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Journal of Colloid and Interface Science 258 (2003) 123–129

JOURNAL OF
Colloid and
Interface Science

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FT-IR investigation of the urea state in lecithin and sodium bis(2-ethylhexyl)phosphate reversed micelles

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Received 28 December 2001; accepted 11 October 2002

Abstract

FT-IR spectra of urea/lecithin/CCl_4 and urea/sodium bis(2-ethylhexyl) phosphate (NaDEHP)/CCl_4 systems as a function of the urea-to-surfactant molar ratio (R_{urea}) at a fixed surfactant concentration (0.1 mol kg^{-1}) have been recorded at 25 °C. Analysis of the absorption spectra leads the to hypothesis that urea is confined within the hydrophilic micellar core of lecithin and NaDEHP reversed micelles. The encapsulation of urea involves some changes of the urea NH stretching band with respect to that of the pure solid urea, attributable to confinement effects. The stretching modes of the surfactant head group are affected by the presence of urea, indicating specific urea-surfactant head group interactions. On the other hand, analysis of the CO stretching band suggests that the urea CO groups are not engaged in urea-surfactant head group interactions.

Keywords: Urea; Solubilization; Lecithin; NaDEHP; Reversed micelles; Confinement effects

1. Introduction

Surfactants are amphiphilic molecules able to self-assemble in liquid systems, giving an extremely wide variety of structures and dynamics. Among all possible molecular aggregates, a very interesting research subject is represented by reversed micelles, which are spontaneously formed by dissolving surfactants in apolar solvents. These dynamic and spatially ordered molecular assemblies are structurally characterized by a micellar core constituted by opportunely arranged surfactant polar heads surrounded by a hydrophobic layer formed by their alkyl chains. The presence of both polar and apolar nanodomains confers on micellar solutions interesting physicochemical properties that could be exploited in many practical applications [1,2].

The most remarkable peculiarity of solutions of reversed micelles is their ability to solubilize a wide variety of substances. Water, aqueous solutions, and highly polar liquid solvents, which have been incorporated within the micellar core are the most extensively studied systems [3–6]. In contrast, confinement of finite amounts of strongly polar solid substances into micellar cores has not received much attention. Considering that confinement can modify the physicochemical properties of a solute with respect to those of bulk or isolated molecules as well as the structure and dynamics of a reversed micelle, investigations devoted to the solubilization of solid substances could be the doorway to new and exciting applications of reversed micelles, such as the preparation of nanoparticles or specialized solid–solid reactions in liquid systems [7,8].

In this way, in a previous work we focused attention on the state of urea confined within sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reversed micelles as a function of the urea-to-surfactant molar ratio (R_{urea}). Spectroscopic data showed that, at $R_{urea} < 0.13$, urea is predominantly dispersed among reversed micelles as monomers while, at greater values of R_{urea}, small clusters stabilized by a monolayer of opportunely oriented surfactant molecules are formed. Moreover, the analysis of both the urea and AOT CO stretching bands provided evidence that these groups are not significantly involved in urea–AOT interactions [9].

With the aim of studying the influence of the nature of the surfactant on the state of urea confined within the micellar core and of putting into evidence similarities and differences, we have extended our FT-IR investigation to reversed

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0021-9797/03/$ – see front matter
doi:10.1016/S0021-9797(02)00073-5

micelles formed by lecithin and sodium bis(2-ethylhexyl) phosphate (NaDEHP) in CCl_4 at a fixed surfactant concentration (0.1 mol kg^{-1}). It must be pointed out that this value is well above the critical micellar concentrations of these surfactants in apolar solvents, assuring that they are in micellar form [10,11]. CCl_4 has been selected as a solvent, given its transparency in the entire IR window.

Urea is a biologically important compound as an end product of the metabolism of ureotelic species; it is also used in the synthesis of some plastics and as a nonlinear optical medium [12]. Besides, it can be considered a convenient model of a wide class of highly hydrophilic solid solutes [13,14]. In the bulk, urea develops an extended network constituted by infinite chains of molecules linked together by two hydrogen bonds in a head-to-tail manner. Each chain is orthogonal to the neighboring chain [15].

