of OH, CO and SO_3^-.

3.1. OH stretching band

It is noteworthy that dimethyl-D-tartrate in a dilute CCl_4 solution, i.e., in the monomeric state, gives a sharp absorption at 3539 cm^{-1} with a shoulder at 3592 cm^{-1} assigned to the stretching vibrations of intramolecularly H–bonded OH groups. In particular, these absorptions are due to the stretching vibration of OH groups that are hydrogen bonded to either C=O or O–CH_3 groups attached to the vicinal chiral carbon [12,13].

On the other hand, when dimethyl-D-tartrate is solubilized in 0.158 M AOT/CCl_4 solutions, the OH band appears broadened and red-shifted suggesting extensive intermolecular H-bonding which, being unconstrained by intramolecular tensions and enhanced by cooperative effects, allows to establish stronger H-bonds as well as to widen the spectrum of differently hydrogen bonded DDT populations [14]. This finding can be taken as a clear indication that DDT is entrapped in the polar domain of the AOT reverse micelles leading to strong DDT/DDT and DDT/AOT interactions. The same behavior has been observed by analyzing the spectra of DLT in AOT/CCl_4 solutions.

However, a closer inspection of the OH band of the confined DDT (see inset of Fig. 1) reveals the occurrence of a spectral feature at 3539 cm^{-1} which can be taken as a clue that part of DDT is dispersed as monomers in the bulk solvent. In order to estimate the fraction of these molecules, we have evaluated the area (A_f) of the OH contribution at 3539 cm^{-1} in terms of Gaussian component of the entire OH band. Then, the fraction of DDT or DLT monomers (X_f) dispersed in the bulk solvent was calculated by

$$X_f = \frac{0.02A_f}{0.158RA_m} \quad (1)$$

where A_m is the area of the OH component at 3539 cm^{-1} of 0.02 M DDT or DLT in CCl_4 and 0.158R is the overall molar concentration of the solubilizate. For all R values and for both enantiomers we have found that $X_f \approx 0.08$ indicating that only a small fraction of the chiral molecules are dispersed in the bulk solvent.

The R dependence of the OH stretching bands of DDT dissolved in AOT/CCl_4 solutions, obtained by subtracting the spectrum

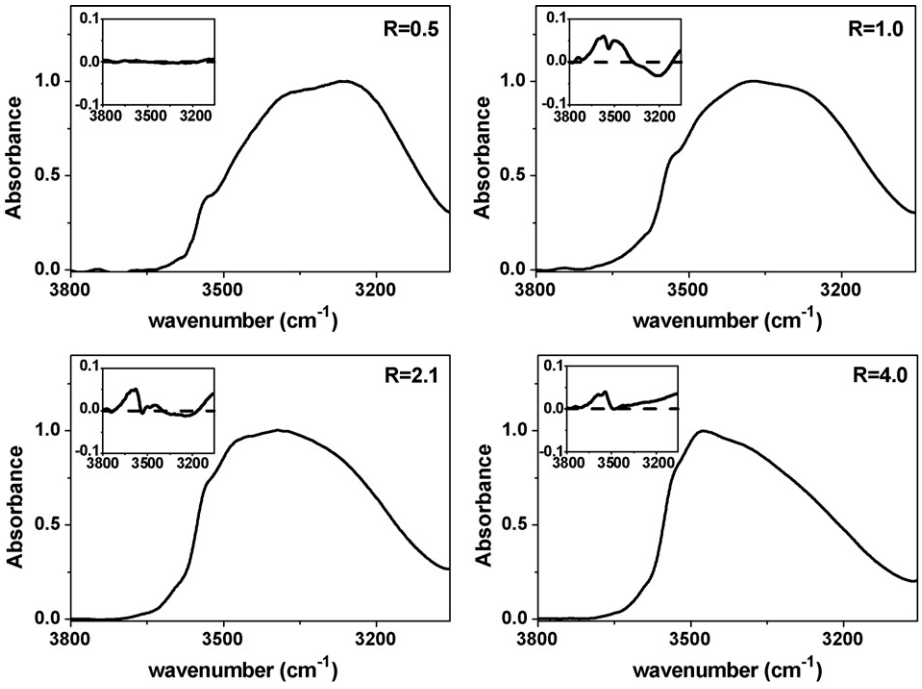

Fig. 3. Normalized OH stretching bands of DDT/AOT/CCl_4 at the R values shown in each panel. In the insets, the difference spectra (DDT/AOT/CCl_4 − DLT/AOT/CCl_4) are shown.

