Hydrotrope-Solubilization Action of Urea in CTAB/n-C_5H_{11}-OH/H_2O System

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Urea can enhance the aqueous solubility of surfactant CTAB (hexadecyltrimethylammonium bromide) when it shows the hydrotrope action. It will show the hydrotrope-solubilization action when the solubilized amount of n-$C_5H_{11}OH$ in O/W microemulsion and that of water in W/O microemulsion are increased. The mechanism of the hydrotrope-solubilization action of urea is the increase of the stability of W/O and O/W microemulsion and structural transition from the lamellar liquid crystalline phase to the bicontinuous structure.

Keywords Urea, hydrotrope-solubilization, microemulsion, lamellar Liquid crystal, bicontinuous

Introduction

In 1916, Neuberg[1,2] found that aqueous solution of certain salts possessed the ability to enhance the solubility in water of several otherwise water-insoluble substances. This phenomenon of increasing the aqueous solubility of substances normally insoluble or sparingly soluble in water, brought about by the third component or additive, is termed hydrotropy or hydrotropism. Yet hydrotrope-solubilization is not the same concept as hydrotropy. Different from surfactant solubilization, which is achieved by association of surfactants and solutes into micelles, microemulsion droplets and liquid crystals,[3-9] hydrotrope-solubilization[10-12] is achieved by a phase transition.

Because the hydrotrope-solubilization action can be applied in practice, people are interested in finding hydrotrope-solubilization agent of new type. In recent years, we have reported systematic studies on the effect of Vitamin C[13-15] as hydrotrope-solubilization agent in CTAB/n-$C_5H_{11}OH$/H_2O system. The hydrotrope-solubilization mechanism obtained in these studies is that the lamellar liquid crystalline phase is destabilized and transformed into isotropic phase with bicontinuous structure by the presence of hydrotrope. As a continuation of the above investigations, in the present paper the effects of urea on the hydrotrope-solubilization behavior in CTAB/n-$C_5H_{11}OH$/H_2O system have been studied.

The structure of urea is simple but its solubility and polarity are strong. The investigations show that urea not only increase the CMC of ionic and non-ionic surfactants, but also lightly reduces the micropolarity at the micellar interface of ionic micelles.[16,17] Two different ways have been used to explain the above results: an indirect mechanism and a direct mechanism.[18] In recent years, Carnero Ruiz has reported systematic studies on the effect of urea on the aggregation behavior of both nonionic[19] and ionic surfactants.[20,21] Some interesting information about structural changes induced by urea in micelles were found. However, the function as hydrotrope for urea has received little attention. In the present paper, we investigate the hydrotrope-solubilization actions of urea in CTAB system. The results reveal that urea can act as hydrotrope or hydrotrope-solubilization agent in the cationic surfactant CTAB system. The presence of urea stabilizes both W/O and O/W microemulsion but destabilizes a lamellar liquid crystal and the phase transition from the lamellar liquid crystalline phase to bicontinuous structure happens.

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Experimental

Materials

The materials used are hexadecyltrimethylammonium bromide (CTAB) (Aldrich, 99 + %), sodium dodecyl sulfate (SDS) (Aldrich, 99 + %), Triton X-100 (Aldrich, 99 + %), urea ($CO(NH_2)_2$) (Aldrich, 99 + %), *n*-pentanol (n-$C_5H_{11}OH$) (Aldrich, 99 + %), and 5-doxyl stearic acid (5-DXSA) (Aldrich, 99 + %). Among the above, only SDS was recrystallized twice in ethanol. Water used was twice distilled.

Determination of partial phase diagram

The isotropic regions of CTAB/n-$C_5H_{11}OH$/H_2O system with and without urea are determined by observing the change point of sample from clarity to cloudy when water or aqueous urea solutions were titrated into the mixture of CTAB and pentanol or pentanol was titrated into the mixture of CTAB and water or aqueous urea solution at 25 ± 0.1℃. The phase boundaries of lamellar liquid crystal phase were determined with an optical microscope with the sample between crossed polarizes and by low angle X-ray diffraction measurements.

Measurement of micropolarity

The steady-state fluorescence spectrum is measured by using pyrene as probe with the excitation wavelength 338 nm and the emission wavelength 384 nm at 25 ± 0.1℃. The intensity ratio of the first to the third peak in the fluorescence spectrum can show the microplarity of probe microenviroment. Furthermore, the location of urea in the microemulsion droplets can be determined from the variety of I_1/I_3 values. All the solution samples are deoxygenated by bubblingnitrogen about 15 min before measurements. The pyrene concentration is 1.4×10^{-7} mol·L^{-1}.