Soybean lecithin is a diacyl phosphatidylcholine mixture occurring widely in biological systems (membranes, animal tissues, and organs). Its biological role is strongly connected with the ability to form micellar aggregates, both in water and in apolar solvents. For these reasons, it is interesting as a suitable surfactant to mime some aspects of cell membranes [16]. By small-angle neutron scattering of solutions of dry lecithin dissolved in deuterated cyclohexane it has been ascertained that, at 25 °C, lecithin forms quite spherical reversed micelles with a radius of about 25 Å [11].

NaDEHP is a surfactant similar in structure to AOT, having identical hydrophobic parts and differing only in the polar head group. It has been widely studied, mainly for its use in metal extraction technology [17]. Small-angle neutron scattering from NaDEHP in benzene indicates the presence of weakly interacting spherical reversed micelles. However, it has been also reported that NaDEHP forms long rodlike reversed micelles when it is totally dried [18]. The structure of lecithin, NaDEHP, and AOT is shown in Fig. 1.

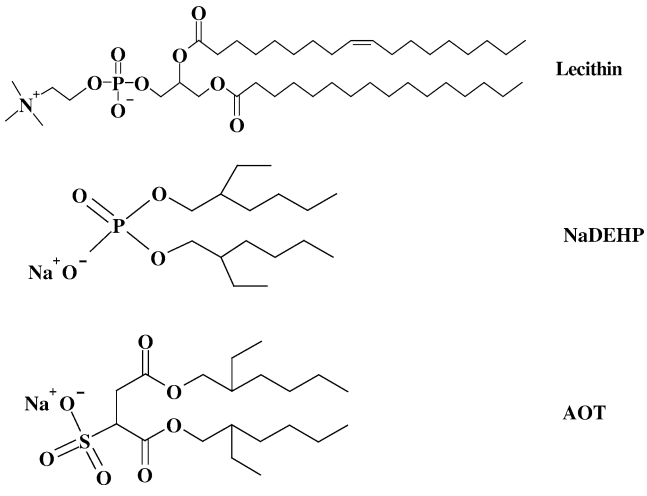

Fig. 1. Schematic representation of the structure of lecithin, NaDEHP, and AOT.

2. Experimental

Urea (Sigma, >99%), bis(2-ethylhexyl) phosphoric acid (HDEHP, Sigma, 95%), lecithin (Lucas Meyer, Epicuron 200), and CCl_4 (Sigma, 99.97%) were used as received.

NaDEHP was synthesized at room temperature from HDEHP by adding solid NaOH (Riedel–de Haën, 99%) in excess of the stoichiometric molar ratio (1 : 1). The mixture was continuously stirred for several days and fluidified by periodic addition of diethyl ether (Riedel–de Haën, 99.5%). Then the mixture was filtered and NaDEHP was precipitated by adding acetone (Merck, >99%) to the liquid phase. After filtration, residual solvent medium was removed from the precipitate by evaporation under vacuum.

To obtain a completely dried solution, a 0.1 mol kg^{-1} solution of lecithin in CCl_4 was stirred for 30 min in the presence of phosphorus pentoxide (Sigma, 99%) and then filtered. This procedure was not used for NaDEHP because a chemical modification of this surfactant takes place. However, we have found that a trace of water in NaDEHP can be removed by evaporation under vacuum of a NaDEHP/*n*-heptane solution. After this treatment, NaDEHP was dissolved in CCl_4 to give a completely dried 0.1 mol kg^{-1} solution.

While urea is practically insoluble in CCl_4, discrete amounts can be dissolved in 0.1 mol kg^{-1} surfactant solutions. The maximum amount of urea which can be dissolved at 25 °C, expressed as urea-to-surfactant molar ratio (R_{urea}), is 1.35 for lecithin and 0.81 for NaDEHP.

FT-IR spectra of all liquid samples were recorded at 25 °C, using a Bruker (IFS25) FT-IR spectrometer in the frequency range 900–4000 cm^{-1}, with a spectral resolution of 2 cm^{-1}. A cell equipped with CaF_2 windows was used and, as background, pure CCl_4.