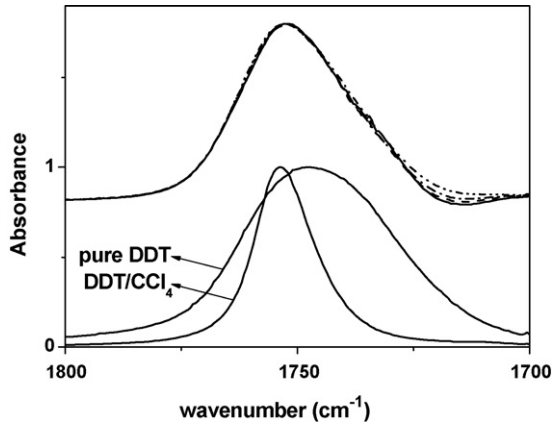

Fig. 4. Normalized CO stretching bands of solid DDT, DDT/CCl_4 ([DDT] = 0.04M) and DDT/AOT/CCl_4 system at various R values ([AOT] = 0.158 M; R = 0.5 solid line; R = 1.0 dashed line; R = 2.1 dashed–dotted line; R = 4.0 dashed–dotted–dotted line).

of AOT/CCl_4 solution and normalized to the same height of the band maximum is shown in Fig. 2. For comparison, the spectra of dimethyl-D-tartrate in the pure solid state are also shown. It can be noted that the OH bands are progressively blue-shifted by increasing R and that, notwithstanding this shift, appreciable spectral differences with respect to the band of pure DDT can be observed. This behavior can be rationalized by hypothesizing that the first DDT molecules are accommodated in the micellar head-group domain so that they form strong H-bonds with the surrounding hydrophilic groups of AOT. Further addition of DDT molecules involves their location in less comfortable sites where DDT/AOT head groups and/or DDT/DDT interactions characterized by less strong intermolecular H-bonds are established. However, taking into account that the OH band of pure DDT is not approached even at the higher R value, the formation of a well-defined internal core composed by DDT molecules can be ruled out. This picture is further circumstantiated by the difference spectra reported in the inset of Fig. 2 obtained by subtracting the normalized OH band at R = 0.5 from those of DDT/AOT/CCl_4 samples at larger R values. It can be noted that by increasing the R value the contribution occurring at about 3500 cm^{-1} increases at the expenses of the contribution occurring at about 3200 cm^{-1}. Similar conclusions can be drawn by analyzing the normalized OH stretching bands of DLT in CCl_4, AOT/CCl_4 solutions and in the pure state.

In order to closely compare the OH stretching bands of DDT and DLT in AOT/CCl_4 solutions, we have reported in each panel of Fig. 3 the normalized bands of DDT at various R values and in the insets the difference spectra (DDT/AOT/CCl_4 − DLT/AOT/CCl_4) at the same R values. An inspection of the insets shows the occurrence of only very small and uncorrelated departures from zero which could be reasonably attributed to minute differences of the water traces present in each pair of enantiomers.

3.2. CO stretching band of D and L-dimethyl tartrate

The DDT CO stretching bands, obtained by subtracting the spectrum of AOT/CCl_4 solution from those of DDT/AOT/CCl_4 samples and normalized to the same height of the CO band maximum, are shown in Fig. 4. For comparison, the normalized CO bands of DDT in CCl_4 and in the pure solid state are also reported. Apart small differences occurring at about 1715 cm^{-1}, it is noteworthy that, by increasing R, no significant variation of the band position and shape occurs. This implies that the environment probed by CO groups of DDT confined in the reverse micelles does not change significantly with R. On the other hand, the small spectral changes observed at about 1715 cm^{-1} can be reasonably attributed to minor perturbation of the environment of the CO group of the AOT β chain induced by the presence of increasing amount of DDT in the reverse micelles [15,16]. Moreover, it can be noted that the frequency at the band maximum (1752 cm^{-1}) and the width at half height (28 cm^{-1}) of dimethyl-D-tartrate confined in AOT reverse micelles are intermediate between that in CCl_4 (1754 and 15 cm^{-1}) and in the pure solid state (1748 and 39 cm^{-1}). This finding emphasizes the peculiar state of DDT confined in reverse micelles confirming that the largest

