Article

Cation-π Interaction between the Aromatic Organic Counterion and DTAB Micelle in Mixed Solvents

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The cation-π interaction between the aromatic organic counterion potassium hydrogen phthalate (KHP) and DTAB micelle in aqueous mixture of EG was investigated, using the techniques of conductivity measurements, UV absorption spectrum and NMR spectrum. The conductivity and UV spectrum studies were with respect to the effect of KHP on DTAB and that of DTAB micelle on KHP, respectively. According to the chemical shift changes of the aromatic ring and the surfactant methylene protons, it can be assumed that KHP penetrated into DTAB micelle with its carboxylic group protruding out of the micellar surface. And the strength of the interaction became weaker with the content of EG in the mixed solvent increasing.

Keywords   cation-π interaction, mixed solvent, ethylene glycol, conductivity, UV spectrum, NMR spectrum

Introduction

Surfactants are widely used in both industry and daily life. The properties of aqueous solution of surfactants have received extensive experimental and theoretical studies over a long period of time. In an attempt to compare the mechanism of the so-called solvophobic effect with the hydrophobic effect, aggregation of several amphiphiles in a nonaqueous polar solvent or its aqueous mixture has received considerable attention recently in the literatures. The previous studies were mostly focused on the thermodynamic properties (especially the cmc determination) and surface properties of micellization,[1-10] or the effect of temperature and pressure on micellization,[11,12] or the vesicle formation,[13] *etc*.

In this paper, a new investigation, about the interaction between the aromatic organic counterion and cationic surfactant micelle in ethylene glycol (EG)/water mixed solvents, was reported. Here, EG was regarded as a cosolvent rather than a cosurfactant forming mixed micelles.

It was well known that the presence of counterions contributed to the stabilization of ionic surfactants. Counterions can reduce the repulsive forces between the hydrophilic parts of the amphiphiles, stabilizing the micelle configuration with reference to a solution of free surfactants. But the association behavior of hydrophobic aromatic counterions was proved to be different from that of inorganic counterions with regard to experimental studies.[14] There exists a strong, noncovalent intermolecular force between aromatic counterions and cationic micelles called cation-π interaction which was

studied in these decades, such as the viscoelasticity phenomenon when organic counterion was present.[15,16] It was assumed that the cation-π interaction would involve a number of intermolecular forces, such as charge-quadrupole, charge-dipole, charge induced dipole, charge transfer and dispersion forces.[17] The orientation of the binding and the effects of counterion structure were discussed, too.[18-21] All these investigations were carried out with water as solvent, but corresponding studies in other polar solvents or mixed solvents were not reported.

The goal of our work was to study the cation-π interaction between the aromatic organic counterion (potassium hydrogen phthalate, KHP) and dodecyl trimethylammonium bromide (DTAB) micelle in aqueous mixture of EG where the mass fraction of EG was 0 (pure water), 20%, 40%, 60% or 80%, using the techniques of conductivity measurements, UV absorption spectrum and NMR spectrum. The conductivity and UV spectrum studies were with respect to the effect of KHP on DTAB and that of DTAB micelle on KHP. While in NMR spectrum, the mutual influence could be observed by the chemical shift changes of the aromatic ring and the surfactant methylene protons. The effects of the EG content on the orientation and the degree of the interaction were discussed.

Experimental

The cationic surfactant DTAB (Acros organics) and KHP (The Third Reagent Plant, Shanghai) were used as received. The solvent EG (Hongsheng Chemical Engi-

neering Plant, Jiangsu) was distilled under the atmospheric pressure. The stable boiling fraction of the distillate was collected and dried with anhydrous sodium sulfate. Water was twice distilled.

The conductivities of the solutions were determined using a DDS-11A conductivity meter (Dazhong Analytical Instrument Plant, Shanghai) with a jacket conductivity cell. The measurement temperature was maintained at (35 ± 0.1) ℃. The UV adsorption spectra of KHP in the presence or absence of DTAB micelle in mixed solvents were recorded on an analytic-jena, specord 200 spectrophotometer (Germany). The sample solutions in the absence of DTAB in mixed solvents were referenced with corresponding solvents and those containing KHP and DTAB were referenced with the blank solutions containing the same DTAB concentration. ^{1}H NMR measurements were carried out with a Bruker DMX 500 NMR spectrometer with the external reference method. The uncertainty of the measurement of chemical shift was 0.005 ppm. The UV and NMR spectra were measured at the room temperature about 25 ℃.