3. Results and discussion

Typical spectra of urea/lecithin/CCl_4 and urea/NaDEHP/CCl_4 systems in the frequency range 900–4000 cm^{-1} are shown in Fig. 2. For comparison, the spectra of lecithin/CCl_4 and NaDEHP/CCl_4 systems are also reported. In both spectra of the surfactant/CCl_4 systems, the absence of the water band, occurring in the frequency range 3000–3800 cm^{-1}, ensures the total absence of water. On the other hand, the presence of urea in the urea/surfactant/CCl_4 systems is pointed out by the appearance of the characteristic NH_2 stretching band (3000–3600 cm^{-1}) and the CO stretching band (1500–1800 cm^{-1}). Moreover, no significant changes of the surfactant CH stretching band (2800–3000 cm^{-1}) with R_{urea} are observed. This emphasizes that urea confinement in the micellar core does not significantly modify the surfactant aggregation state, the lateral packing order of the surfactant chains in the micellar aggregate, or their conformational dynamics [9,19].

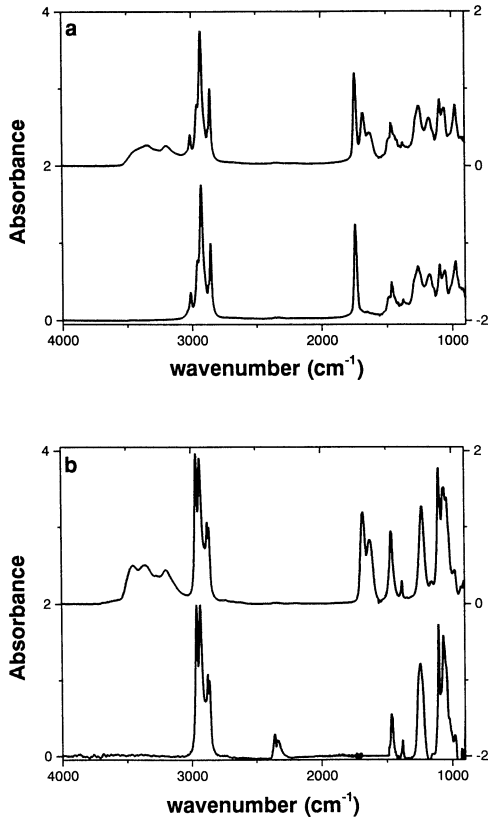

Fig. 2. Infrared spectra of urea/lecithin/CCl_4 system at $R_{urea} = 0.99$ (upper spectrum) and lecithin/CCl_4 system (lower spectrum), (a) and urea/NaDEHP/CCl_4 system at $R_{urea} = 0.81$ (upper spectrum) and NaDEHP/CCl_4 system (lower spectrum) (b).

In order to draw an exhaustive picture of urea encapsulated within the micellar core, among all bands, whose main frequency assignments are collected in Table 1, we have analyzed those due to the stretching of NH_2, CO, and PO_4^- groups.

3.1. NH_2 stretching bands

The symmetric and antisymmetric NH_2 stretching bands due to the intramolecular coupling of equivalent NH bonds of monomeric urea occur at 3440 and 3548 cm^{-1}, respectively [20,21]. When urea is dissolved in a series of halogen derivatives of aliphatic hydrocarbons, these bands are broadened (widths in the range 21–38 cm^{-1}) and shifted toward lower wavenumber (shifts in the range 20–40 cm^{-1}) [22]. In solid urea, the occurrence of strong hydrogen bonding redshifts these bands about 100 cm^{-1}, further increasing their width (widths of about 60–70 cm^{-1}) [23]. Moreover, in the same spectral region, new bands appear, which are absent in monomeric urea and urea solutions. These bands, occurring at 3141, 3208, and 3257 cm^{-1}, have been assigned to combinations or overtones of NH_2 vibrations of strongly hydrogen bonded urea molecules [24].

By comparing the NH_2 stretching bands of solid urea and urea trapped into the micellar core of lecithin, NaDEHP, and AOT reversed micelles, reported in Fig. 3, a surfactant-dependent shape of the bands is immediately noted, implying the occurrence of specific urea–surfactant head group interactions. In addition, some changes in the position, width, and relative intensity of each gaussian component with respect to those of pure solid urea can be also noted.