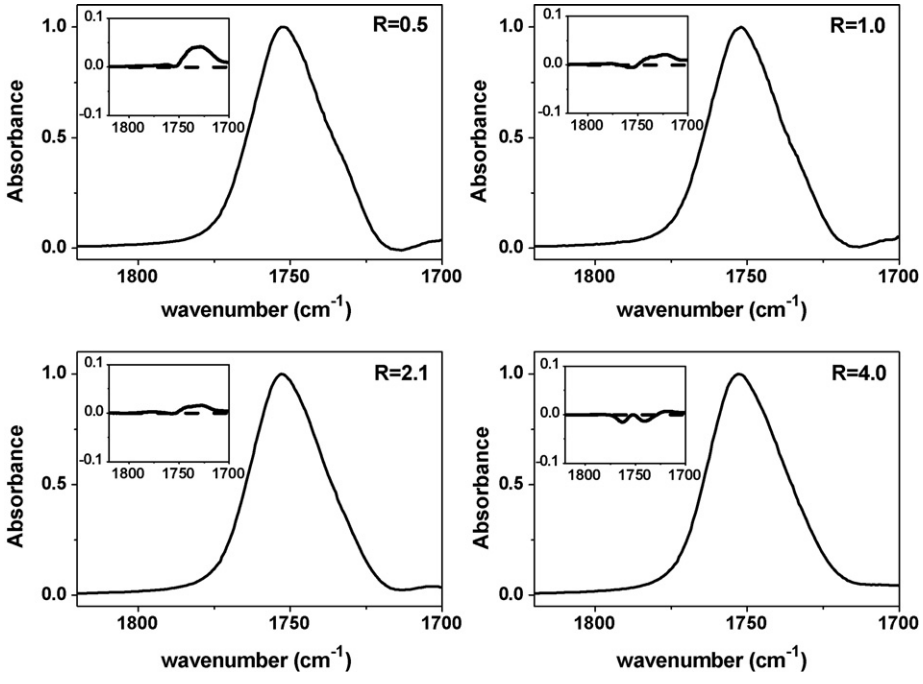

Fig. 5. Normalized CO stretching bands of DDT in DDT/AOT/CCl_4 at the R values shown in each panel. In the insets, the difference spectra (DDT/AOT/CCl_4 − DLT/AOT/CCl_4) are shown.

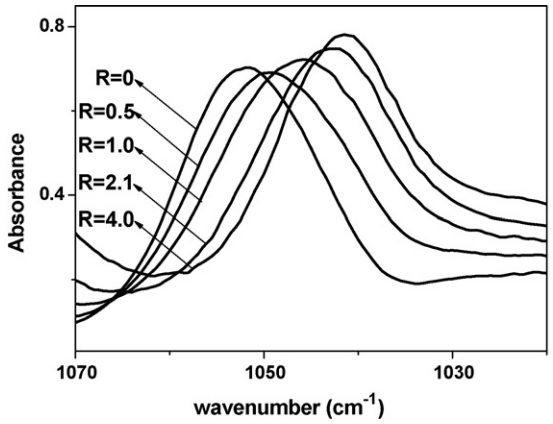

Fig. 6. AOT SO_3^- stretching bands in DDT/AOT/CCl_4 system at various R values.

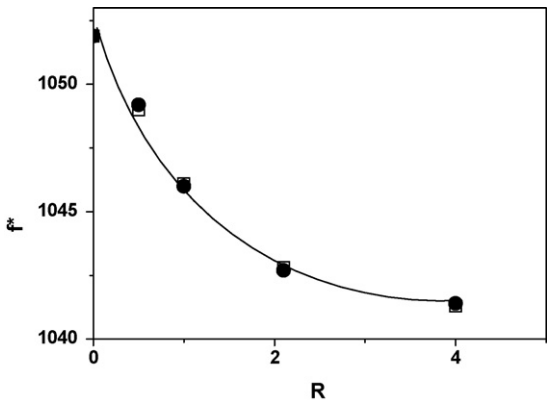

Fig. 8. f^* values of the AOT SO_3^- head-group stretching band for the DDT/AOT/CCl_4 (●) and DLT/AOT/CCl_4 (□) systems as a function of R.

amount of DDT is entrapped in the reverse micelles and that its CO groups are engaged in interactions with the OH groups of surrounding DDT molecules and/or with the hydrophilic head groups of AOT. The similar behavior has been observed by analyzing the CO stretching band of DLT in AOT/CCl_4 solutions. Moreover, as it is shown in the insets of Fig. 5, apart minor changes observed at about 1715 cm^{-1} no significant difference between the CO band of the two enantiomers has been detected implying that the CO groups of both compounds experience the same local environment.

