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Investigation of interaction between phenol and cetylpyridinium chloride micelle in the absence and in the presence of electrolyte by ^{1}H NMR spectroscopy

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ABSTRACT

In recent years, the micellar enhanced ultrafiltration (MEUF) of phenol in wastewater using cetylpyridinium chloride (CPC) as surfactant has gained many attentions. However, so far no research has focused on the interaction between phenol and CPC micelle. In this study, the interaction between phenol and CPC micelle with and without electrolyte was investigated by using ^{1}H NMR spectroscopy. In the absence of electrolyte, at low phenol concentrations (0.5 mM and 1 mM) phenol was solubilized at the micelle–water interface by the ion interaction between $C_6H_6O^-$ and $C_5H_5N^+$, and in the hydrophilic head group region of CPC micelle by the polar interaction between phenol and CPC micelle. When phenol concentration range was from 1 mM to 8 mM, the micelle–water interface and the hydrophilic head group region of CPC micelle saturated with $C_6H_5O^-$ and phenol, then phenol penetrated into the palisade layer deeper but was still close to the hydrophilic head group of CPC micelle. The presence of NaCl and Na_2SO_4 had almost no influence on the solubilization of phenol in CPC micelle, however, the presence of Na_2CO_3 promoted the solubilization of phenol in CPC micelle significantly. In the presence of Na_2CO_3, more $C_6H_5O^-$ ions were solubilized at the water–micelle interface by the ion interaction between $C_6H_6O^-$ and $C_5H_5N^+$. At low Na_2CO_3 concentration the micelle–water interface of CPC micelle saturated with $C_6H_5O^-$, and benzene ring penetrated into the palisade layer of CPC micelle, but deeper penetration was not observed with the increase of Na_2CO_3 concentration. Excessive $CO_3{}^{2-}$ could make some $C_6H_5O^-$ transfer from CPC micelle to water, resulting in the decrease of the solubilization extent of phenol in CPC micelle.

1. Introduction

In recent years, the micellar enhanced ultrafiltration (MEUF) has been studied as a viable alternative technique which is effective and economical to remove phenol in wastewater. In MEUF of phenol, phenol in aqueous solution is solubilized by micelle of surfactant then an appropriate ultrafiltration membrane is employed to reject both micelle and phenol. Therefore, the ability of micelle to solubilize phenol has a key influence on the performance of MEUF of phenol. Until now many researches about the MEUF of phenol in aqueous stream have been conducted [1–5], but they have not focused on the interaction between phenol and micelle.

The location in the micelle where the solubilization of phenol occurs can reflect the type of the interaction between micelle and phenol, and the ability of micelle to solubilize phenol. Generally, micelle consists of two parts: one is the core of micelle which is composed of hydrophobic hydrocarbon chains; the other is the surface of micelle which is composed of hydrophilic head groups and water of hydration. Solubilization is known to occur at four sites in micelle: (i) at the micelle–water interface, (ii) between the hydrophilic head groups, (iii) in the palisade layer of the micelle, namely, between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups that comprise the outer core of the micelle interior, and (iv) in the inner hydrophobic core of micelle [6]. These solubilization sites can be determined by using nuclear magnetic resonance (NMR) [7], ultraviolet (UV) spectroscopy [8], and X-ray diffraction [9]. NMR chemical shifts depend on the molecular environment of the nuclei, so changes in chemical shifts of surfactants as a function of solubilizate concentration provide precise information on the location of a solubilizate with respect to the micelle nuclei. In the field of colloid and interface science, some researches have been conducted to investigate the solubilization sites of phenol in micelles by using NMR. Suratkar and Mahapatra [6] investigated the site of incorporation of phenol in sodium dodecyl sulfate (SDS) micelle by ^{1}H NMR spectroscopy and concluded that at higher concentration phenol penetrates into the palisade layer of SDS micelle. Jacobs et al. [10] using ^{1}H NMR spectroscopy concluded that phenol orients itself in anionic SDS micelles in such a manner that the hydroxyl group is close to the polar surface. Mata et al. [11] studied a phenol-induced structural transition in aque-

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ous cetyltrimethyl ammonium bromide (CTAB) solution by using ^{1}H NMR and considered that phenol is located at micelle–water interface and do not penetrate the micellar core even at high concentrations of phenol. Chaghi et al. [12] studied the interaction of phenol with cationic micelles of CTAB by ^{1}H NMR in the range of low additive and surfactant concentrations, and concluded that the preferential location of phenol is in the outer micelle parts then additional phenol molecules are located increasingly deeper within the micelle core.

In the most of researches about the MEUF of phenol, CPC was usually used to form micelle to solubilize phenol. In our previous work [13], in order to promote the performance of MEUF of phenol, electrolyte including sodium chloride (NaCl), sodium sulfate (Na_2SO_4) and sodium carbonate (Na_2CO_3) was added into the phenol/CPC system. Compared with NaCl and Na_2SO_4, Na_2CO_3 could improve the performance of MEUF of phenol greatly. As a result, the aim of this study is to investigate the interaction between phenol and CPC micelle with and without electrolyte by using ^{1}H NMR. ^{1}H NMR studies primarily focused on elucidating the nature of the interaction between phenol and CPC micelle, and the solubilization site of phenol in CPC micelle, mainly from the dependence of chemical shifts of all the CPC protons on phenol or Na_2CO_3 concentration.