Table 1
Infrared frequencies and assignments of functional groups of urea, lecithin, and NaDEHP in the range 1000–4000 cm^{-1}

Wavenumber (cm^{-1})				Group assignment
Monomeric urea	Solid urea	Urea/lecithin/CCl_4	Urea/NaDEHP/CCl_4	
3548	3442	3450	3463	$\nu_{as}(NH_2)$
3440	3344	3348	3354	$\nu_s(NH_2)$
	3257	3263	3259	Combinations of NH_2 vibrations
	3208	3200	3202	
	3141	3152	3155	
		3011		ν(HC=)
		2958	2960	$\nu_{as}(CH_3)$
		2929	2932	$\nu_{as}(CH_2)$
		2873	2875	$\nu_s(CH_3)$
		2855	2861	$\nu_s(CH_2)$
		1741		ν(CO) of lecithin
1734	1682	1680	1680	$\nu(CO) + \nu(CN) + \delta(NH_2) + \rho(NH_2)$ of urea
1594	1636	1627	1625	$\delta(NH_2) + \nu(CN)$
	1599	1615	1611	$\delta(NH_2) + \nu(CO)$
1394	1465			$\nu_{as}(CN_2) + \delta(NH_2) + \rho(NH_2)$
		1466	1463	$\nu_{as}(CN_2) + \delta_{as}(CH_3) + CH_2$ sciss
		1378	1380	$\delta_s(CH_3) + \delta_s(CH_2)$
			1341	CH_2 wag
		1251	1227	$\nu_{as}(PO_4^-)$
	1153	1173	1152	$\rho(NH_2) + \nu(CN_2) + \nu(CO)$
		1092	1099	CH_2 wag, CH_2 twist
		1058	1036	δ(P–O–C), $\nu_s(PO_4^-)$
1014				$\nu_s(CN_2)$

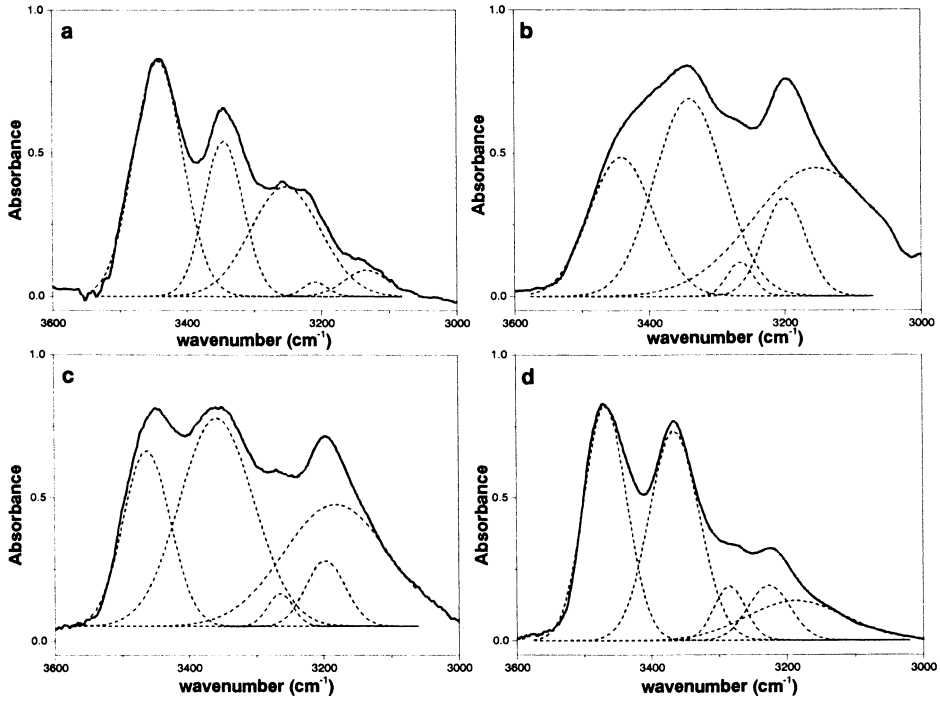

Fig. 3. Comparison between the NH_2 stretching bands of pure urea (a), urea/lecithin/CCl_4 system at $R_{urea} = 0.99$ (b), urea/NaDEHP/CCl_4 system at $R_{urea} = 0.81$ (c), and urea/AOT/CCl_4 system at $R_{urea} = 0.91$ (d).