3.3. AOT SO_3^- stretching band

The band maxima of the AOT SO_3^- symmetric stretching absorption in DDT/AOT/CCl_4 samples display a progressive shift to lower frequency as R increases together with an intensity enhancement only at the higher R values (see Fig. 6). The observed trend indicates a progressive increase of the fraction of AOT SO_3^- groups engaged in tartrate–surfactant head-group interactions whereas the behavior of the band intensity reveals that these interactions do not affect significantly the dipole moment of the SO_3^- oscillators, except for the supersaturated samples. Moreover, as it is shown in the insets of Fig. 7, no significant difference between the normalized AOT SO_3^- bands of samples containing the two enantiomers at the same R is observed, implying that the AOT SO_3^- group does not distinguish between the enantiomer type. The dependence of the frequency (f^*) at the band maximum with R for both solubilizates is depicted in Fig. 8. It can be noted that, after an initial rapid decrease, the f^* value trends to a plateau. This behavior is similar to that shown by cyanamide when it is confined within AOT reverse micelles and similarly it makes possible to state that solubilizate/surfactant interactions mainly occur between the OH group of DDT or DLT and the SO_3^- surfactant ionic head groups tending to the complete saturation at the higher R [8,17].

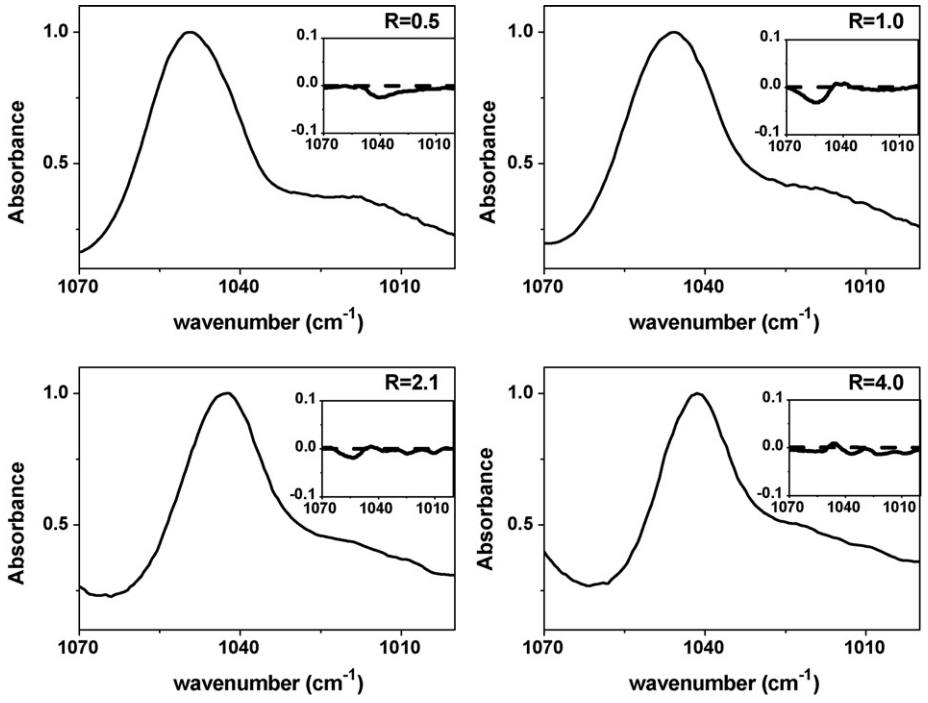

Fig. 7. Normalized AOT SO_3^- stretching bands in DDT/AOT/CCl_4 system at the R shown in each panel. In the insets, the difference spectra (DDT/AOT/CCl_4 – DLT/AOT/CCl_4) are shown.