2. Materials

The cationic surfactant cetylpyridinium chloride (CPC) (purity > 99%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and recrystallized twice from ethanol/acetone (weight ratio of 1:3). The CMCs of CPC in H_2O and D_2O were 0.91 mM and 0.66 mM determined by using surface tension method at 25 °C. Phenol and electrolytes were analytical pure and not further purified.

2.1. Instrument and methods

^{1}H NMR spectra were recorded on a Varian INOVA400 apparatus in D_2O at 25 ± 0.5 °C. Chemical shifts were obtained in δ unit (ppm). For chemical shift measurements, a carbon tetrachloride solution of tetramethylsilane (10%) contained in a capillary was used as an external reference, and its chemical shift was taken as 0.000 ppm.

To investigate the interaction between phenol and CPC micelle, the CPC concentration was fixed at 20 mM and the phenol concentration varied to be 0.5 mM, 1 mM, 2 mM, 3 mM and 8 mM. To investigate the interaction between phenol and CPC micelle in the presence of electrolyte, the CPC concentration and the phenol concentration were 20 mM and 2 mM, and the concentrations of Na_2CO_3, NaCl and Na_2SO_4 were the same (10 mM). It was further investigated the interaction between phenol and CPC micelle in the presence of Na_2CO_3 from the dependence of chemical shifts on Na_2CO_3 concentration. When the CPC concentration and the phenol concentration were 20 mM and 2 mM, the Na_2CO_3 concentration varied to be 1 mM, 3 mM, 5 mM, 10 mM and 20 mM.

The size of CPC micelle in the presence of Na_2CO_3, NaCl and Na_2SO_4 had been determined by DLS (Dynamic light scattering) with Zetasizer Nano-Zs (Malvern Instruments, UK).

3. Results and discussion

Fig. 1 represents the ^{1}H NMR spectra of CPC with and without phenol. It is shown seven proton signals of CPC in ^{1}H NMR spectrum: (a, a′)-CH, (b, b′)-CH and c-CH, α- and β-methylene, 13 bulk methylene as well as the terminal methyl proton ($-CH_3$). Interestingly, the 13 bulk methylene protons of CPC resolved into two well-defined peaks. The downfield signal of this doublet was assigned to the two methylene groups (γ-$(CH_2)_2$) which are attached to the β-methylene group; the upfield signal was assigned to the 11 methylene groups (ε-$(CH_2)_{11}$) which are attached to the terminal methyl group. The signals of CPC except ε-$(CH_2)_{11}$ and $-CH_3$ were found to shift to the upfield in the presence of phenol. This phenomenon indicated that the presence of phenol changed the molecular environment of CPC nuclei. Ring current-induced shifts of the ^{1}H resonance signals of micelles have been admitted as the evidence for the interaction between aromatic molecules and micelles [6,11,12,14]. Further experiments show details.

As shown in Fig. 2, in the presence of increasing concentrations of phenol, all group protons of CPC except ε-$(CH_2)_{11}$ and $-CH_3$ shift to higher magnetic field but to varying extents, whereas ε-$(CH_2)_{11}$ and $-CH_3$ remain downfield shifts.

Fig. 3 shows the dependence of shift extents (δ_0–δ) of all the CPC protons on the phenol concentration. δ_0 and δ represent chemical shifts of all the CPC protons without and with phenol, respec-

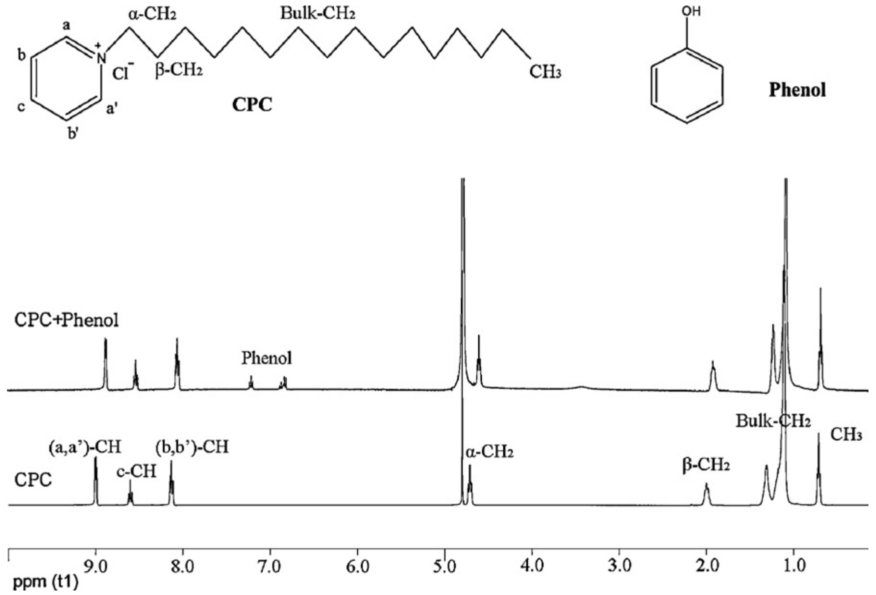

Fig. 1. ^{1}H NMR spectra of CPC in the presence and in the absence of phenol.

