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Adsorption of cationic–anionic surfactant mixtures on activated carbon

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Abstract

This paper reported the adsorption of cationic–anionic surfactant mixtures, such as octyltriethylammonium bromide/sodium dodecylbenzenesulfonate (OTEAB/SDBS) and dodecylpyridinium chloride/sodium octanesulfonate (DPC/SOS), on activated carbon (AC) in deionized water and in mineralized water systems. The AC surface chemistry was characterized by X-ray photoelectron spectroscopy and ζ-potential determinations. It was observed that in deionized water solution, the addition of SOS obviously promoted the adsorption of DPC, while the existence of OTEAB increased the adsorption of SDBS first and then decreased that slightly with increasing SDBS concentration. In mineralized water solution, the addition of cationic (anionic) surfactants reduced the adsorption of anionic (cationic) surfactants. It was shown that the adsorption of the surfactants on the AC was predominated mainly by the hydrophobic interaction between AC surface and surfactants because of the low oxygen content and very low ζ-potential on the AC surface. There might exist synergism between cationic and anionic surfactants when adsorbing on AC in deionized water due to the electrostatic interaction between oppositely charged surface active ions. Such synergism might be greatly weakened when a large number of inorganic salts exist owing to the "screen" effect of the counter ions of the salt on the electrostatic attraction of oppositely charged surface active ions.

Keywords: Activated carbon; Adsorption; Interfacial properties; Surface properties

1. Introduction

It is well known that the mixtures of cationic–anionic surfactants possess much higher surface activities than their individual components [1–4]. Moreover, such a synergism can be obtained even if they were mixed unequimolarly in a large range of ratios [1,4]. It is of importance to check if such a synergism in the interfaces of air/liquid or liquid/liquid still exists in solid/liquid interfaces. In some cases, such a synergism is necessary. However, in some cases, it should be avoided. For example, in the case of enhanced oil recovery [5,6], on the one hand, we hope to optimize the use of the synergism between cationic and anionic surfactants to reduce both surfactant concentration and oil/water interfacial tension, however, on the other hand, we always wish the adsorption of surfactants on the surfaces of rock and soil as less as possible. A lot of work has been done on the adsorption of surfactants at solid/liquid interfaces [7–9]. However, most of works focused on the use of single surfactants [10–12]. While the studies involving surfactant mixtures were mainly on the same type surfactants or ionic–nonionic surfactant mixtures

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[13–15]. To the best of our knowledge, investigation on the adsorption of cationic–anionic surfactant mixtures on activated carbon was rare. In this paper, we will report the adsorption of cationic–anionic surfactant mixture systems, including octyltriethylammonium bromide/sodium dodecylbenzenesulfonate and dodecylpyridinium chloride/sodium octanesulfonate, on activated carbon. Since the practical systems usually contained a lot of salts, and the inorganic salts could influence the adsorption of single surfactants, especially ionic surfactants, at solid/liquid interface [10–12,16], we prepared the solution by using both deionized water and mineralized water, and the effect of the inorganic salts on the adsorption of the surfactant mixtures was discussed.

2. Experiments

2.1. Materials

Octyltriethylammonium bromide (OTEAB) and sodium octanesulfonate (SOS) were prepared by the procedure described in our previous paper [3]. Dodecylpyridinium chloride (DPC) and sodium dodecylbenzenesulfonate (SDBS) were purchased from Beijing Chemical Co., A.R. grade. No surface tension minima were found for all the surfactants, which implied that no surface-active impurities existed [4]. Water was of Millipore quality.

Activated carbon (AC), the third grade graininess, was obtained from Beijing Guanghua Timber Mill, which was treated using water, anhydrous acetic acid and hydrofluoric acid successively as described in our previous work [17]. The treatment by anhydrous acetic acid was for removing compounds of alkali metals and ferrum, and the purpose of the hydrofluoric acid treatment was to remove other impurities [18]. The original ash content of AC used in this work was about 5%. After the treatments, it was found that the sample contained ash less than 0.06%.

The mineralized water was prepared as the following composition [19]: $CaCl_2$, 222 $mg\,L^{-1}$; $MgCl_2 \cdot 6H_2O$, 256 $mg\,L^{-1}$; $NaHCO_3$, 833 $mg\,L^{-1}$; Na_2SO_4, 120 $mg\,L^{-1}$; NaCl, 4718 $mg\,L^{-1}$. All salts were A.R. grade.