Results and discussion

Conductivity studies

Conductivity measurement is an empirical method to obtain the critical micelle concentration (cmc) of an ionic surfactant. As can be seen in Figure 1, conductivity (κ) plots in mixed solvents as a function of DTAB concentration c are demonstrated and the conductivity plots when KHP is present with the concentration ratio of DTAB to KHP being 2︰1 are shown in Figure 2. Because of the solubility of KHP, conductivity measurements in mixed solvents were only carried out in the solutions where EG contents were 0, 20%, 40% and 60%. The data points above and below the inflection were fit to the equations of the form $\kappa = Ac + B$ (where, κ is the conductivity, c is the concentration of DTAB, and A and B are the slope and intercept, respectively), giving two linear segments corresponding to the monomeric and micellar forms of the surfactants. Solving the two equations simultaneously, the points of intersection were obtained and identified with cmc, which were shown in Table 1. Compared to the cmc values in water and pure EG,[22,11] it can be sure that our measurements were reasonable.

It can be seen that the cmc value increases drastically with the EG content in the solvent system increasing whether KHP is absent or present. The micellar properties of ionic surfactants in EG/water mixed solvents have been studied widely.[8,23] All these investigations suggested that EG as a cosolvent was to decrease the hydrophobic effect because of the decrease of the cohesive energy and dielectric constant. Therefore, the addition of EG mainly produced an increase in cmc, a decrease in the micellar aggregation numbers and an increase in the effective headgroup area which is not

beneficial for the close packing of surfactants. In pure water and other EG/water mixed solvents, the cation-π interaction is demonstrated by the decrease in the cmc for the DTAB-KHP mixed micelle system in comparison to DTAB alone. The penetration of KHP into surfactant headgroups contributes to a reduction of the headgroup electrostatic repulsion and an increase in the total aggregate volume with respect to the formation of the prolate mixed micelle. But the magnitude of lowering of the cmc decreases with the content of EG, which provides insight into the degree that the interface is stabilized.
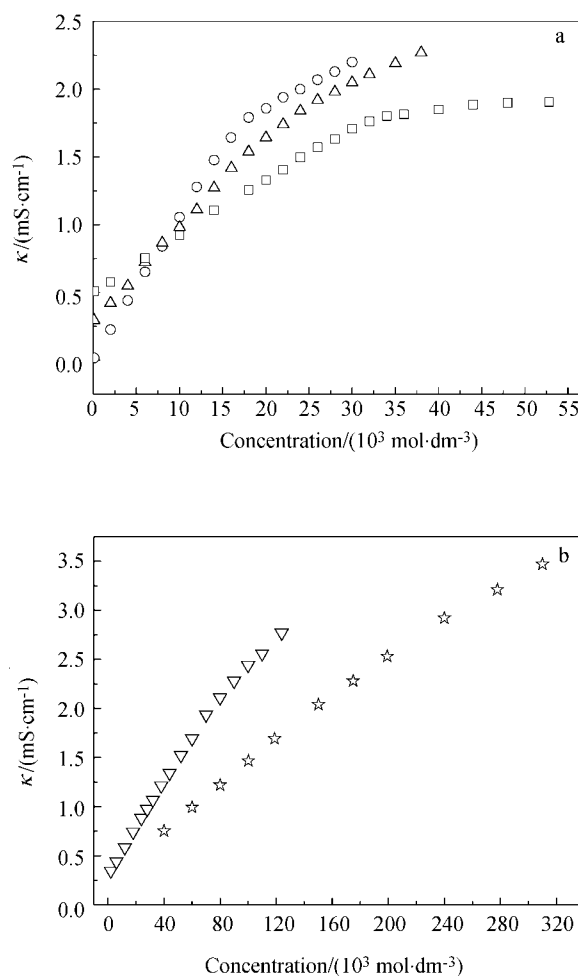

Figure 1 Specific conductivity κ vs concentration c of DTAB in the EG/water mixed solvents. (a) the EG content: (○) 0, (△) 20%, (□) 40%; (b) the EG content: (▽) 60%, (☆) 80%.