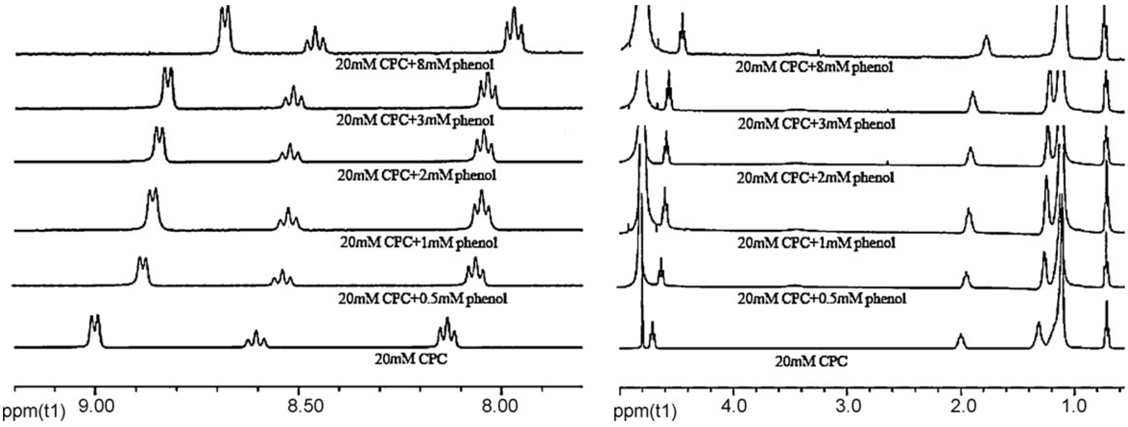

Fig. 2. ^{1}H NMR spectra of CPC protons at various phenol concentrations.

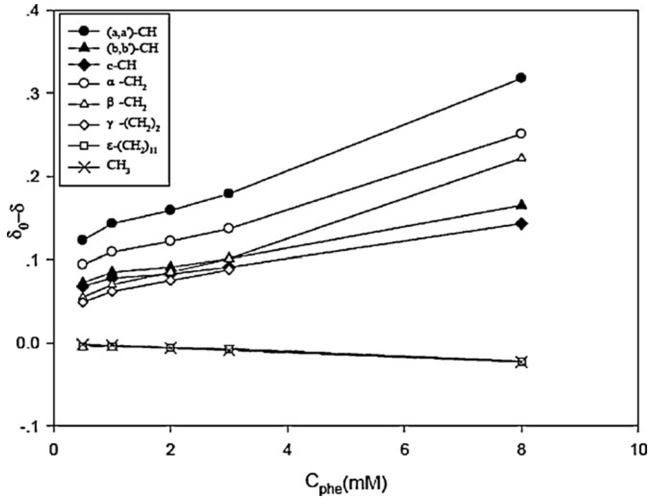

Fig. 3. The dependence of shift extents (δ_0–δ) of all the CPC protons on the phenol concentration.

tively when the CPC concentration was fixed at 20 mM. The positive value of (δ_0–δ) represents the upfield shift and the negative one represents the downfield shift. With the increase of the phenol concentration, positive extents (δ_0–δ) of all the CPC protons except ε-(CH$_2$)$_{11}$ and –CH$_3$ increased at different rates, and negative shift extents (δ_0–δ) of ε-(CH$_2$)$_{11}$ and –CH$_3$ increased linearly at the same rate.

Table 1 shows shift extents (δ_0–δ) of all the CPC protons at various phenol concentrations. When the phenol concentration was 0.5 mM and 1 mM, shift extents of all the CPC protons were ordered as (a, a′)-CH > α-CH$_2$ > (b, b′)-CH > c-CH > β-CH$_2$ > γ-(CH$_2$)$_2$ > ε-(CH$_2$)$_{11}$ > –CH$_3$; with phenol concentration increased, it was found that the order of chemical shifts of (b, b′)-CH and c-CH in pyridine ring and β-CH$_2$ changed. When the phenol concentration was 2 mM, it was observed (b, b′)-CH > β-CH$_2$ > c-CH; when it was 3 mM, the order was (b, b′)-CH=β-CH$_2$ > c-CH; when the phenol concentration was 8 mM, it was found β-CH$_2$ > (b, b′)-CH > c-CH.