2.2. Characterization of activated carbon

The specific surface area, pore volume and pore size distribution of AC were determined by a nitrogen gas adsorption analysis, using a Micromeritics ASAP 2010C instrument at −196 °C. The mesoporous and microporous properties were estimated by BJH [20] and H–K method [21], respectively.

X-ray photoelectron spectroscopy (XPS) was used to analyze the oxygen content and surface functional groups of AC. XPS was performed with an Axis Ultra spectrometer (Kratos, UK).

Elemental analysis of AC samples was used to determine the overall oxygen content of AC, which was performed using Elementar Vario EL (Germany).

The ζ-potentials of AC particles in deionized water and in mineralized water were measured using Zeta potential analyzer (Zeta-plus, Brookhaven Instruments Corp.).

2.3. Determination of isotherm

The samples were prepared by adding 0.02 g AC into 25 ml surfactant solution. To obtain the adsorption isotherms of the mixed surfactant, the surfactant mixture solutions were prepared, followed by the addition of the adsorbent. The adsorption equilibrium was obtained by shaking the solutions for 10 h in an air-thermostat at 25.0 ± 0.5 °C. The concentrations of DPC and SDBS were determined by UV absorption (UV-3100, Shimdazu) at 257 and 260 nm, respectively. The apparent amount adsorbed (Γ) was obtained from a mass balance analysis [8]. Prior to the determination of isotherm, all solutions were adjusted to pH ~7 by using HCl and NaOH. The pH was determined using a pH meter (PHS-3C, Shanghai Leisheng Instrument Co., China).

2.4. Determination of critical micelle concentration (cmc) of surfactants

The cmc values of surfactants were determined by surface tension method [4]. The surface tension was measured by drop volume method [4].

3. Results and discussion

3.1. Isotherms of DPC and SDBS on activated carbon

In order to examine the adsorption properties of mixed cationic–anionic surfactants, the adsorption of single ionic surfactants on AC was determined as shown in Fig. 1.

It could be seen that at the same surfactant concentration, the amount adsorbed of both DPC and SDBS in mineralized water is larger than that in deionized water. Moreover, it was also observed that the amount adsorbed of DPC was slightly higher than that of SDBS when their equilibrium concentrations were same.

3.2. Adsorption of mixed cationic–anionic surfactants on AC/deionized water interface

Fig. 2a showed the isotherm of DPC on AC/deionized water interface when 4 $mmol\,dm^{-3}$ SOS existed.

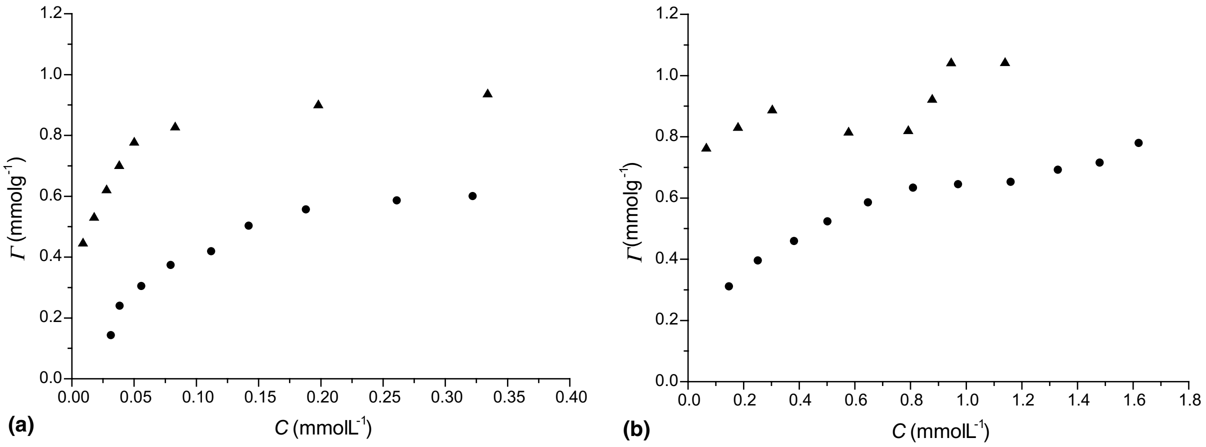

Fig. 1. Adsorption isotherms of DPC (a) and SDBC (b) on AC in deionized water (●) and in mineralized water (▲) (25 °C).

