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Thermodynamics of interaction between sodium dodecyl sulphate with 3-alkoxyl-2-hydroxypropyl trimethyl ammonium chlorides in aqueous systems

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Abstract

Interactions between sodium dodecyl sulphate (SDS) and four new surfactants, 3-alkoxyl-2-hydroxypropyl trimethyl ammonium chlorides (C*n*NCl) in aqueous systems were investigated using titration microcalorimetry. Pseudo-critical micellar concentration (pcmc), and thermodynamic parameters of the formation of mixed micelle for two binary surfactant systems at a certain concentration of C*n*NCl were estimated from the calorimetric data and the titration curve with methods from the literature. Changes in enthalpy and entropy of formation of the mixed micelle were discussed in the light of the structure of the surfactants and the iceberg model. The deduced conclusion is that interactions between hydrophobic chains of SDS and C*n*NCl are more important than the electrostatic attraction of the negatively charged head group of SDS with the positively charged head of C*n*NCl in the synergistic interaction between the anionic and cationic surfactants while the size of iceberg around the surfactant monomer is not sensitive to length of the hydrophobic chain.

Keywords: Microcalorimetry; Sodium dodecyl sulphate; 3-Alkoxyl-2-hydroxypropyl trimethyl ammonium chloride; Micelle; Hydrophobic interaction

1. Introduction

Since the end of 1980s, a large number of researches have been done on anionic and cationic mixed surfactant systems to clarify the aggregation behaviour [1–12] with special interest in formation of vesicles [13–17] due to their application in a variety of industries, such as in the production of cosmetics, pharmaceuticals and textiles. In these worldwide studies, NMR and ESR spectra [9], UV-spectra [8,17], fluorescence [12], electric conductivity [11,13], TEM [13,16], DSC [16], polarizing microscopy [13,15], X-ray diffraction analysis [15] etc. have been used besides surface tension measurement. However, reports of research on anionic and cationic mixed surfactant systems utilizing calorimetry are sparse, although the method has been widely used to study on other types of surfactant systems [17–21]. The present work investigates the mixed surfactant aqueous systems of sodium dodecyl sulphate (SDS) with each of four 3-alkoxyl-2-hydroxypropyl trimethyl ammonium chlorides (C*n*NCl). Pseudo-critical micelle concentrations (pcmc) at a certain concentration of C*n*NCl for

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two binary surfactant systems were determined with the calorimetric data, and thermodynamic parameters of the formation of micelles were estimated, which was discussed in the light of iceberg model and the structure of surfactants.

2. Experimental

2.1. Materials

3-Alkoxyl-2-hydroxypropyl trimethyl ammonium chlorides were synthesized with the method described earlier [22] and purified by recrystallization in ethyl alcohol (AR grade), here alkoxyl $= C_nH_{2n+1}O$, $n =$ 8, 12, 14, 16, and each specific quaternary ammonium salt surfactant is also simply designated by C*n*NCl; sodium dodecyl sulphate (SDS, reagent grade) was purchased from Shanghai Chemical Reagent Company (Shanghai, China) and purified by recrystallization twice in absolute alcohol. All surfactants used in this work meet the criterion for purity [23], i.e. there was no minimum in the concentration dependence of surface tension versus the logarithm of surfactant concentration in aqueous solution. The critical micelle concentration (cmc) of SDS in water at 25 °C was 6.62×10^{-3} mol dm^{-3} in good agreement with the reported value [2] of 6.78×10^{-3} mol dm^{-3}, and cmc of each C*n*NCl was 12.9×10^{-3}, 5.45×10^{-3}, 2.04×10^{-3}, and 1.02×10^{-3} mol dm^{-3}, respectively, corresponding to $n = 8$, 12, 14, and 16, at the same temperature, determined with electric conductivity and dropping volume methods in this laboratory. Water used in preparation of solutions was obtained by redistillation in the presence of basic potassium permanganate.