In literatures about the solubilization of aromatic compounds in cationic micelles [15–17], the authors concluded that highly polar solutes tend to solubilize in the vicinity of the micelle surface due to ion interactions or polar interactions between the organic solutes and micelles. As well known, phenol possessing phenolic-OH is a polar aromatic compound and can ionize partially to $C_6H_6O^-$ and H^+ in the aqueous solution. CPC possesses the cationic head group of pyridine ring $C_5H_5N^+$, so phenol can be solubilized in CPC micelle by two interactions: one is the ion interaction between $C_6H_6O^-$ and $C_5H_5N^+$, the other is the polar interaction between phenol and CPC micelle. When the phenol concentration was low (0.5 mM and 1 mM), the order of shift extents of all the CPC protons indicated that the benzene ring of phenol was close to the pyridine ring and α-CH$_2$ of CPC, so phenol was solubilized at the micelle–water interface and in the head group region of CPC micelle by the two interactions mentioned above. When the phenol concentration was 2 mM, shift extents of all the CPC protons increased simultaneously, but the order changed and the shift extent of β-CH$_2$ was greater than that of c-CH. This phenomenon meant that phenol was solubilized not only at the micelle–water interface and in the head group region but also in the palisade layer. Phenol penetrated into the palisade in such a way that the phenolic-O$^-$ group was fixed on the surface of the CPC micelle and its benzene ring resided inside the CPC micelle in the hydrocarbon region. As phenol concentration gradually increased, shift extents of all the CPC protons kept increasing, but the increase rate of the shift extent of β-CH$_2$ was faster than that of (b, b′)-CH. Therefore, when the phenol concentration was 8 mM, the shift extent of β-CH$_2$ was greater than that of (b, b′)-CH. It shows that phenol penetrated into the palisade deeper on the increasing phenol concentration. However, the shift extent of β-CH$_2$ was always less than those of (a, a′)-CH and α-CH$_2$. This indicated that although phenol penetrated into the palisade deeper, it was still close to the head group of CPC micelle.

Contrary to upfield shifts of α-CH$_2$, β-CH$_2$ and γ-(CH$_2$)$_2$, ε-(CH$_2$)$_{11}$ and –CH$_3$ remained downfield shifts on the addition of phenol. This could be explained in terms of their chemical environment which became less polar [12]. When the phenol concentration was low, it was solubilized at the micelle–water interface. Upon the increasing phenol concentration, phenol penetrated into the

Table 1
Shift extents (δ_0–δ) of all the CPC protons at various phenol concentrations.

Phenol concentration (mM)	(a, a′)-CH	(b, b′)-CH	c-CH	α-CH$_2$	β-CH$_2$	γ-(CH$_2$)$_2$	ε-(CH$_2$)$_{11}$	–CH$_3$
0.5	0.123	0.072	0.068	0.094	0.055	0.049	−0.004	−0.002
1	0.143	0.085	0.078	0.109	0.070	0.062	−0.004	−0.003
2	0.159	0.091	0.083	0.122	0.085	0.075	−0.006	−0.006
3	0.179	0.101	0.091	0.137	0.101	0.088	−0.007	−0.009
8	0.318	0.165	0.143	0.251	0.222	–	−0.022	−0.023

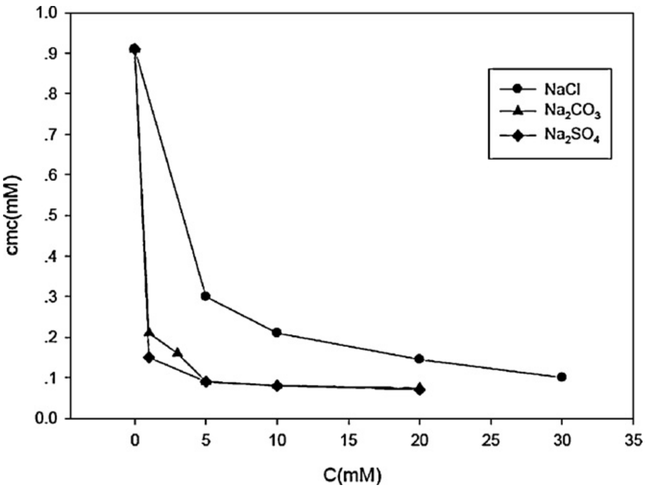

Fig. 4. The dependence of the CMC of CPC on the electrolyte concentration.

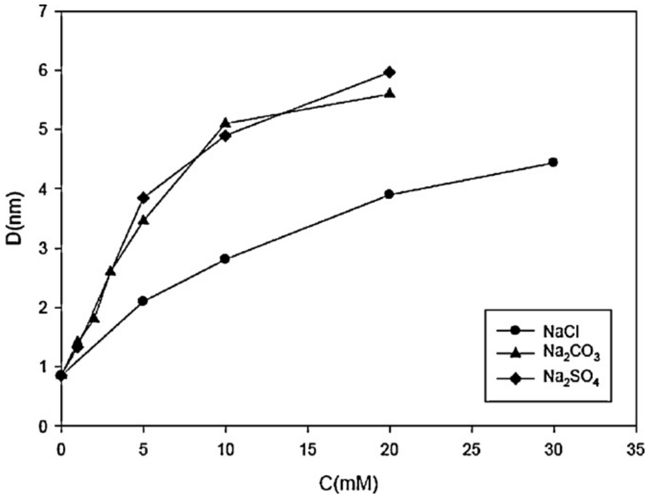

Fig. 5. The dependence of the size of CPC micelle on the electrolyte concentration. CPC: 20 mM.