Table 2
Single-component parameters obtained by deconvolution of the NH band in the frequency region 3000–3600 cm^{-1}

Position/width/area[a]	Position/width/area	Position/width/area	Position/width/area	Position/width/area
		Pure urea		
3442/74/43.5	3344/58/23.5	3257/91/24.6	3208/42/2.7	3141/71/5.7
		Lecithin/CCl_4 system		
		$R_{urea} = 0.11$		
3432/102/16.5	3336/120/39.2	3268/33/1.7	3199/64/12.2	3137/156/30.4
		$R_{urea} = 0.51$		
3442/85/13.5	3341/116/40.3	3267/34/1.8	3199/64/11.8	3139/161/32.6
		$R_{urea} = 0.99$		
3447/81/15.0	3345/114/40.3	3265/36/1.9	3200/62/10.8	3149/162/32.0
		$R_{urea} = 1.35$		
3450/75/14.8	3348/114/43.2	3263/45/3.1	3200/58/10.4	3152/148/28.5
		NaDEHP/CCl_4 system		
		$R_{urea} = 0.12$		
3460/77/21.0	3348/113/37.4	3262/36/2.6	3195/74/15.0	3142/140/24.0
		$R_{urea} = 0.52$		
3461/77/23.1	3350/109/38.5	3261/47/5.2	3201/58/9.1	3155/117/24.1
		$R_{urea} = 0.81$		
3463/68/20.0	3354/118/44.7	3259/48/5.7	3202/54/9.6	3155/99/20.0

[a] Position (cm^{-1}), width (cm^{-1}), area (%).

To obtain detailed information about the state of urea and its evolution with R_{urea}, deconvolution of the NH_2 band of all the investigated samples as sum of gaussian components has been done and results are shown in Table 2 and in Fig. 4. For comparison, the parameters obtained by deconvolution of the NH_2 band of urea/AOT/CCl_4 samples and of pure urea are also shown in Fig. 4 [9].

The following conclusions can be reached from the figure. (a) Most of the component positions show a modest shift to longer wavenumber with respect to those of pure