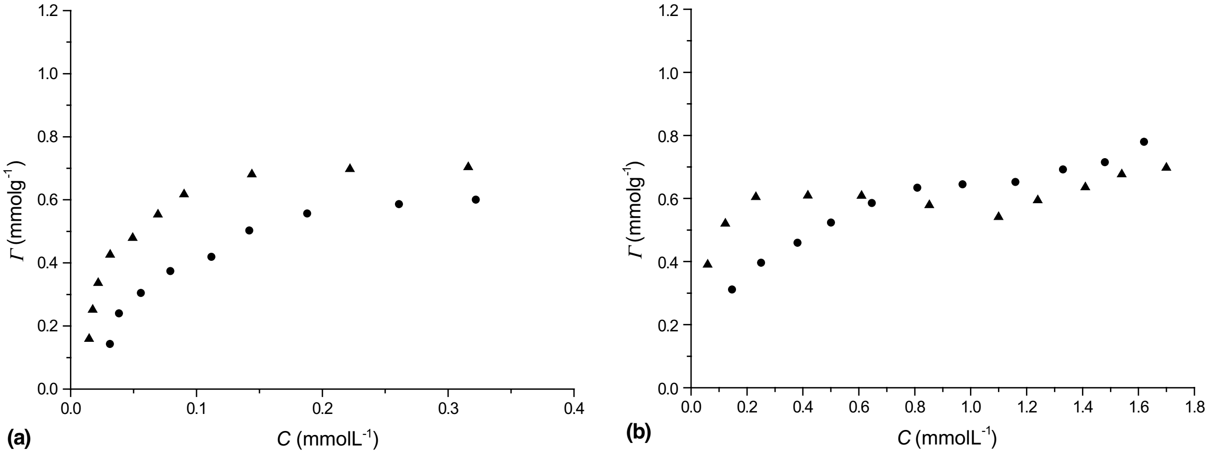

Fig. 2. Adsorption isotherms of DPC with 4 mmol dm^{-3} SOS (a, ▲) and SDBC with 0.5 mmol dm^{-3} OTEAB (b, ▲) on AC in deionized water (25 °C). (a, ●): DPC without SOS, (b, ●): SDBC without OTEAB.

Fig. 2b showed the isotherm of SDBS with adding 0.5 mmol dm^{-3} OTEAB. It could be seen from Fig. 2 that, comparing to the isotherm without SOS, the existence of SOS increased the amount adsorbed of DPC. While the existence of OTEAB increased the amount adsorbed of SDBS at first and then decreased slightly with increasing SDBS concentration.

3.3. Adsorption of mixtures of cationic–anionic surfactants on AC/mineralized water interface

Fig. 3 showed the isotherms of the mixtures of cationic–anionic surfactants on AC in mineralized water. It could be seen from Fig. 3 that the existence of 4.0 mmol dm^{-3} SOS reduced the amount adsorbed of DPC (Fig. 3a), and in the same fashion, the existence of 0.5 mmol dm^{-3} OTEAB reduced the adsorption of SDBS (Fig. 3b). Such results were totally different from those in deionized water.

3.4. Surface properties of AC and the possible adsorbing mechanism

The adsorption ability of AC was known to relate with its surface chemical composition, specific surface area and pore structure [22], which was affected by different AC raw materials as well as the different treatment methods [23,24]. One needs to know the surface properties of AC in order to discuss the adsorption mechanism. Table 1 showed the AC specific surface area and pore structure determined by a nitrogen gas adsorption analysis.

It could be seen that the AC we used contained both mesopores and micropores, but the pore structure was dominated by micropores.

Pendleton et al. [23,25] and Lee and Reucroft [26] had demonstrated that AC surface chemistry was more important than poresize distribution in terms of their ability to control the adsorption of surfactant from di-