CPC micelle gradually. Because of the nonpolarity of the benzene ring, the micelle inner became less polar. As a consequence, the resonance signals of ε-$(CH_2)_{11}$ and $–CH_3$ kept shifting to downfield.

Interestingly, it was worth noting that with the increase of the phenol concentration two peaks of γ-$(CH_2)_2$ and ε-$(CH_2)_{11}$ were merged gradually and combined into one peak unresolved at 8 mM. This is contrary to the splitting of the bulk methylene signals of SDS and CTAB due to the addition of phenol [6,12]. These authors suggested that phenol molecules penetrate into the micelle core, effectively shielding up to the methylene protons. This contradiction may be interpreted by the ^{1}H NMR spectra of CPC in the absence of phenol. As shown in Fig. 1, in the absence of phenol the 13 bulk methylene protons of CPC resolved into two well-defined peaks of γ-$(CH_2)_2$ and ε-$(CH_2)_{11}$, however, the bulk methylene protons of SDS and CTAB in the absence of phenol were singlet [6,12].

Electrolyte can weaken the repulsive forces between head groups of ionic surfactant, which are normally fighting against the aggregation of surfactant monomers, so the critical micellar concentration (CMC) of surfactant decreases and the volume of micelle increase. As a result, the presence of electrolyte can enhance the solubilization extent of solubilizates in micelles inner [18–20]. In this study, in the presence of Na_2CO_3, NaCl and Na_2SO_4, the CMC of CPC and the size of CPC micelle at the CPC concentration of 20 mM were determined, as shown in Figs. 4 and 5.

The interaction between phenol and CPC micelle in the presence of electrolyte was investigated by using ^{1}H NMR spectra, too. Table 2 shows shift extents (δ_0–δ) of all the CPC protons in the presence of various electrolytes. Herein δ_0 represented chemical shifts of all the CPC protons when the concentrations of CPC and phenol were 20 mM and 2 mM. In the presence of NaCl and Na_2SO_4, shift extents (δ_0–δ) of all CPC protons are negligible, but in the presence of Na_2CO_3 they are great. This indicated that the presence of NaCl and Na_2SO_4 could not enhance the solubilization extent of phenol in CPC micelle, but the presence of Na_2CO_3 could. According to the surface tension determination, the presence of Na_2CO_3, NaCl and Na_2SO_4 did decrease the CMC of CPC remarkably, moreover, the CMC in the presence of Na_2CO_3 and Na_2SO_4 were similar. A conclusion could be made that although the presence of NaCl and Na_2SO_4 decreased the CMC and increased the volume of CPC micelle, phenol was still difficult to be solubilized in the inner of CPC micelle due to its hydrophilicity. The increase of the solubilization extent of phenol in CPC micelle in the presence of Na_2CO_3 was attributed to the fact that Na_2CO_3 could react with phenol to produce more $C_6H_5O^-$, which could be solubilized at the micelle–water interface. Consequently, the ion interaction between $C_6H_6O^-$ and $C_5H_5N^+$ played more important role in the solubilization of phenol in CPC micelle than the polar interaction between phenol and CPC micelle in the presence of electrolyte. The shift extents of (a, a′)-CH, α-CH_2 and β-CH_2 are greater than those of other protons of CPC, which can still prove it.

The addition of Na_2CO_3 can promote the dissociation of phenol. The higher the dissociation degree is, the more the quantity of phenoxide ion is. The dissociation degree of phenol can be calculated according to [H^+] in the aqueous solution and the dissociation equilibrium constant of phenol of 1.3×10^{-10}. Table 3 shows the pH of the aqueous solutions of phenol/Na_2CO_3 and dissociation degrees of phenol with the addition of various concentrations of Na_2CO_3. The dissociation degree of phenol enhances sharply then slowly with the increase of Na_2CO_3 concentration.

The interaction between phenol and CPC micelle in the presence of Na_2CO_3 was examined further from the dependence of proton shifts of CPC on Na_2CO_3 concentration. Fig. 6 shows ^{1}H NMR spectra of CPC protons in the system of phenol/CPC at various Na_2CO_3 concentrations.

The dependence of shift extents (δ_0–δ) of all the CPC protons on the Na_2CO_3 concentration is shown in Fig. 7. δ_0 and δ represent chemical shifts of all the CPC protons with and without Na_2CO_3, respectively when the concentrations of CPC and phenol were fixed at 20 mM and 2 mM. The positive value of (δ_0–δ) represents the upfield shift and the negative one represents the downfield shift.