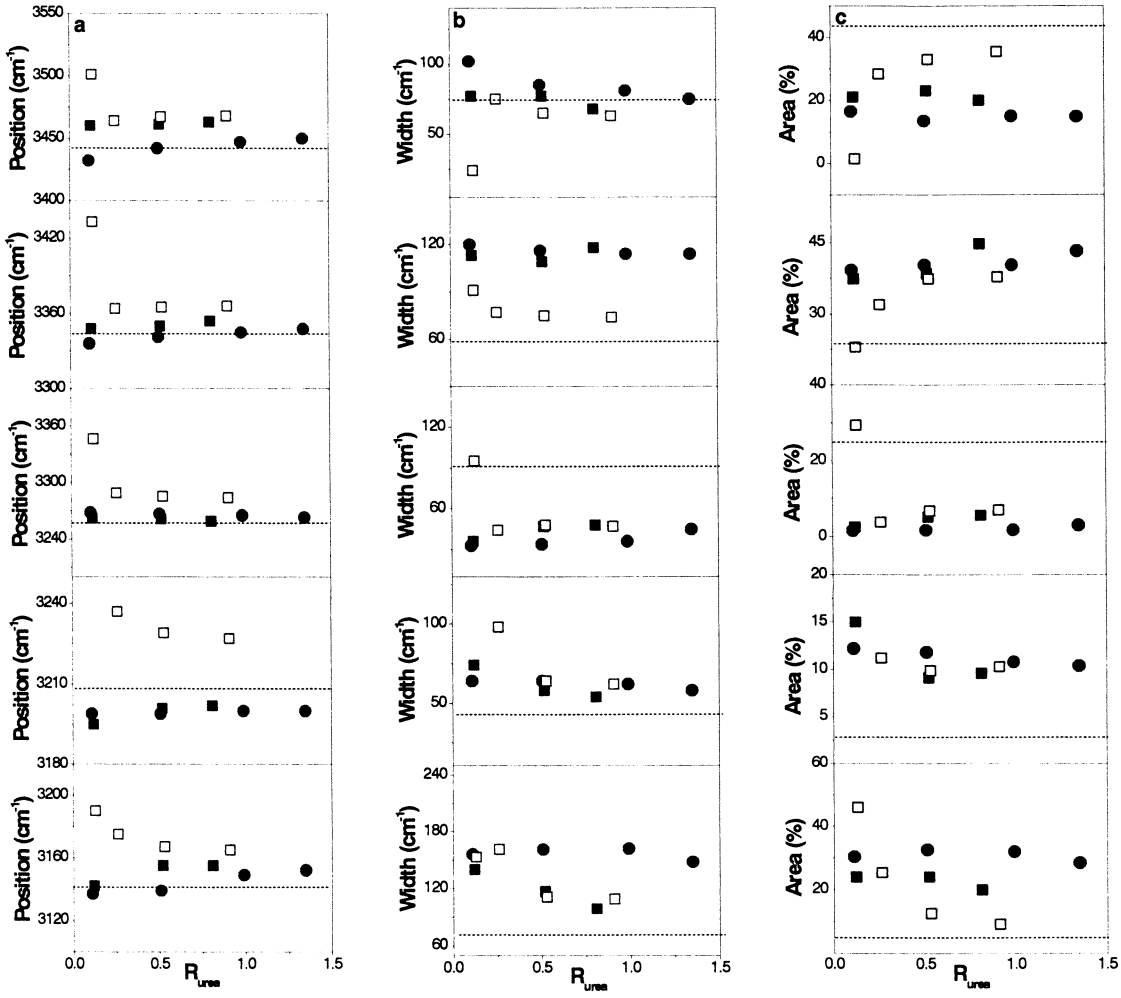

Fig. 4. Position (a), width (b), and area (c) of the NH_2 band components of the urea/lecithin/CCl_4 (•), urea/NaDEHP/CCl_4 (■), and urea/AOT/CCl_4 (□) systems as a function of R_{urea}. Dotted lines represent the values of pure solid urea.

solid urea, which, in the case of lecithin, is practically absent. The red shift of the band components when urea is entrapped in AOT reversed micelles is generally larger than that in NaDEHP reversed micelles. Moreover, apart from the lowest R_{urea} values, no significant dependence of the component positions on R_{urea} can be detected. These observations suggest that only a part of the urea–urea hydrogen bonds are replaced by urea–surfactant head group interactions and that the strength (S) of these intermolecular interactions is in the order $S_{urea–urea} \approx S_{urea–lecithin} > S_{urea–NaDEHP} > S_{urea–AOT}$. (b) Most of the component widths are markedly larger than that of pure urea. Exceptions are the component occurring at about 3442 cm^{-1}, which displays nearly the same width values, and that occurring at about 3257 cm^{-1}. Moreover, no significant dependence of the component width on R_{urea} can be detected. It must be pointed out that an increase of the component width can be attributed to an increase of the molecular motional dynamics and/or to an increase of the populations of the oscillators vibrating within a limited range of frequencies. (c) The area of the component occurring at about 3442 cm^{-1}, assigned to the NH_2 antisymmetric stretching, is markedly smaller than that of pure solid urea, whereas the area of the component occurring at about 3344 cm^{-1}, assigned to the NH_2 symmetric stretching, is markedly larger. Taking into account that the intensity of an absorption band is proportional to the variation of the molecular dipole moment ($\partial\mu/\partial q$) with the normal coordinate, the area changes indicate that the quantities $\partial\mu/\partial q$ associated to symmetric and antisymmetric NH_2 stretchings are differently perturbed by micellar confinement. This effect could arise from the replacement of part of the urea–urea hydrogen bonds with urea–surfactant head group interactions. On the other hand, the changes of the area of the components occurring at smaller wavenumber could be taken as an indication that some changes in the populations of the strongly hydrogen-bonded urea molecules occur.