Low angle X-ray diffraction

Low angle X-ray diffraction measurements were obtained from D/max-A X-ray diffractometer at room temperature. $\lambda = 0.15418$ nm.

Determination of ESR *spectra*

Electron spin resonance (ESR) experiments were performed on a Varian E-115 X-band spectrometer at 25℃. All samples of the ESR experiments contained 2×10^{-3} mol·L^{-1} 5-DXSA and were deoxygenated with nitrogen before performance.

Determination of diffusion coefficient

A three-electrode arrangement in a conventional three-compartment cell was used. A platinum foil-working electrode, a platinum foil-auxiliary electrode, and a saturated calomel electrode (SCE) reference electrode were used. All the solutions were deoxygenated by bubbling nitrogen. The potential was swept linearly at 36 mv·s^{-1} at 25 ± 0.1℃.

Electrochemical experiments were performed using an electrochemical analyzer system with an SHD-1 bipotentiosat (Yinbing Electrochemical Apparatus Co., Jilin, China), rotating ring-disk electrode (Jiangsu Fourth Meters Co.).

Results and discussion

1. *Hydrotrope-solubilization action of urea*

Fig. 1a—c illustrate the partial phase diagrams of the CTAB/n-$C_5H_{11}OH$/$CO(NH_2)_2$(aq.) system. Fig. 1 shows that with the addition of urea there are three changes in the CTAB/n-$C_5H_{11}OH$/H_2O system: (1) The solubility of CTAB in water increases, which reveals the hydrotrope action of urea for CTAB. But both the solubility of CTAB and water in pentanol and pentanol in water shows no obvious change. (2) The solubilized amount of pentanol in the O/W microemulsion increases and so does the maximum amount of water solubilized in W/O microemulsion. Thus, the region of W/O and O/W come close with the addition of urea and join with each other when 30% urea solution is used through the bicontinuous structure region (BI) which will be discussed later. (3) The area of the lamellar liquid crystalline phase region (LC) shrinks. It is obvious that the existence of urea would stabilize the structure of O/W and W/O, and the increase of film intensity of microemulsion droplets is the only way to strengthen the stability of both O/W and W/O microemulsion. So it

can be concluded that urea should be located in the interface of microemulsion droplets by some way.

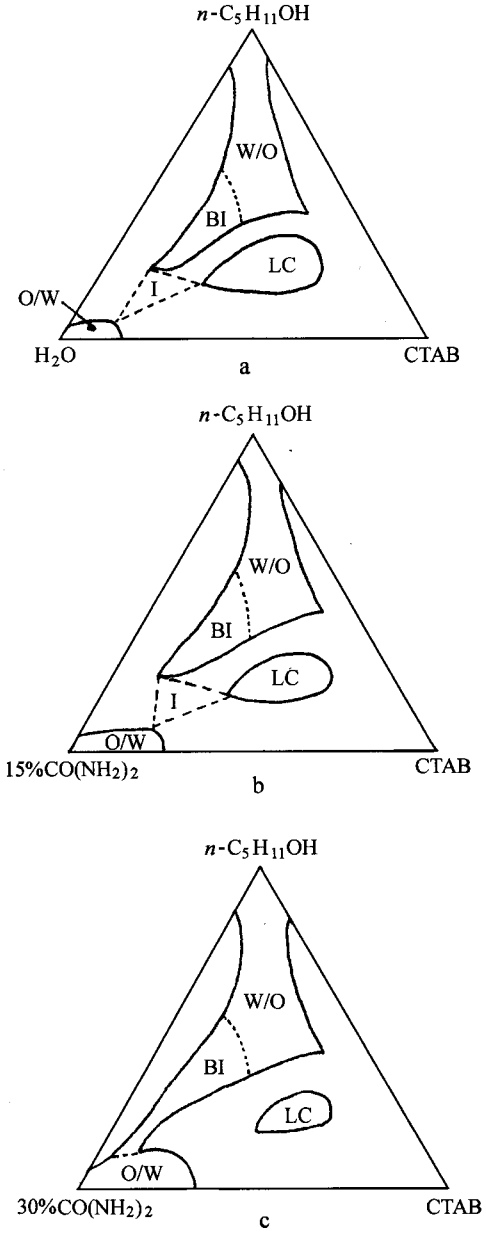

Fig. 1 Effect of urea on the phase behavior, I: Three-phase region.