Obviously, it shows an inflexion point for all the CPC protons except ε-$(CH_2)_{11}$ and $–CH_3$ when the Na_2CO_3 concentration is 5 mM. When the Na_2CO_3 concentration is below 5 mM, shift extents (δ_0–δ) of protons increase sharply; when it is above 5 mM, variation trend is in the opposite direction. And the curve of ε-$(CH_2)_{11}$ and

Table 2
Shift extents (δ_0–δ) of all the CPC protons in the presence of various electrolytes (CPC: 20 mM; phenol: 2 mM; electrolytes: 10 mM).

Electrolyte	(a, a′)-CH	(b, b′)-CH	c-CH	α-CH_2	β-CH_2	γ-$(CH_2)_2$	ε-$(CH_2)_{11}$	$–CH_3$
NaCl	−0.0610	−0.0380	−0.0350	−0.0420	−0.0100	−0.0180	−0.002	−0.001
Na_2CO_3	0.2350	0.0630	0.0550	0.1620	0.1560	–	−0.0320	−0.029
Na_2SO_4	0.006	−0.0360	−0.0200	−0.004	0.0320	0.0200	0.0000	0.0000

Table 3
The pH of the aqueous solutions of phenol/Na_2CO_3 and dissociation degrees of phenol with the addition of various concentrations of Na_2CO_3 at 25 °C, phenol concentration fixed at 2 mM.

	Na_2CO_3 (mM)					
	0	1	3	5	10	20
pH	6.43	9.61	10.08	10.3	10.46	10.71
Dissociation degree of phenol (%)	0.035	34.6	61.0	72.2	78.9	87.0

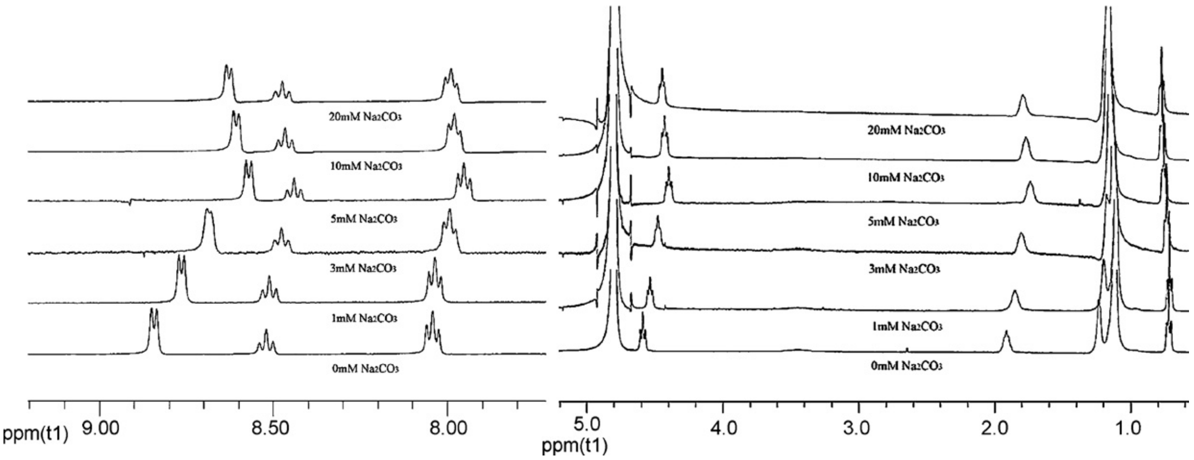

Fig. 6. ^1H NMR spectra of CPC protons in the system of phenol/CPC at various Na_2CO_3 concentrations. CPC: 20 mM; phenol: 2 mM.

$-CH_3$ shows descendent trend and gradual linear. On the whole, they were ordered as (a, a′)-CH > α-CH_2 > β-CH_2 > (b, b′)-CH > c-CH > γ-$(CH_2)_2$ > ε-$(CH_2)_{11}$ > $-CH_3$. The shift extents of α-CH_2 and β-CH_2 were similar, and the shift extent of (b, b′)-CH has no obvious difference with that of c-CH. In the aqueous solution Na_2CO_3 could react with phenol to produce $C_6H_5O^-$, H^+ and $NaHCO_3$, namely, at the same phenol concentration the quantity of $C_6H_5O^-$ in the presence of Na_2CO_3 was more than that in the absence of Na_2CO_3, resulting in the solubilization of phenol at the water–micelle interface mostly by the ion interaction between $C_6H_6O^-$ and $C_5H_5N^+$. Furthermore, it was observed that when Na_2CO_3 concentration was 3 mM two peaks of γ-$(CH_2)_2$ and ε-$(CH_2)_{11}$ were merged into one peak unresolved. According to Table 3, when the Na_2CO_3 concentration increased from 0 mM to 3 mM, the dissociation degree of phenol enhanced sharply. This revealed that at low Na_2CO_3 concentration the micelle–water interface of CPC micelle saturated with $C_6H_5O^-$, and the benzene ring penetrated into the palisade layer of CPC micelle. Furthermore, as observed, change trends of chemical shifts of all the CPC protons were similar, so the inference could be drawn that phenol did not penetrate into the palisade of CPC micelle deeper with the increase of Na_2CO_3 concentration. In summary, the precise solubilization site of benzene ring should be between α-CH_2 and β-CH_2 according to the similarity of their shift extents.