2.2. Microcalorimetric measurements

The calorimeter was an isothermal titration microcalorimeter Thermal Activity Monitor TAM LKB2277 (Thermometric, Sweden) controlled by Digitam 4.1 software. This instrument has a precision of electrical calibration better than ±1% and the accuracy can be checked by measuring the dilution enthalpy of a concentrated sucrose solution (0.985 mol dm^{-3}). The result value (-0.648 ± 0.012 kJ mol^{-3}) agreed well with the literature [24] value (-0.643 ± 0.015 kJ mol^{-1}). SDS solution (5.00×10^{-2} mol dm^{-3}) was injected in small aliquots (15 μl) into the 4 ml stainless steel ampoule containing 2 ml dilute C*n*NCl solution (5.00×10^{-3} mol dm^{-3}), using a 500 μl Hamilton syringe controlled by a 612 Lund Syringe Pump. The interval between two injections was 35–45 min, which was sufficiently long for the signal to return to the baseline. The stirrer in the ampoule was at a constant speed of 50 rpm. All experiments were performed at 298.15 ± 0.01 K.

3. Results and discussion

3.1. Apparent interaction enthalpy ($\Delta_{int}H_m$) of SDS with CnNCl and hydrophobic interaction

The titration processes for SDS in C8NCl, C12NCl and C14NCl were found to be exothermic (Fig. 1(a)), while that for SDS in C16NCl was found to change from strong exothermic to weak exothermic and finally to weak endothermic (Fig. 1(b)). For deducing the dilution heats of SDS and C*n*NCl solutions, we performed titration experiments of SDS solution into pure water and pure water into the C*n*NCl solutions, respectively. The former titration process was weakly endothermic and the latter ones were even weaker endothermic so that the dilution heats could be neglected. Now the apparent interaction enthalpy ($\Delta_{int}H_m$) of SDS with C*n*NCl can be defined as $\Delta_{int}H_m = \Delta_{obs}H_m(2) - \Delta_{obs}H_m(1)$, here $\Delta_{obs}H_m$ (1) and $\Delta_{obs}H_m$ (2) are observed enthalpies of dilution of concentrated SDS solution added into pure water and solution of C*n*NCl, respectively. The apparent interaction enthalpies ($\Delta_{int}H_m$) calculated from the titration data are gathered in Table 1.

In comparing the apparent interaction enthalpy of SDS with C*n*NCl at low SDS concentration, it can be seen that the longer the hydrophobic chain of C*n*NCl is, the stronger the interaction between SDS and it will be. This tendency is shown by Fig. 2, which means that hydrophobic interaction between hydrophobic chains of SDS and C*n*NCl is more important than the static electric attraction of the negatively charged head group of SDS with the positively charged head of C*n*NCl in the synergistic interaction between the anionic and cationic surfactants.