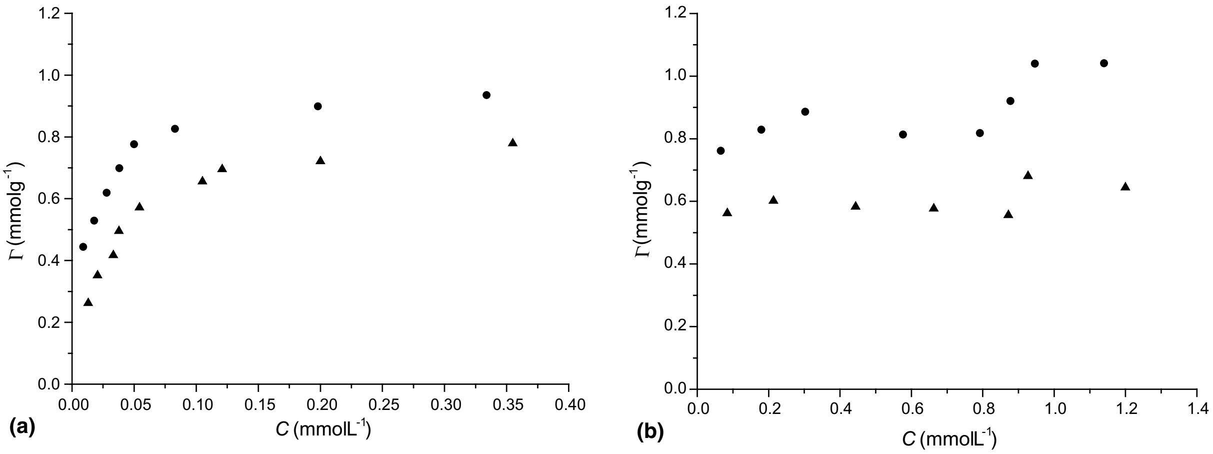

Fig. 3. Adsorption isotherms of DPC with 4 mmol dm^{-3} SOS (a, ▲) and SDBC with 0.5 mmol dm^{-3} OTEAB (b, ▲) on AC in mineralized water (25 °C). (a, ●): DPC without SOS, (b, ●): SDBC without OTEAB.

Table 1
The specific surface area, pore volume and pore diameter of activated carbon

Specific surface area	1049.5 $m^2 g^{-1}$
Total pore volume	0.64 $cm^3 g^{-1}$
Mesopore volume	0.27 $cm^3 g^{-1}$
Micropore volume	0.37 $cm^3 g^{-1}$
Average mesopore diameter	4.24 nm
Average micropore diameter	0.82 nm

lute aqueous conditions. AC surfaces exhibited chemical heterogeneity due to the presence of heteroatoms, O, N, H, P, and/or S [27]. Among those heteroatoms, oxygen was found to have strongest impact on solution adsorption [23,27]. We investigated the surface chemistry of AC by elemental analysis, XPS and the ζ-potential measurements.

Fig. 4 showed the XPS spectrum. We applied the spectrum of various C—O and C—C structures to fit the C 1s spectrum. Fig. 4 suggested the presence of varied oxygen-containing groups on AC surface, their concentrations were listed in Table 2. The oxygen and carbon content on the AC surface were also shown in Table 2. Using elemental analysis, the total oxygen and carbon content in the AC samples were also obtained as shown in Table 2.

Comparing with the phosphoric acid-activated AC samples reported by Pendleton et al. [23], it was found that the oxygen content in the AC samples used in our experiments was relatively low.

A complete analysis of the surfactant–AC adsorption process required that surface charges be addressed as an adsorption variable as the C—O structures would be susceptible to ionization and/or polarization processes on immersion in the aqueous phase. These sites would provide an electron-rich environment for electrophilic interactions [23]. We measured the ζ-potential of AC particles at different pH (Fig. 5).

Fig. 5 showed that the ζ-potential of AC particles was very low, only −0.2 mV in neutral water (it was reported that the ζ-potentials of the AC treated using acetone and ultra-pure water [28] and the AC treated at 700 °C were close to zero [29]). It was known that the relationship between ζ-potential and surface charge density σ [30] could be expressed as

$$\sigma = \pm\left[\frac{kT\varepsilon}{2\pi}\right]^{1/2}\left\{\sum_i n_i\left[\exp\left(-\frac{Z_i e\zeta}{kT}\right)-1\right]\right\}^{1/2}, \tag{1}$$

where ε, e, κ and T were dielectric constant of medium, electron charge, Boltzmann constant and temperature respectively, n_i and z_i were i ion number per unit liquid and the valence of i ion respectively. Because of the low ζ-potential of AC used in our work, the surface charge in deionized water was not large, which corresponded to its relatively low oxygen content as above described.

In the mineralized water at pH 2.19, 3.89, 6.19 and 8.5, the ζ-potentials of AC particles were all zero. The total concentration of inorganic salts in the mineralized water used in this work was about 0.09 mol dm^{-3}. According to the equation for calculating diffusion electric bilayer ($1/\kappa$) [30]

$$\frac{1}{\kappa} = \frac{3\times 10^{-10}}{z(c)^{1/2}(m)}, \tag{2}$$

(where z and c were ion valence number and electrolyte concentration respectively), the thickness of diffusion electric bilayer was about 10^{-9}–10^{-10} m. The lowering of diffusion electric bilayer thickness significantly decreased ζ-potential. Therefore, the AC surface was uncharged in mineralized water among a broad pH range.