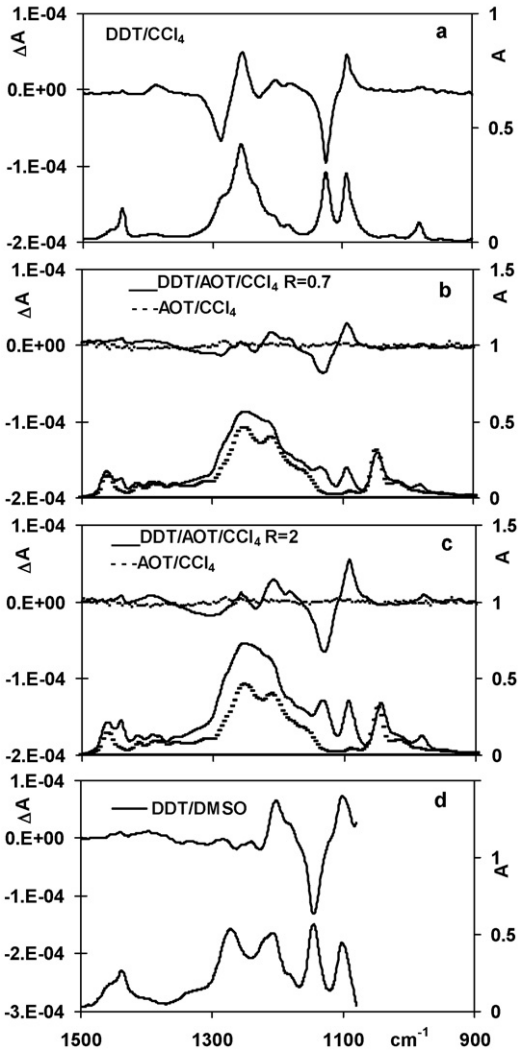

Fig. 9. VCD and absorption spectra of (a) DDT/CCl_4 [0.04 M] 200 μm cell; (b) DDT/AOT/CCl_4 ([AOT] = 0.158M, R = 0.7) 50 μm cell compared to AOT/CCl_4; (c) DDT/AOT/CCl_4 ([AOT] = 0.158 M, R = 2) 50 μm cell, compared to AOT/CCl_4; (d) DDT/DMSO [0.41 M] 50 μm cell.

3.4. 1050–1300 cm^{-1} VCD signals of dimethyl-D-tartrate

As already reported in the literature [12,18], two strong positive VCD couplets (the positive components of positive doublets being at lower wavenumbers than the negative ones) are observed in CCl_4 solutions, the first one at 1095–1126 cm^{-1} in correspondence with two absorption peaks, the second at 1257–1290 cm^{-1} in correspondence with a large structured absorption peak, centred at 1257 cm^{-1}. If we consider the spectra of DDT in AOT/CCl_4 (Fig. 9), we see that the first couplet is not much perturbed both in absorption and VCD spectra with just a blue shift of the higher frequency component of about 10 cm^{-1}. The second VCD couplet instead changes quite dramatically. This fact can be appreciated already from absorption data, especially considering the difference spectra with respect to AOT, where the two shoulders observed on the two sides of the peak at 1257 cm^{-1} in CCl_4 solutions increase in intensity in AOT micelles (Fig. 9b and c).

Considering VCD, in correspondence with the couplet obtained in CCl_4, one observes a broadened negative feature at about 1300 cm^{-1} and a positive band at 1212 cm^{-1}. A detailed normal mode analysis is quite a hard task since it should take into account

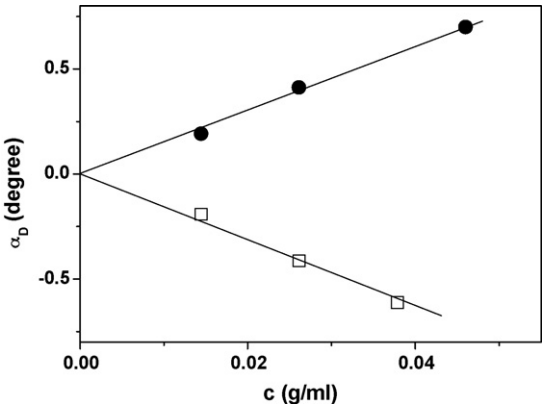

Fig. 10. Observed optical rotation (α_D) at sodium D line of DDT/AOT/CCl_4 ([AOT] = 0.158 M (●) and DLT/AOT/CCl_4 ([AOT] = 0.158 M (□) as a function of dimethyl tartrate concentration (c) measured in a 1 dm cell.