Table 1 Variation of the cmc values of DTAB in EG/water mixed solvents in the absence or presence of KHP

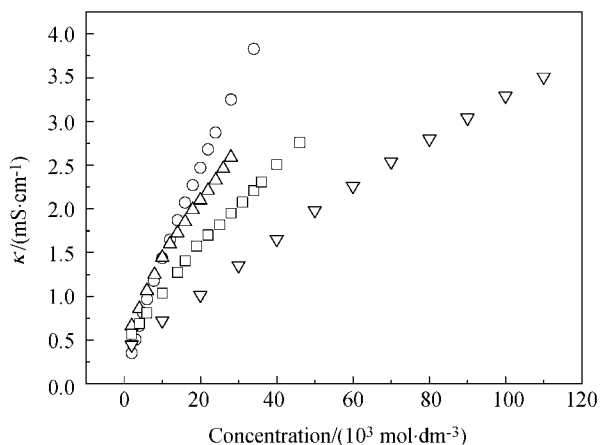| w_{EG}/%	cmc/(10^3 mol•dm^{-3})		
	DTAB alone	KHP+DTAB	Variation
0	16.5	5.4	−11.1
20	22.3	11.8	−10.5
40	28.6	18.7	−9.9
60	68	59	−9
80	186	—	—

Figure 2 Specific conductivity κ vs. concentration c of DTAB in the presence of KHP in the EG/water mixed solvents. The EG content: (○) 0, (△) 20%, (□) 40%, (▽) 60%.

UV spectrum study

UV spectra can provide a sensitive technique for the study of the solubilization of solute molecules by the micelles of the surfactants. The variations in the maximal absorption wavelength of KHP (1.5×10^{-3} mol•dm^{-3}) in the presence of DTAB (0.1 mol•dm^{-3}) in mixed EG/water solvents where the EG content was 0, 20%, 40% or 60% are also shown in Table 2. The effect of DTAB addition on the spectra of KHP is that they change considerably in the maximal absorption wavelength: a red shift is obviously observed in the presence of DTAB. Earlier reports prove that the red shift resulted from the cation-π interaction between KHP and DTAB micelle in such a way that the unsaturated aromatic ring penetrated into DTAB micelle.[16] But the major aspect of the cation-π interaction is not electrostatic attracting interaction between the cation group of DTAB and the anion carboxylic group. In fact, such attracting interaction will weaken the conjugation effect of KHP, which will conduce to the blue shift of the spectra of KHP in presence of DTAB with comparison to KHP alone, while not red shift. It has been concluded that a complete, quantitative description of the cation-π interaction would involve a number of intermolecular forces, and the major aspect is electrostatic interaction of the cation with the quadrupole moment of the aromatic.[17]

Table 2 Variations of the maximal absorption wavelength of KHP in EG/water mixed solvents in the absence or presence of DTAB

w_{EG}/%	λ_{max}/nm		
	KHP	KHP+DTAB	Variation
0	282	287	5
20	283	287	4
40	284	287	3
60	286	287	1
80	287	287	0

Nevertheless, it must be pointed out that when the mass fraction of EG is 80%, red shift effect can not be observed, perhaps because of the unformation of DTAB micelle with lower DTAB concentration than the cmc value (see Table 1) in this mixed solvent.

It also can be seen from Table 2 that the spectrum of KHP shifts to longer wavelength in absence of DTAB as the EG content increases, just like the addition of DTAB. The variations in the UV spectra of *p*-toluenesulfonate in aqueous solution in the presence of CTAB and in ethanol solution in the absence of CTAB, respectively, have been reported by Sepulveda.[19] The similar influence of CTAB micelle and ethanol was received and proved because of the decrease of the dielectric constant by systematic experiments. Our results were similar with Sepulveda's foundation.

It is more interesting to note that the maximal absorption wavelength λ_{max} keeps constant in any solvent system rather than changes with the EG content. This result must be governed by the balance between the enhancement of EG to the red shift of KHP and the hindrance of EG to the strength of the cation-π interaction between KHP and DTAB micelle. The hindrance effect can also be seen from the magnitudes of the red shift decreasing with the EG content. It may be explained for the hindrance of close packing with addition of EG as discussed earlier in conductivity studies.

NMR spectral study

NMR techniques are frequently used to investigate the average position of the organic counterions within the micellar interface. The penetration into the interface and specific orientation of KHP are clearly assigned from the observable chemical shift changes of the aromatic ring and the surfactant methylene protons.

The NMR spectrum of DTAB in the absence or presence of KHP in mixed EG/water solvents where the content of EG is 40% is represented in Figure 3, and that of KHP in the absence or presence of DTAB is demonstrated in Figure 4. It is obvious that the α-methylene, β-methylene protons of DTAB and the proton in position a of KHP all show an upfield shift while proton b of KHP shows a downfield shift. The detailed chemical shifts of these protons in five EG/water solvents with different ratio are shown in Table 3.