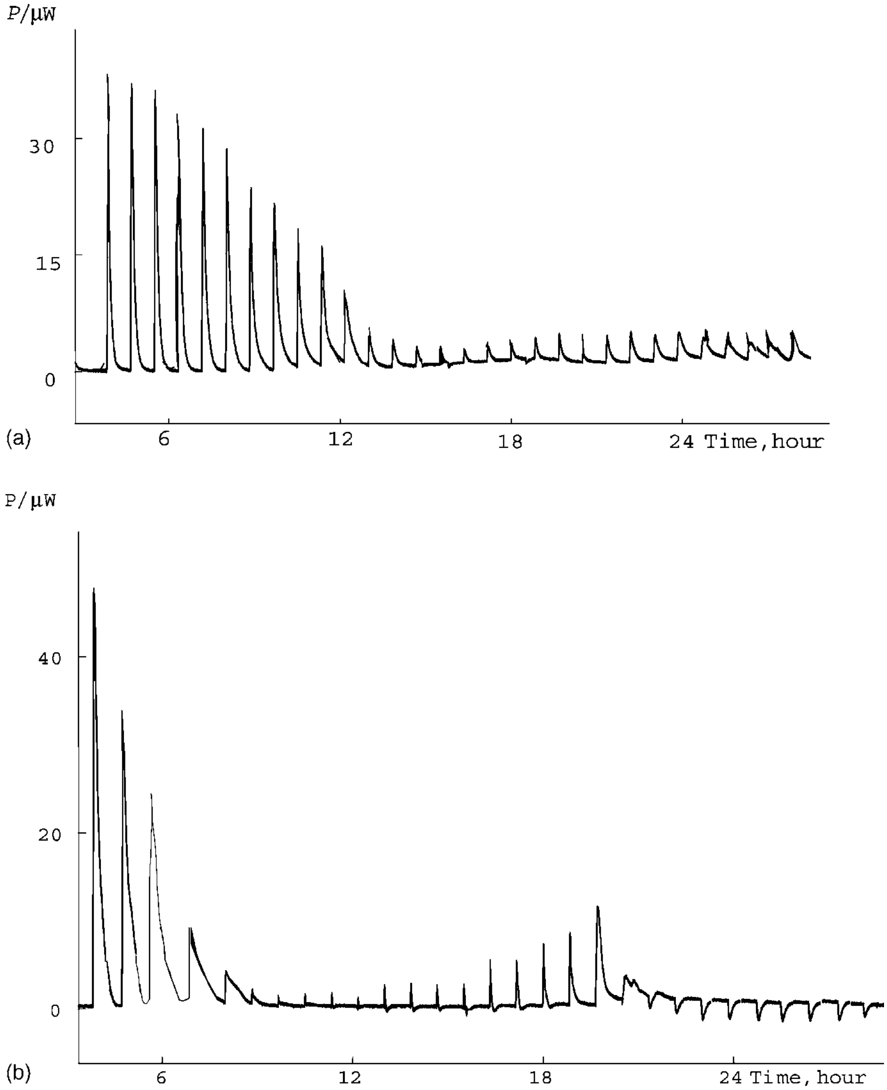

Fig. 1. (a) Enthalpy diagram of the thermometric titration of 2 ml C12NCl at the concentration of 5 mM with 50 mM SDS at 298.15 K in aliquots of 15 μl (*p* is power of released heat energy in μw). (b). Enthalpy diagram of the thermometric titration of 2 ml C16NCl at the concentration of 5 mM with 50 mM SDS at 298.15 K in aliquots of 15 μl (*p* is power of released heat energy in μW).

3.2. Thermodynamic parameters of mixed micelle forming processes and structures of surfactants

The plot of calorimetric data for the concentrated SDS solution with the dilute solution of C14NCl shown as Fig. 3 is similar to that for the SDS solution with water [24], which clearly shows that mixed micelles are formed in SDS-C*n*NCl aqueous systems. But the steep segment of the curve is not corresponding to critical micelle concentration (cmc) of the binary surfactant system, it only shows that the formation of mixed micelle starts at a certain concentration of C*n*NCl. In order to distinguish between this special concentration and real mixed cmc, we call it *pseudo-critical micelle concentration* (pcmc). According to the phase separation model [1,26], interaction between the two types of surfactants can be shown by the following processes when the

Table 1
Apparent interaction enthalpy ($\Delta_{\mathrm{int}}H_{\mathrm{m}}$) of SDS with C*n*NCl calculated with microcalorimetric titration data at 298.15 K

C_{SDS} (mol dm^{-3})	$-\Delta_{\mathrm{int}}H_{\mathrm{m}}$ (kJ mol^{-1}) (SDS)			
	$n = 8$	$n = 12$	$n = 14$	$n = 16$
0.372	7.463	16.560	24.581	36.137
0.739	7.168	16.342	23.660	33.463
1.100	6.759	16.124	23.588	31.276
1.456	6.299	15.985	22.489	22.826
1.807	6.113	16.480	22.207	17.934
2.153	6.001	16.577	22.178	14.536
2.494	5.845	16.147	21.332	12.155
2.830	5.869	16.196	21.015	10.470
3.162	5.995	15.753	20.421	9.288
3.488	5.980	15.415	19.258	8.288
3.811	6.070	14.788	18.157	7.518
4.128	6.132	13.650	16.863	6.786
4.442	6.130	12.698	15.593	6.190
4.751	6.202	11.878	14.470	5.702
5.056	6.148	11.095	13.506	5.314
5.357	6.037	10.425	12.675	4.962
5.654	5.944	9.866	11.975	4.690
5.947	5.781	9.315	11.354	4.464
6.236	5.592	8.872	10.743	4.496
6.552	5.396	8.436	10.177	4.713
6.803	5.222	8.044	9.740	4.567
7.082	5.031	7.773	9.388	4.439
7.356	4.899	7.535	9.147	4.180
7.627	4.766	7.354	8.910	3.937
7.895	4.676	7.180	8.733	3.726
8.159	4.574	7.008	8.593	3.544
8.420	4.436	6.864	8.395	3.349
8.678	4.319	6.710	8.194	3.178
8.932	4.188	6.568	7.983	3.039
9.184	4.068	6.413	7.792	2.908