3.5. Possible adsorbing mechanism

It was known that surfactant adsorption was the result of several interactions at the solid–solution

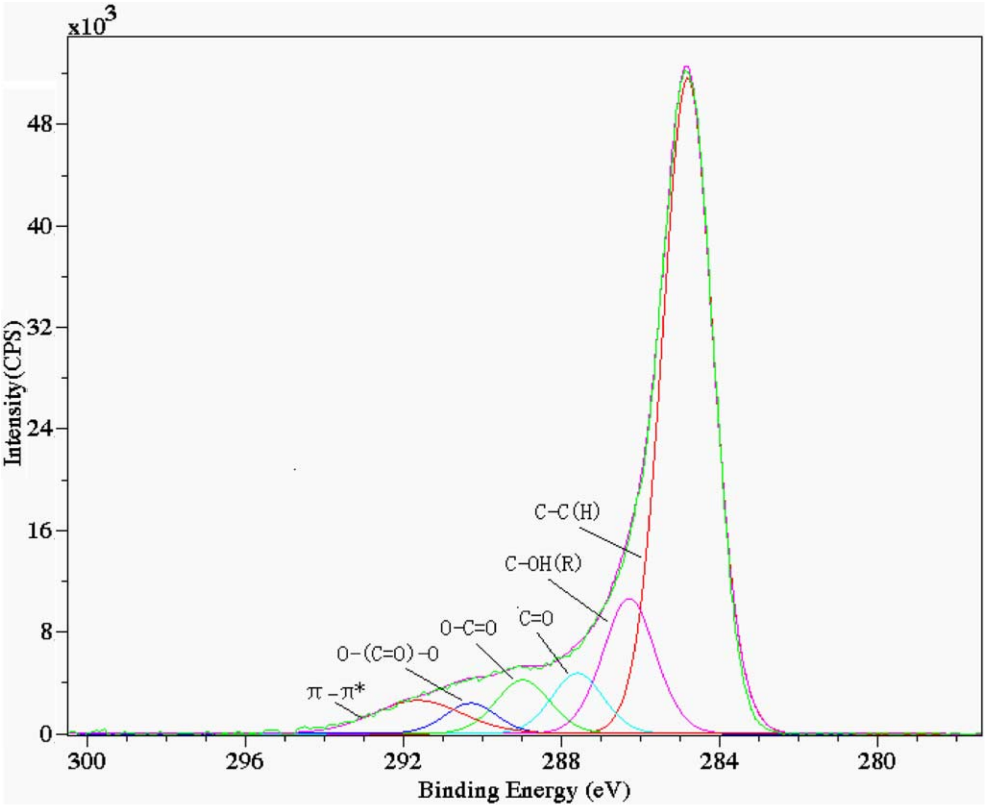

Fig. 4. Curve fitting of the XPS spectrum of activated carbon C 1s peak.

Table 2
The concentration of AC functional groups and oxygen and carbon content

Surface functional groups (%)	
Graphic/(C—C)	65.5
C—O—R(H)	13.9
C═O	6.1
HO—C═O	5.6
O—(C═O)—O	3.1
π—π*	5.8
Oxygen content (%)	
6.8 (surface)	6.2 (bulk)
Carbon content (%)	
93.2 (surface)	88.45 (bulk)

interface. To name a few, for example, the direct interactions between surfactant and activated carbon could be hydrophobic bonding, hydrogen bonding, dispersion forces, electrostatic attraction, and ion exchange to replacing counterions [22]. Moreover, other interactions would also contribute the surfactant adsorption, such as the interaction between surfactant molecules at the adsorbent–solution interface, which leaded to the formation of interfacial aggregates [23].

Pendleton et al. found an opposite relationship between the amount adsorbed of ionic surfactants and the oxygen content of AC [23,31,32]. Because the increasing of AC oxygen content resulted in an increasingly hydrophilic surface, they concluded that the adsorption of ionic surfactants on AC relied mainly on surface-solute hydrophobic interactions.