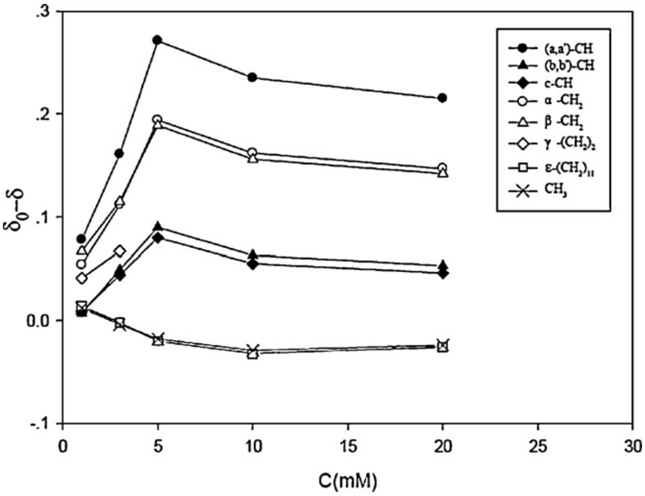

Fig. 7. The dependence of shift extents (δ_0–δ) of CPC protons on the Na_2CO_3 concentration in the system of phenol/CPC. CPC: 20 mM; phenol: 2 mM.

Interestingly, the resonance signals of ε-$(CH_2)_{11}$ and $-CH_3$ remained downfield shifts on the addition of Na_2CO_3, and this trend was the same as on the addition of phenol. This could be interpreted in terms of their chemical environment which became less polar, too. But the less polarity of their chemical environment mainly resulted from counter-ions including $CO_3{}^{2-}$, $HCO_3{}^-$ and $C_6H_5O^-$ binding to the headgroups in the CPC micelle mantle [21]. With the increase of Na_2CO_3 concentration, more counter-ions bound to the headgroups of CPC micelle, consequently, the resonance signals of ε-$(CH_2)_{11}$ and $-CH_3$ kept shifting to downfield.

When the Na_2CO_3 concentration was above 5 mM, the dissociation degree of phenol enhanced slowly, and excessive $CO_3{}^{2-}$ could adsorb on the surface of CPC micelle by the electrostatic attraction between $CO_3{}^{2-}$ and $C_5H_5N^+$. They could compete with $C_6H_5O^-$. Obviously, negative divalent was easier to adsorb on the surface of CPC micelle than negative one valence $C_6H_5O^-$, and could occupy more adsorption sites of CPC micelles. Consequently, some $C_6H_5O^-$ transferred from the surface of CPC micelles to water, and shift extents of all the CPC protons except ε-$(CH_2)_{11}$ and $-CH_3$ decreased. However, the gross quantity of counter-ions binding to the headgroups in the CPC micelle mantle did not decrease, so the inflexion point of shift extents of ε-$(CH_2)_{11}$ and $-CH_3$ protons did not exist at the Na_2CO_3 concentration of 5 mM.

4. Conclusions

From measurement of the chemical shifts of the protons of CPC, it was possible to elucidate the interaction between phenol and CPC micelle with and without electrolyte. At low phenol concentration

(0.5 mM and 1 mM), phenol was solubilized at the micelle–water interface by the ion interaction between $C_6H_6O^-$ and $C_5H_5N^+$, and in the head group region of CPC micelle by the polar interaction between phenol and micelle; with the increase of the phenol concentration (above 2 mM), the micelle–water interface and the head group region of CPC micelles saturated with $C_6H_5O^-$ and phenol, then phenol penetrated into the palisade layer of CPC micelle deeper and deeper, but it was still close to the head group of CPC micelle under the phenol concentration range in this study.

Compared with NaCl and Na_2SO_4, the presence of Na_2CO_3 promoted the solubilization of phenol in CPC micelle significantly due to the enhancement of dissociation degree of phenol. The addition of Na_2CO_3 produced more $C_6H_6O^-$ at the same phenol concentration. The ion interaction between $C_6H_6O^-$ and $C_5H_5N^+$ played more important role in the solubilization of phenol in CPC micelle than the polar interaction between phenol and CPC micelle in the presence of Na_2CO_3. At low Na_2CO_3 concentration the micelle–water interface of CPC micelle saturated with $C_6H_5O^-$, and the benzene ring penetrated into the palisade layer of CPC micelle between α-CH_2 and β-CH_2. When the Na_2CO_3 concentration exceeded 5 mM, excessive ${CO_3}^{2-}$ could compete with $C_6H_5O^-$ and occupy more adsorption sites of CPC micelles. Consequently, some $C_6H_5O^-$ transferred from CPC micelles to water, and shift extents of all the CPC protons except N-$(CH_2)_{11}$ and –CH_3 decreased.