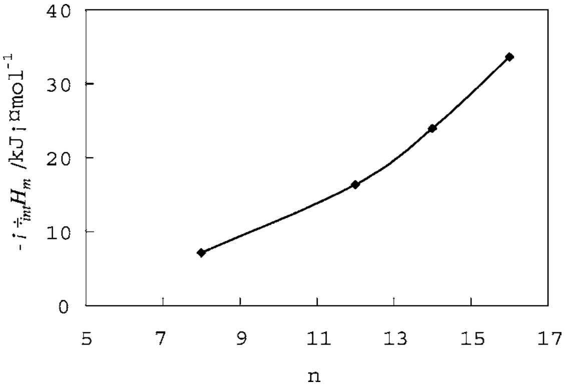

Fig. 2. Apparent interaction enthalpy ($\Delta_{\mathrm{int}}H_{\mathrm{m}}$) of SDS with C*n*NCl at low SDS concentration versus the number of carbon atoms, *n* in C*n*NCl.

concentration of SDS (C_{SDS}) in the range from pcmc (in 5×10^{-3} mol dm^{-3} C*n*NCl solution) to cmc (in water). Firstly, the micelles of SDS in concentrated solution being added into the dilute solution of C*n*NCl dissociate into monomers:

$$\text{SDS (in micelle)} \rightarrow \text{SDS (monomer)} \tag{1}$$

Then the monomer of SDS interacts with monomer or micelle of C*n*NCl, forming mixed micelles:

$$\begin{aligned}&\text{SDS} + b\text{C}n\text{NCl}\\&\quad = \text{SDS}\,(\text{C}n\text{NCl})_b(\text{mixed micelle}, X_{\mathrm{SDS}}^{\mathrm{m}})\end{aligned} \tag{2}$$

Here micelle is regarded as a phase different from aqueous phase, and Process (2) is similar to a heterogeneous reaction. Enthalpy change of equilibrium (2) or formation enthalpy of the mixed micelle, $\Delta_{\mathrm{pcmc}}H_{\mathrm{m}}$, can be estimated with the method from the literatures [24,25], i.e., $\Delta_{\mathrm{pcmc}}H_{\mathrm{m}}$ can be obtained from the difference between the apparent interaction enthalpy ($\Delta_{\mathrm{int}}H_{\mathrm{m}}$) of the two flat linear segments of the curve, as shown in Fig. 3. Change of Gibbs free energy ($\Delta_{\mathrm{pcmc}}G_{\mathrm{m}}$) is related to pcmc of SDS and C*n*NCl and molar fraction of SDS ($X_{\mathrm{SDS}}^{\mathrm{m}}$) in micelle. Approximately, the pseudo-critical micelle concentrations (pcmc) of the binary mixture surfactant aqueous solutions, are at about $(4.54 \pm 0.26) \times 10^{-3}$ mol dm^{-3} of SDS (the corresponding molar ratios, $n_{\mathrm{SDS}}/n_{\mathrm{C}n\mathrm{NCl}}$ are about 1/1), when $n = 12$, 14. This means that electric neutral micelle is most stable since there is no repelling force between head group of surfactant ions. For $n = 12$ or 14, b in Eq. (2) is approximately equal to 1 and the equilibrium concentration of SDS or C*n*NCl is equal to the pcmc. Two other thermodynamic function changes ($\Delta_{\mathrm{cmc}}G_{\mathrm{m}}$, $\Delta_{\mathrm{cmc}}S_{\mathrm{m}}$) can be obtained with the formulae [1,26]:

$$\Delta_{\mathrm{cmc}}G_{\mathrm{m}} = -RT\ln\left(\frac{a_{\mathrm{C,m}} \cdot a_{\mathrm{A,m}}}{a_{\mathrm{C}} \cdot a_{\mathrm{A}}}\right) \tag{3}$$

$$\Delta_{\mathrm{cmc}}S_{\mathrm{m}} = \frac{\Delta_{\mathrm{cmc}}H_{\mathrm{m}} - \Delta_{\mathrm{cmc}}G_{\mathrm{m}}}{T} \tag{4}$$