quite a few conformations: nine of these had been considered by Buffeteau et al. [12] and give a good prediction of the IR and VCD spectra of dimethyl tartrate (in their case DLT) in CCl_4, where one single conformation, among the nine examined, is found to be populated 70%, and thus it grossly accounts for the observed bands. The normal modes originating the first couplet commented here are due to C–O stretchings of the two HC*OH groups plus little contributions from deformation modes of C*H and OH. The higher frequency band of the second couplet is due to bending of C*H and OH of the two HC*OH groups, the lower frequency one is quite delocalised and is due to C–C/C–O stretchings of the $COOCH_3$ groups plus deformations of C*H and OH of the two central groups HC*OH. To mimic all possible geometries of DDT in interaction with AOT is beyond the scope of this work. However it has already been reported in the literature [18] that the couplet at 1257–1290 cm^{-1}, observed also in $CDCl_3$, changes in case of DMSO solutions, while the lower frequency couplet is less affected by changing the solvent. For sake of comparison we report our own spectra recorded in DMSO. The band at 1126 cm^{-1} of the first couplet is blue shifted by 20 wavenumbers changing from CCl_4 to DMSO and the couplet at 1250–1300 cm^{-1} is nearly lost, while a band at 1204 cm^{-1} is recorded. We conclude that VCD spectral data suggest that in presence of AOT and DMSO the hydroxyls are strongly perturbed: we infer that both the SO_3^- group in AOT and the SO group in DMSO break intramolecular H-bonds and give rise to intermolecular H-bonds, as suggested also from the OH stretching spectroscopic region previously commented on. This fact inevitably changes the OH orientation of DDT, thus particularly affecting the bands originated by their deformation modes, and possibly influences the population of conformers and even their type, due to the diminished presence of stabilizing intramolecular H-bonds.

3.5. Optical rotation of dimethyl-tartrates in AOT reverse micelles

The observed optical rotation (α_D) at sodium D line of DDT/AOT/CCl_4 and DLT/AOT/CCl_4 solutions as a function of dimethyl tartrate concentration (c) is shown in Fig. 10. The linear trends indicate that effects due to dimethyl tartrate concentration are negligible. Thus, by least square analysis of these experimental data, the specific rotation values of DDT ($+15.2 \pm 0.4$ deg ml g^{-1} dm^{-1}) and DLT (-15.8 ± 0.6 deg ml g^{-1} dm^{-1}) were calculated. Apart the sign, it is worth to note the concordance of these quantities within the experimental errors, confirming that the AOT reverse micelles do not discriminate the two enantiomers.

Moreover, since the specific rotation ($[\alpha_D]$) of chiral compound in different media is influenced by the dielectric constant of the solvent and reflects solvent-induced effects on its preferential conformation(s), it is of interest to compare the $[\alpha_D]$ value of DDT in AOT reverse micelles (+15.2 deg ml g^{-1} dm^{-1}) with that in some conventional solvents such as CCl_4 (+43.0 deg ml g^{-1} dm^{-1}), DMSO (−3.1 deg ml g^{-1} dm^{-1}) and water (−20.8 deg ml g^{-1} dm^{-1}) [19,20]. From the comparison of these values and according to literature, it can be argued that the polarity probed by DDT in the micellar environment is intermediate between that in CCl_4 and DMSO [21]. Further contributions could arise from specific effects on the dimethyl tartrate conformations due to its confinement in the AOT reverse micelles.

4. Conclusions

Through a FT-IR investigation, detailed information on 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 obtained. The analysis of the spectral features of the most significant IR active groups (OH, CO and SO_3^-) allows to hypothesize that both enantiomers are mainly confined in the reverse micelles and located in proximity to the surfactant head-group region. Also VCD spectroscopy is here demonstrated to be highly sensitive to the interactions of the chiral molecules with solvent or with surfactant agents, revealing very evident modifications of the signals and confirming the hypothesis of interactions of dimethyl tartrate with polar head of AOT.

The entrapment of dimethyl tartrates within reverse micelles involves marked changes of the typical H-bonding of dimethyl tartrate in the pure solid state and as monomers attributable to the establishment of system-specific solubilizate/surfactant head-group interactions and confinement effects. Experimental data allow also to rule out the formation of a well-defined internal core formed by the chiral molecules even at the higher R investigated including supersaturated samples. By an accurate comparison of the spectral behavior of the two enantiomers, the occurrence of significant differences in these interactions has been excluded, leaving without a direct experimental evidence able to explain their different solubility in AOT micellar solution. Unless one wants to speculate about minute energy differences between the two enantiomers [22], one needs to consider the possibility of different amounts of water or chiral contaminant traces in the micellar solutions and/or recognition of a single AOT configuration.

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