2. *Mechanism of the hydrotrope-solubilization action of urea*

Location of urea in CTAB/n-$C_5H_{11}OH/H_2O$ *microemulsion system*

The location of urea in the microemulsion of CTAB/n-$C_5H_{11}OH/H_2O$ system can be verified by the micropolarity of microemulsion droplets.[15] The micropolarity can be determined by the I_1/I_3 value of pyrene located in the microemulsion droplets (Table 1). When urea is added in the O/W microemulsion of CTAB/n-$C_5H_{11}OH/H_2O$ system, the value of I_1/I_3 decreases from 1.24 (sample 1 in Table 1) to 1.16 (sample 4). It is clear that the addition of urea can make the pyrene transfer to the inside of the interface of the microemulsion droplets. As we know, pentanol can be used as cosurfactant and usually exists among the polar groups of surfactant molecules in the O/W microemulsion droplets so that the decrease of I_1/I_3 value must be caused by the location of urea between the pentanol and pyrene in the interface of O/W droplets. Similarly, because of the location of urea in the W/O microemulsion droplets of CTAB/n-$C_5H_{11}OH/H_2O$ system, pyrene transfers to outside of interface of W/O droplets and the I_1/I_3 values decrease from 1.13 (sample 5) to 1.06 (sample 6).

Since urea is located in the interface of the microemulsion droplets, the film intensity of the microemulsion droplets is strengthened. Hence, the stability of both O/W and W/O microemulsion of CTAB/n-$C_5H_{11}OH/H_2O$ system is increased, as is reflected by the expansion of O/W and W/O regions in the phase diagrams described in Fig. 1.

The location of urea in the microemulsion of CTAB/n-$C_5H_{11}OH/H_2O$ system can be also verified by the ESR technique.[22] The ESR spectrum of microemulsion is always made up of three peaks (Fig. 2). In the analysis of the ESR spectra, the hyperfine splitting constant (A_N) of probe is regarded as a useful micropolar reporter and the rotational correlation time (τ_c) may be taken as the time needed for a probe molecule to rotate for an angle of π. As an approximation, the rotational correlation time can be calculated from the following equation:[23]

$$\tau_c = 6.6 \times 10^{-10} W_0[(h_0/h_{-1})^{1/2} + (h_0/h_{+1})^{1/2} - 2] \quad (1)$$

where W_0 represents the peak line width of the ESR midfield line (in Gauss), and h_{-1}, h_0, h_{+1} are the peak to peak heights of the low-, mid-, high-field lines, respectively. The data in Table 2 show that, with the addition of urea, the probe hyperfine splitting constants (A_N) of both O/W and W/O microemulsions of CTAB/

Table 1 Effect of urea on the micropolarity (I_1/I_3) for CTAB/n-$C_5H_{11}OH$/H_2O system

Samples	CTAB (wt%)	n-$C_5H_{11}OH$ (wt%)	H_2O (wt%)	$CO(NH_2)_2$ (wt%)	Media	I_1/I_3
1	5	3	92		O/W	1.24
2	5	3	87	5	O/W	1.22
3	5	3	72	20	O/W	1.18
4	5	3	62	30	O/W	1.16
5	5	85	10		W/O	1.13
6	5	80	10	5	W/O	1.06

n-$C_5H_{11}OH$/H_2O systems decrease. This reveals that with the addition of urea the probe molecules are located in a reduced micropolarity at the binding sites of the probe in the microemulsion, as is reflected by the drop of the I_1/I_3 value of pyrene described in Table 1. The data in Table 2 also show that, the τ_c values decrease with the addition of urea. The possible reason for this result is that urea molecules exist in the interface of the microemulsion droplets, which leads to the film intensity of the microemulsion droplets strenthened, but make the probe molecules rotate in a relatively larger space, so that the τ_c values decrease.

Table 2 Parameters, A_N, τ_C and S, for CTAB/n-$C_5H_{11}OH$/$CO(NH_2)_2$(aq.) system

Samples	Media	$CO(NH_2)_2$ (wt%)	CTAB/$CO(NH_2)_2$(aq.) (W/W)	n-$C_5H_{11}OH$ content (wt%)	τ_c (s) $\times 10^{10}$	A_N (mT)	S
1	O/W	0	0.14	5	2.32	1.51	
2	O/W	15	0.14	5	1.45	1.46	
3	O/W	30	0.14	5	1.41	1.41	
4	W/O	0	1.95	50	1.52	1.51	
5	W/O	15	1.95	50	1.39	1.50	
6	W/O	30	1.95	50	1.37	1.49	
7	LC	0	1.00	20			0.57
8	LC	15	1.00	20			0.51
9	LC	30	1.00	20			0.42