Here a_{C} and a_{A} are, respectively, activities of the cationic surfactant and the anionic surfactant in bulk phase at the pcmc. Both a_{C} and a_{A} are approximately equal to the pcmc because the ionic strength of the aqueous system is very low; $a_{\mathrm{C,m}}$ and $a_{\mathrm{A,m}}$ are activities of the cationic surfactant and anionic surfactant

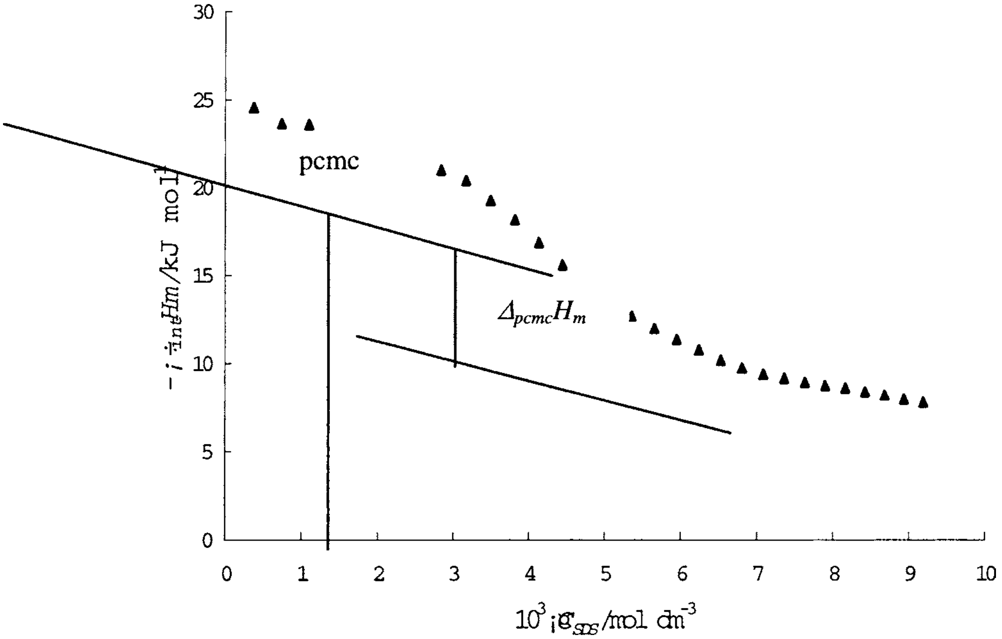

Fig. 3. A typical plot of apparent interaction enthalpy ($\Delta_{\mathrm{int}}H_{\mathrm{m}}$) of SDS with C*n*NCl versus the concentration of sodium dodecyl sulphate (C_{SDS}) calculated from the results of titration experiment ($n = 14$), and method to obtain pcmc and $\Delta_{\mathrm{pcmc}}H_{\mathrm{m}}$.

in the mixed micelles. Exactly determination of values for $a_{\mathrm{C,m}}$ and $a_{\mathrm{A,m}}$ is difficult. To simplify calculation, we suppose either $a_{\mathrm{C,m}}$ or $a_{\mathrm{A,m}}$ is equal to 1, at $X^{\mathrm{m}}_{\mathrm{SDS}} = 0.5$, which means that an imaginary standard state for each surfactant in micelle is used. The measured and calculated thermodynamic parameters for $n = 12$ and 14 are shown in Table 2.