3.2. Urea CO stretching bands

The spectra of urea/lecithin/CCl_4 and urea/NaDEHP/CCl_4 systems in the frequency region 1500–1800 cm^{-1} are reported in Fig. 5. For comparison, the spectrum of pure urea

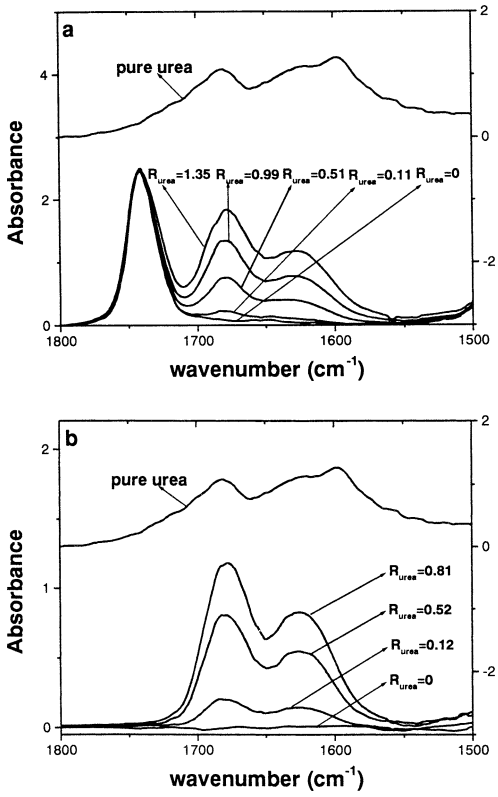

Fig. 5. Comparison between the CO stretching band of pure urea and those of urea/lecithin/CCl_4 (a) and urea/NaDEHP/CCl_4 (b) systems at various R_{urea} values.

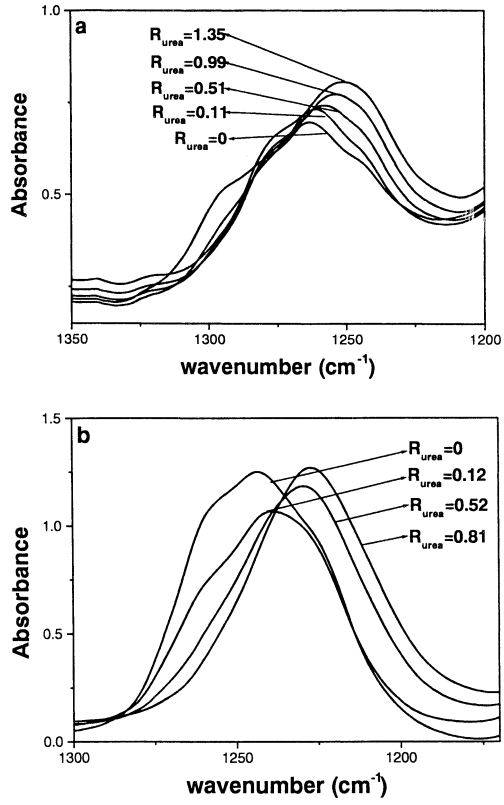

Fig. 6. PO_4^- antisymmetric stretching bands of urea/lecithin/CCl_4 (a) and of urea/NaDEHP/CCl_4 (b) systems at various R_{urea} values.

is also shown. It can be noted that at $R_{urea} > 0$ the spectra are constituted of the band assigned to the CO stretching of urea (1682 cm^{-1}), with some contributions of ν(CN), $\delta(NH_2)$, and $\rho(NH_2)$, and those mainly due to the urea NH_2 bendings (1612 and 1630 cm^{-1}) [25]. In the case of lecithin, another band occurring at 1730 cm^{-1} due to the lecithin CO stretching can be noted.