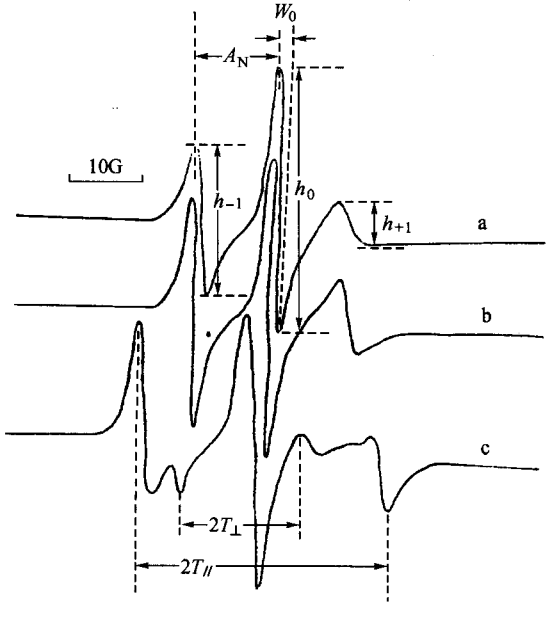

Fig. 2 ESR spectras for CTAB/n-$C_5H_{11}OH$/H_2O system, (a) O/W; (b) W/O; (c) LC.

Location of urea in lamellar liquid crystal of CTAB *system*

In lamellar liquid crystal, there is a relationship between d_0 and d as follows:[24]

$$d = d_0(1 + R)/(1 + \alpha R) \quad (2)$$

in which d is the interlayer space of the lamellar liquid crystal and can be determined by small-angle X-ray diffraction, d_0 is the interlayer space without the solvent and can be obtained by extrapolating to a zero-solvent content in Fig. 3, R is the volume ratio of the solvent to other compositions, and α is a volume fraction of the solvent penetration from the solvent layer to the amphiphilic bilayer in the lamellar structure.

Algebraic manipulation gives a simple expression for α:[25]

$$\alpha = 1 - (\partial d/\partial R)/d_0 \quad (3)$$

Fig. 3 shows the results determined by small-angle X-ray diffraction for the CTAB/n-$C_5H_{11}OH$/$CO(NH_2)_2$ (aq.) system. The values of α and d_0 are shown in Table 3. As Fig. 3 and Table 3 show, the higher the aqueous concentration of urea is, the smaller the value of d_0. If most of the urea molecules existed in solvent layer, the addition of urea would have increased the value of d_0 rather than decreased it. Besides, since urea is insoluble in oil phase, it would not exist in oil layer. Thus, some urea molecules should exist in the amphiphilic bilayer.

Table 3 Interlayer spacing (d_0) and the solvent penetration (α) in the lamellar liquid crystal. CTAB/n-C_5H_{11} OH = 2.33 (W/W)

$CO(NH_2)_2$ (wt%)	d_0 (nm)	α
0	2.59	0.412
15	2.51	0.332
30	2.43	0.219

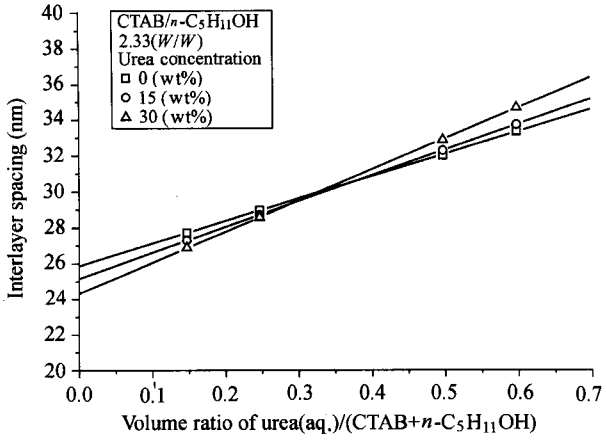

Fig. 3 Effect of urea on the interlayer spacing of the CTAB/n-$C_5H_{11}OH$/H_2O lamellar liquid crystal.

On the other hand, the data in Table 3 show that the values of solvent penetration α decrease with the increase of urea concentration. The possible reason is that urea molecules exist in the amphiphilic bilayer and some water molecules go back to the solvent layer.