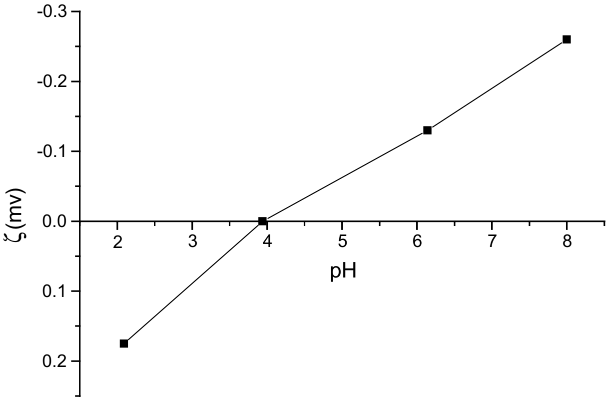

Fig. 5. The relationship of ζ-potential of activated carbon and pH (25 °C).

Because the AC used in our work contained relatively low oxygen content and low surface charges, we assumed that the electrostatic action might not significantly contribute the adsorption of surfactants. The adsorption of ionic surfactants on AC might be predominated by the hydrophobic interaction between surfactant and AC surface.

Although the surface charge in deionized water was not large, but there still existed weak electrostatic interaction between weakly negatively charged AC surface and cationic surfactant. This might explain why the amount adsorbed of DPC was slightly larger than that of SDBS (Fig. 1).

For the mixtures of cationic–anionic surfactants, there existed electrostatic attractions between the oppositely charged headgroups of surfactants [1–4]. The adsorbed ionic surfactant could make the AC surface charged, which might promote the adsorption of oppositely charged another ionic surfactants. In other words, there might exist synergism between cationic and anionic surfactants when they adsorbed on the AC surface. Based on this, we could explain the results in Fig. 2a. Because the concentration of SOS was much higher than that of DPC, the amount adsorbed of SOS should be larger than that of DPC, which made the AC surface negatively charged, thus promotes the adsorption of DPC. In the same way, for SDBS-OTEAB mixing systems (Fig. 2b), when the concentration of OTEAB was much higher than that of SDBS, the amount adsorbed of SDBS could be increased because of the synergism between SDBS and OTEAB. However, if the concentration of OTEAB was lower than that of SDBS, the promoting effect of adsorbed OTEAB on the adsorption of SDBS was no longer obviously, OTEAB even could induce a lowering of the adsorption of SDBS because OTEAB molecules occupied part of AC surface (Fig. 2b). Therefore, it could be concluded that the cooperating adsorption in cationic–anionic surfactant mixtures was in fact due to the electrostatic interaction between oppositely charged surface active ions.

It was well known that inorganic salts could impact the adsorption of ionic surfactants at solid/liquid interface [10–12,16]. However, such an effect might have some differences on single ionic surfactants and on mixed cationic–anionic surfactants. For single ionic surfactants, the counter ions of salts reduced the repulsion between ionic surfactant headgroups, thus inducing the lowering of cmc of surfactants [8], as shown in Table 3. The lowering of cmc value made surfactants form adsorbed micelles before the cmc [9]. It was known that the formation of adsorbed micelles could increase the adsorption dramatically [9]. This might explain why the amount adsorbed of both DPC and SDBS in mineralized water was larger than that in deionized water at the same surfactant concentrations (Fig. 1). At the same time, the ''salt out'' effect of surfactants in mineralized water could also induce the increase of amount adsorbed [9].

Table 3
cmc of surfactants determined by surface tension method (25 °C)

	In deionized water ($\mathrm{mol\,dm^{-3}}$)	In mineralized water ($\mathrm{mol\,dm^{-3}}$)
DPC	1.5×10^{-2}	3.6×10^{-3}
SDBS	1.8×10^{-3}	1.5×10^{-4}

For the mixtures of cationic–anionic surfactants in mineralized water, the charged headgroups of ionic surfactants were surrounded or screened by counter ions of electrolytes, which weakened the attraction between cationic and anionic surfactants [33,34]. Consequently, the adsorbed surfactant molecules could not effectively attract oppositely charged surfactant molecules by electrostatic attractive action, in other words, the cooperative adsorption action was weakened in mineralized water systems. Furthermore, there might exist competitive adsorption between cationic and anionic surfactants, which resulted in the adsorption of each surfactant in mixed systems lower than that in their single system, by which we could explain the results in Fig. 3.

In conclusion, the adsorption of surfactants on the AC used in our work relied mainly on the hydrophobic interaction between AC surface and surfactants. There existed synergism between cationic and anionic surfactants when adsorbing on AC in deionized water due to the electrostatic interactions between oppositely charged surface active ions. However, when a large number of inorganic salts existed, the synergism adsorption of mixed surfactants might be weakened greatly due to the ''screen'' effect of the salt counter ions on the electrostatic attraction of oppositely charged surface active ions.

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Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2004.11.039.

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