The results of this study would aid in gaining a sound scientific understanding of the factors governing the effective solubilization of phenol in CPC micelles and enhancing the performance of the MEUF of phenol effectively.

Acknowledgements

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References

[1] J. Sabaté, M. Pujolà, J. Llorens, Comparison of polysulfone and ceramic membranes for the separation of phenol in micellar-enhanced ultrafiltration, J. Colloid Interface Sci. 246 (2002) 157–163.
[2] F.I. Talens-Alesson, H. Adamczak, J. Szymanowski, et al., Micellar-enhanced ultrafiltration of phenol by means of oxyethylated fatty acid methyl esters, J. Membr. Sci. 192 (2001) 155–163.
[3] M. Syamal, P.K. Sirshendu De, Bhattacharya, Phenol solubilization by cetyl pyridinium chloride micelles in micellar enhanced ultrafiltration, J. Membr. Sci. 137 (1997) 99–107.
[4] C.C. Tung, Y.M. Yang, C.H. Chang, et al., Removal of copper ions and dissolved phenol from water using micellar-enhanced ultrafiltration with mixed surfactants, Waste Manage. 22 (2002) 695–701.
[5] J. Sabaté, M. Pujolà, E. Centelles, et al., Determination of equilibrium distribution constants of phenol between surfactant micelles and water using ultrafiltering centrifuge tubes, Colloid Surf. A 150 (1999) 229–245.
[6] V. Suratkar, S. Mahapatra, Solubilization site of organic perfume molecules in sodium dodecyl sulfate micelles: new insights from proton NMR studies, J. Colloid Interface Sci. 225 (2000) 32–38.
[7] J.C. Eriksson, G. Gillberg, NMR-studies of the solubilisation of aromatic compounds in cetyltrimethylammonium bromide solution. II, Acta Chem. Scand. 20 (1966) 2019–2027.
[8] J.R. Cardinal, P. Mukherjee, Solvent effects on the ultraviolet spectra of benzene derivatives and naphthalene. Identification of polarity sensitive spectral characteristics, J. Phys. Chem. 82 (1978) 1614–1620.
[9] W. Philippoff, Micelles and X-rays, J. Colloid Interface Sci. 5 (1950) 169–191.
[10] J.J. Jacobs, R.A. Anderson, T.R. Watson, Interaction in phenol–sodium dodecyl sulphate–water systems, J. Pharm. Pharmacol. 23 (1971) 148–149.
[11] J.P. Mata, V.K. Aswal, P.A. Hassan, P. Bahadur, A phenol-induced structural transition in aqueous cetyltrimethylammonium bromide solution, J. Colloid Interface Sci. 299 (2006) 910–915.
[12] R. Chaghi, L.-C. de Menorval, C. Charnay, et al., Interactions of phenol with cationic micelles of hexadecyltrimethylammonium bromide studied by titration calorimetry, conductimetry, and ^{1}H NMR in the range of low additive and surfactant concentrations, J. Colloid Interface Sci. 326 (2008) 227–234.
[13] G.M. Zeng, K. Xu, J.H. Huang, et al., Micellar enhanced ultrafiltration of phenol in synthetic wastewater using polysulfone spiral membrane, J. Membr. Sci. 310 (2008) 149–160.
[14] B.J. Kim, S.G. Oh, S.S. Im, Investigation on the solubilization locus of aniline–HCl salt in SDS micelles with H NMR spectroscopy, Langmuir 17 (2001) 565–566.
[15] S.R. Jadhav, N. Verma, A. Sharma, et al., Flux and retention analysis during micellar enhanced ultrafiltration for the removal of phenol and aniline, Sep. Purif. Technol. 24 (2001) 541–557.
[16] S.N. Bhat, G.A. Smith, E.E. Tucker, et al., Solubilization of cresols by 1-hexade cylpyridinium chloride micelles and removal of cresols from aqueous streams by micellar-enhanced ultrafiltration, Ind. Eng. Chem. Res. 26 (1987) 1217–1222.
[17] C. Treiner, A.K. Chattopadhyay, Correlation of Partition Coefficients for Polar Aromatic and Aliphatic Molecules between Trimethyldodecylammonium Bromide Micelles + Water and Octanol + Water Systems at 298.15 K, J. Colloid Interface Sci. 109 (1986) 101–108.
[18] N. Zaghbani, A. Hafiane, M. Dhahbi, Removal of Safranin T from wastewater using micellar-enhanced ultrafiltration, Desalination 222 (2008) 348–356.
[19] N. Zaghbani, A. Hafiane, M. Dhahbi, Separation of methylene blue from aqueous solution by micellar enhanced ultrafiltration, Sep. Purif. Technol. 55 (2007) 117–124.
[20] M.J. Rosen, Surfactants and Interfacial Phenomena, 3rd ed., Wiley-Interscience, New York, 2004.
[21] L.J. Magid, Z. Han, G.G. Warr, et al., Effect of counter-ion competition on micellar growth horizons for cetyltrimethylammonium micellar surfaces: electrostatics and specific binding, J. Phys. Chem. B 101 (1997) 7919–7927.