It can be seen from the data in Table 1 that the interaction between SDS and C8NCl is so weak that pcmc and $\Delta_{\mathrm{pcmc}}H_{\mathrm{m}}$ cannot be exactly determined. The cause might be that the hydrophobic chain of C8NCl is much shorter than that of SDS, and hence hydrophobic interaction between the two types of surfactants is weak. On the other hand, interaction between SDS and C16NCl is very strong when the concentration of SDS is very low (Fig. 1(b)), while the interaction evidently becomes weaker as the concentration of SDS gets higher. In fact, the original concentration of C16NCl (5.00×10^{-3} mol dm^{-3}) is evidently higher than its cmc in water. When SDS solution is added into the solution, monomer anions of SDS escaped from the original anionic micelle to insert themselves into the micelle of C16NCl so that several cations of C16NCl interact with one anion of SDS when the concentration of SDS is low and a large energy is released (about 34 kJ mol^{-1} SDS, Fig. 1(b), Table 1 and Fig. 2), while the amount of the released heat is rapidly reduced one aliquot after another. After the molar ratio, $n_{\mathrm{SDS}}/n_{\mathrm{C16NCl}}$ in the mixed micelle reaches 1/1, the titration process changes from weak exothermic to endothermic (Peak 21 in Fig. 1 (b)), which indicates that static electric repelling must be overcome before SDS monomer ions transfer from SDS micelle to mixed micelle when the ratio of $n_{\mathrm{SDS}}/n_{\mathrm{C14NCl}}$ in the micelle is larger than 1/1. This shows it again that electric neutral

Table 2
Estimated formation thermodynamic parameters of mixed micelle at 1/1 molar ratio, $n_{\mathrm{SDS}}/n_{\mathrm{C}n\mathrm{NCl}}$ at 298.15 K[a]

n	$\Delta_{\mathrm{pcmc}}G_{\mathrm{m}}$ (kJ mol^{-1})	$\Delta_{\mathrm{pcmc}}H_{\mathrm{m}}$ (kJ mol^{-1})	$T\Delta_{\mathrm{pcmc}}S_{\mathrm{m}}$ (kJ mol^{-1})
12	−13.37	−9.36 ± 0.32	4.06
14	−13.37	−13.78 ± 0.54	−0.41

[a] The error of each $\Delta_{\mathrm{pcmc}}H_{\mathrm{m}}$ is from calculation according to results of three replicates.

micelle is most stable. If a plot of the apparent interaction enthalpy ($\Delta_{\text{int}}H_{\text{m}}$) of SDS with C16NCl versus concentration of SDS (C_{SDS}) is drawn, the segment of the curve corresponding to low concentration range of SDS will be so steep that the formation heat of the mixed micelle cannot be obtained.

3.3. Calorific effects and Entropy effects of formation of SDS-C12NCl and SDS-C14NCl mixed micelle at 1:1 molar ratio

Thermodynamic data in Table 2 show an interesting phenomenon, i.e., the released heat ($-\Delta_{\text{pcmc}}H_{\text{m}}$) of the formation of the mixed micelle increases 4.4 kJ mol^{-1} and the formation entropy ($\Delta_{\text{pcmc}}S_{\text{m}}$) simultaneously decreases an equivalent amount, maintaining the formation Gibbs free energy ($\Delta_{\text{pcmc}}G_{\text{m}}$) as a constant with the length of the hydrophobic chain of C*n*NCl extending an ethylidene groups (CH_2CH_2). To explain this phenomenon, two important factors should be considered. One is the collapse of the iceberg structure around the hydrophobic part of surfactant ion monomers when micelles are formed, which causes both enthalpy and entropy increase [27]. The other is that interaction between hydrophobic tails causes both enthalpy and entropy decrease, when the surfactant monomers get into micelles from bulk aqueous solution. The longer the hydrophobic tail is, the greater the decrease of the enthalpy and entropy will be. The values of $\Delta_{\text{pcmc}}H_{\text{m}}$ and $T\Delta_{\text{pcmc}}S_{\text{m}}$ (Table 2) simultaneously drop to larger negative level with the change of the length of hydrophobic chain of C*n*NCl. This indicates that the former factor is much less important than the latter one, namely, change of the size of the iceberg structure is not evident as the hydrophobic tail of surfactant becomes longer, because the alkoxyl ($C_nH_{2n+1}O$) chain can coil itself more easily as the number of carbon atoms becomes larger.

Additionally, electrostatic interaction between ionic heads of anionic and cationic surfactant, and interaction between surfactant ions and their counterions, and the existence of inorganic ions (Na^+ and Cl^-) can all influence the thermodynamic properties of the binary surfactant systems. However, all these interactions change in the same way in the titration experiments of this work, so their effects on the tendency of the changes of thermodynamic functions need not to be considered here.

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