Whatever the EG content is, the chemical shifts of the α-methylene and β-methylene protons all decrease with addition of KHP, which gives clear evidence that the aromatic ring of KHP is embedded in the surfactant headgroup, and the ring current effect of the aromatic ring induces shielding of DTAB headgroup protons. However, the chemical shifts of the proton in position a of KHP decreases with addition of DTAB, while that of proton b increases. The opposite shift of protons a and b is due to the orientation of KHP penetrating into DTAB micelle. The previous investigations have proposed

Table 3   Chemical shifts (δ) of methylene protons in DTAB and protons a and b in KHP

$w_{EG}/\%$	DTAB		KHP		DTAB＋KHP			
	β-CH$_2$	α-CH$_2$	H$_a$	H$_b$	β-CH$_2$	α-CH$_2$	H$_a$	H$_b$
0	1.8013	3.4126	7.5844	7.7519	1.5890	3.2452	7.3978	8.0839
20	1.8020	3.4013	7.6008	7.7979	1.6402	3.2703	7.4492	8.0968
40	1.8057	3.3770	7.6350	7.8886	1.6758	3.2781	7.4883	8.0996
60	1.8114	3.3636	7.6669	7.9852	1.7432	3.3076	7.5744	8.1101
80	1.8354	3.3793	7.7037	8.0956	1.8084	3.3515	7.6847	8.1272
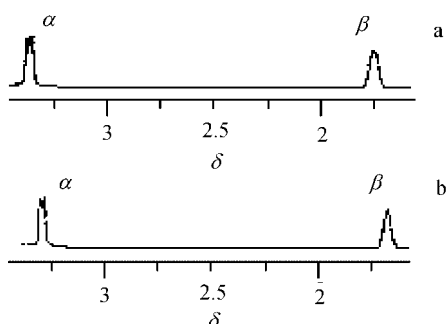
Figure 3 ^{1}H NMR of the methylene protons in DTAB in 40% EG. (a) In the absence of KHP, (b) in the presence of KHP.
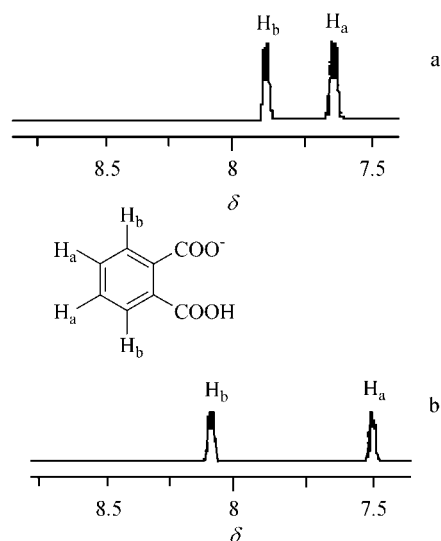
Figure 4 ^{1}H NMR of aromatic ring protons in KHP in 40% EG. (a) In the absence of DTAB, (b) in the presence of DTAB.

many different penetration model, applied in different systems. For example, Sepulveda believed that *p*-toluene sulfonate would be located in the CTAB (cetyl trimethyl ammonium bromide) micelles with its benzene ring immersed in the micelles.[19] While Rao suggested other two models depending on the structure of the additive.[18] Here, according to our experimental fact, it can be assumed that KHP penetrates into DTAB micelle with one of Rao's model: the carboxylic group of KHP protrudes out of the micellar surface. Therefore, the proton in position a is in a medium of weaker polarity, resulting in the upfield shift. The chemical shift in-

creasing of proton b which is still in the solvent environment is due to the decrease in the density of electron atmosphere.

As discussed in UV study, the addition of EG produces hinderance to the strength of the cation-π interaction as well as decreasing of the degree of KHP penetrating into DTAB micelle due to that the magnitudes of the chemical shift changes decrease with the EG content.

Conclusions

The conductivity and UV spectrum studies were with respect to the effect of KHP on DTAB and that of DTAB micelle on KHP, respectively. In any content of EG in mixed solvent, the cation-π interaction between the aromatic organic counterion KHP and DTAB micelle in aqueous mixtures of EG is demonstrated by the decrease in the cmc for the DTAB-KHP mixed micelle system in comparison to DTAB alone, and the presence of DTAB micelle produces a red shift of the UV spectrum of KHP. In NMR spectrum, two kind of protons of KHP show an opposite shift in chemical shift, giving the evidence that KHP penetrates into DTAB micelle with its carboxylic group protruding out of the micellar surface. But it must be noted that the strength of this interaction and the degree of KHP embedded into DTAB micelle both decrease as the EG content increases, because of the decreasing of hydrophobic effects and the dielectric constant produced by EG.

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