The comparison among the CO band positions of monomeric urea (1734 cm^{-1}) [20], urea dissolved in a series of halogen derivatives of aliphatic hydrocarbons (1700 cm^{-1}) [22], urea dissolved in acetonitrile (1695 cm^{-1}) [25], and pure solid urea (1682 cm^{-1}) suggests that it is strongly affected by changes of the urea CO group surroundings. However, analyzing the position and the width of the CO band of urea confined in lecithin and NaDEHP reversed micelles, the absence of significant changes with respect to pure solid urea, as well as of R_{urea} dependence, was ascertained. Similar behavior was observed by analyzing the urea CO band of the urea/AOT/CCl_4 system [9]. Since the position of the CO band is a sensitive probe of its environment, it can be unambiguously stated that the CO group of confined urea is not involved in urea/surfactant interactions but rather in urea/urea interactions, i.e., hydrogen bonded with urea NH_2 groups [25–27]. The implication is that urea is entrapped in the micellar core, probably forming hydrogen-bonded aggregates constituted by molecules linked in a head-to-tail manner. It is of interest that, by molecular orbital calculations on one-dimensional urea aggregates, it has been found that for oligomers larger than the decamer, this hydrogen-bonding pattern is the most energetically favored [14].

A perusal of the lecithin CO stretching band, consisting of two underlying component bands occurring at 1730 and 1741 cm^{-1}, indicates that this band is also practically unaffected by the presence of urea [27]. This finding, similar to that found by analyzing the AOT CO band, indicates that urea encapsulation in the micellar core does not involve interactions between lecithin CO and urea NH_2 groups.

3.3. PO_4^- antisymmetric stretching bands

The establishment of specific interactions between surfactant PO_4^- and urea NH_2 groups is evidenced by a progressive shift to lower frequencies of the lecithin and NaDEHP PO_4^- antisymmetric stretching bands with the increase of R_{urea} shown in Fig. 6. It can be also noted that urea addition induces a change in the shape and intensity of the PO_4^- band. The shift of the PO_4^- band to lower frequency and the parallel decrease of the width are gauges of the strengthening of the hydrogen bonds and of the decrease of the PO_4^- motional dynamics [28].

In order to monitor the influence of urea on the PO_4^- band, the frequency (f^*) at the maximum of the band as a function of R_{urea} has been reported in Fig. 7. A linear dependence of f^* on R_{urea} can be noted. This behavior, similar to that ob-

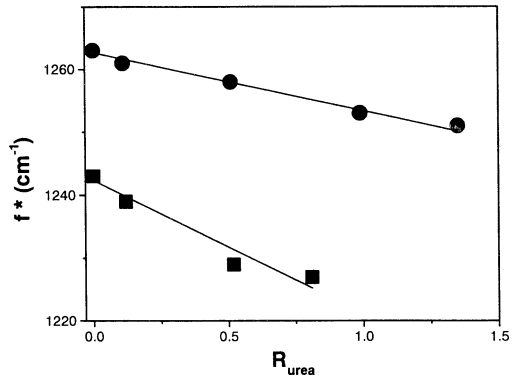

Fig. 7. Peak frequency (f^*) of the PO_4^- antisymmetric stretching band of urea/lecithin/CCl_4 (•) and urea/NaDEHP/CCl_4 (□) systems as a function of R_{urea}.

served when urea is added to AOT reversed micelles, indicates that addition of urea influences the PO_4^- band even at the higher R_{urea} values; i.e., urea molecules are mainly located in proximity to the surfactant head group interface and an internal core in the urea molecular aggregate never develops [9].

4. Summary

The state of finite amounts of urea confined in the micellar cores of lecithin and NaDEHP reversed micelles has been investigated by FT-IR spectroscopy. Analysis of the spectra leads to the hypothesis that urea is entrapped within the micellar core as small urea molecular aggregates. Besides, the comparison of the NH_2 stretching band of urea confined in lecithin, NaDEHP, and AOT reversed micelles with that of pure solid urea suggests that the state of urea is modestly impacted by confinement in reversed micelles. On the other hand, the analysis of the surfactant PO_4^- band indicates that urea entrapment is sustained by favorable interactions arising from hydrogen bonding between urea NH_2 and surfactant PO_4^- groups. Surprisingly, urea CO groups are not involved in these interactions. Besides, the monotonic variation of the PO_4^- band position with R_{urea} suggests that, even at the higher R_{urea} values, urea molecules are mainly located in proximity to the surfactant head group interface and an internal core in the urea molecular aggregates never develops.

Acknowledgment

Financial support from MURST, 60%, is gratefully acknowledged.

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