The existence of urea in the amphiphilic bilayer would make the arrangement of surfactant molecules in a lower order. As the result, the liquid crystal phase is destabilized. This result can be verified by the ESR technique. In lamellar liquid crystal, the anisotropic degree of the probe rotating motion (S) can be calculated from the following equation:[26]

$$S = (T_{//} - T_{\perp})/[T_{ZZ} - 1/2(T_{XX} + T_{YY})] \quad (4)$$

where T_{ZZ}, T_{XX} and T_{YY} are measures of the probe hyperfine splitting vector along N—O spindle ($T_{ZZ} = 3.2$ mT, $T_{XX} = T_{YY} = 0.6$ mT). $T_{//}$ and $T_{\perp}$ can be got from ESR spectra directly. $S = 1$ for solid, and $S = 0$ for isotropic solution.

The data in Table 2 show that the values of the anisotropic degree of the S decrease with the increase of urea concentration. This means that with the addition of urea the liquid crystal phase is destabilized. As the result, the region of lamellar liquid crystal shrinks and is transformed into the isotropic region BI (Fig. 1).

Structure determination of the isotropic region

The electrode for the CTAB micelle solution is a reversible system. The diffusion coefficient of the CTAB micelle can be calculated from the following equation at 25℃:[27]

$$i_p = 2.69 \times 10^5 \, n^{3/2} \, C_0 D_0^{1/2} V^{1/2} A \quad (5)$$

in which i_p is the cathodic peak current in amperes, C_0 is the solution concentration in mol·cm^{-3}, v is the potential sweep rate in $V \cdot s^{-1}$, A is the total surface area of the Pt electrode, and D_0 is the particle diffusion coefficient in the solution in cm^2·s^{-1}. The electrons per molecule oxidized or reduced, n, can be obtained from the relation of the peak potentials E_p to half-peak potentials $E_{p/2}$. For the CTAB reaction at the platinum electrode, $n \approx 1$.[28]

Fig. 4 illustrates the typical curves of the diffusion coefficient of CTAB micelles. From Fig. 4 we can see that the diffusion coefficient increases with the increase of the content of urea solution and there are two sudden changes on the curves of the diffusion coefficient. According to the determination of the microemulsion structure with diffusion coefficient, the point of inflection is corresponding to the structure change:[29] (1) When the solvent content is lower, the diffusion coefficients increase with a very low speed and the corresponding systems show W/O structure; (2) When the solvent content is higher, the diffusion coefficients greatly increase with solvent content and the corresponding structure is O/W; (3) When the solvent content is medium, the corresponding system shows bicontinuous structure (BI).

Based on the above principle and by labeling the sudden changes in the isotropic region in Fig. 1, the isotropic region in Fig. 1 can be devided into three areas: W/O, O/W and bicontinuous.

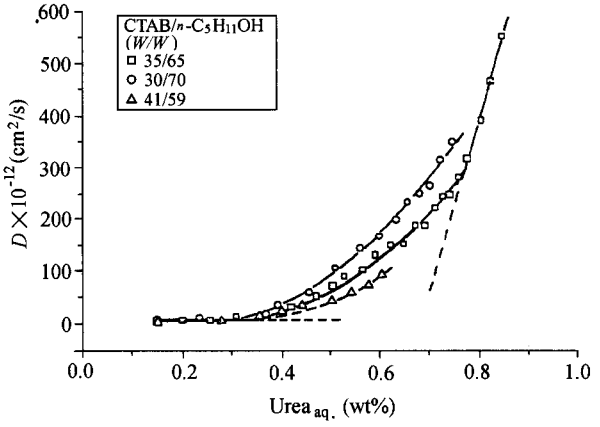

Fig. 4 Diffusion coefficients of CTAB micelles with the content of urea solution (30 wt%).

From Fig. 1, it is clear that between the lamellar liquid crystal region and the isotropic region there exists a three-phase region (I in Fig. 1) which is composed by O/W, BI and LC. With the addition of urea, the O/W region increasesslightly, but the lamellar liquid crystal region shrinks obviously and the bicontinuous region increases apparently. It is obvious that in the three-phase region the swell of the bicontinuous region is caused by the reduce of the lamellar liquid crystal region. Therefore, the existence of urea results in the phase transition from the lamellar liquid crystalline phase to bicontinuous structure.

Mechanism of the hydrotrope-solubilization action of urea

From Fig. 1 and the above discussion, with the addition of urea, the stability of microemulsions increases but that of lamellar liquid crystal decreases. Hence, the microemulsion regions increase but the lamellar liquid crystal regions decrease. Obviously, the hydrotrope-solubilization action of urea is related to the effect of urea to the stability of lamellar liquid crystal of CTAB/n-C_5H_{11}-OH/H_2O system. So the mechanism of urea on the CTAB/n-$C_5H_{11}OH$/H_2O system is that the lamellar liquid crystal phase is transformed into the bicontinuous phase with the addition of urea.

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