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SHORT COMMUNICATION

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Striking differences between alkyl sulfate and alkyl sulfonate when mixed with cationic surfactants

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Abstract The properties of alkyl sulfate and alkyl sulfonate are similar except for their Krafft points. However, alkyl sulfate and alkyl sulfonate behave quite differently when they are mixed with cationic surfactants and show some totally unexpected results. In this work sodium alkyl sulfate ($C_nH_{2n+1}SO_4Na$,C_nSO_4)–alkyl quaternary ammonium bromide [$C_nH_{2n+1}N(C_mH_{2m+1})_3Br$, C_nN, $m=1$–4] mixtures and sodium alkyl sulfonate ($C_nH_{2n+1}SO_3Na$, C_nSO_3)–C_nN mixtures were studied. It was found that, in contrast to the single surfactants, C_nSO_3–C_nN mixtures were much more soluble than C_nSO_4–C_nN mixtures. Besides, the two kinds of catanionic surfactant mixtures were quite different in their phase behavior and aggregate properties. The results were interpreted in terms of the interactions between surfactant molecules, which were very different in the two kinds of mixed systems owing to the distinction between alkyl sulfate and alkyl sulfonate in the molecular charge distribution.

Keywords Catanionic surfactant mixtures · Headgroup effect
Aqueous two-phase system

Introduction

Considerable studies have been done on catanionic surfactants mixtures [1, 2, 3, 4, 5], owing to their overwhelmingly higher surface activity than their individual components. However, most studies focused mainly on their surface and bulk properties. There have not been so many studies on the effects of surfactant structures, and they have mainly focused on the alkyl chain symmetry or asymmetry effect [6, 7, 8], while studies on the headgroup effect are lacking [9, 10, 11]. On the other hand, alkyl sulfates instead of alkyl sulfonates are usually used in various studies on catanionic surfactant mixtures.

The single surfactant systems of alkyl sulfate and alkyl sulfonate are similar except for their Krafft points, for example, the critical micelle concentrations (cmc) of sodium dodecyl sulfate and sodium dodecyl sulfonate are 8.7×10^{-3} and 9.7×10^{-3} mol l^{-1}, respectively. However, this study shows that alkyl sulfate and alkyl sulfonate behave quite differently when mixed with cationic surfactants, even with some unexpected results and in contrast to the single components. In this work, the aqueous solubility, phase behavior and aggregate properties of C_nSO_4–C_nN mixtures and C_nSO_3–C_nN mixtures were studied and compared; the results are expected to contribute to the studies on the effect of surfactant headgroups.

Experimental

Materials

Sodium octyl/decyl sulfate (C_8SO_4, $C_{10}SO_4$) was synthesized from chlorosulfonic acid and octanol/decanol, and then the solution was neutralized. The crude product was recrystallized five times from ethanol. Sodium dodecyl sulfate ($C_{12}SO_4$) purchased from Sigma was used as received. Sodium octyl sulfonate (C_8SO_3) was synthesized from 1-bromide octane and sodium sulfite. The crude product was recrystallized five times from ethanol. Sodium decyl sulfonate ($C_{10}SO_3$), purchased from Tokyo Kasei, A.R. grade, was used as received. Sodium dodecyl sulfonate ($C_{12}SO_3$), a product of Beijing Chemical Co., C.P. grade, 97%, was recrystallized from water and ether. Alkyltrimethyl/ethyl/butylammonium bromide (C_nNM, C_nNE, and C_nNB) was synthesized from 1-bromoalkane and trimethyl/ethyl/butylamine. The crude products were recrystallized five times from mixed ether–acetone solvent.

The purity of all the surfactants was examined, and no surface tension minimum was found in the surface tension curve. All the solutions were prepared using deionized water.

Dynamic light scattering

Dynamic light scattering (DLS) measurements were made using a spectrometer of standard design (ALV-5000/E/WIN multiple tau digital correlator) and a Spectra Physics 2017 200-mW Ar laser (514.5-nm wavelength). All measurements were made at a scattering angle of 90°, and the intensity autocorrelation functions were analyzed using the method of Cumulant and Contin. The solutions were centrifuged at a speed of 12,000 rpm for 30 min before the light scattering experiments. The experimental temperature was maintained at 25 °C.

Surface tension measurement

The surface tension of the surfactant solutions was measured by the drop-volume method.

Results and discussion

Solubility

It was observed that C_nSO_3–C_nN mixtures were unexpectedly much more soluble in water than C_nSO_4–C_nN mixtures. As we all know, the aqueous solubility of alkyl sulfonate is much lower than that of alkyl sulfate, so it is usually taken for granted that when mixed with cationic surfactants the catanionic mixtures of alkyl sulfonate must be much less soluble than those of alkyl sulfate. Therefore, alkyl sulfonate is usually not mixed with cationic surfactants, which is almost a general rule in applications of catanionic surfactant mixtures. However, our results showed that C_nSO_3–C_nN was much more soluble than C_nSO_4–C_nN. We have obtained some homogeneous solutions in C_nSO_3–C_nNE equimolar mixed systems with high concentration in previous work [12].

The phase states of C_nSO_4–C_nN and C_nSO_3–C_nN mixed systems at equimolar composition and $c_T = 0.1$ mol l^{-1} (c_T is the total surfactant concentration) were studied (Table 1). The results showed that the aqueous solubility of C_nSO_3–C_nN was much higher than that of C_nSO_4–C_nN. Usually, C_nSO_4–C_nN will precipitate even at very low concentration when its composition approaches equimolar, for example, the $C_{10}SO_4$–$C_{10}NE$ equimolar mixed system formed precipitates at $c_T = 3.0$ mmol l^{-1}. In contrast, C_nSO_3–C_nN can form homogeneous solutions even at equimolar composition and high concentrations, for example, $C_{10}SO_3$–$C_{10}NE$ and other catanionic mixed systems forming homogeneous solutions (Table 1) can still form homogeneous solutions when c_T increases to 0.2 mol l^{-1} even with 0.1 mol l^{-1} NaBr added.

Krafft point

The differences between the two kinds of catanionic surfactant mixtures also reflect on their Krafft points. For the single system, the Krafft points of C_nSO_3 are much higher than those of C_nSO_4, for example, the Krafft points of $C_{12}SO_4$ and $C_{12}SO_3$ are 9 and 38 °C, respectively. However, when they are mixed with cationic surfactants, the variation of their Krafft points is just the opposite. For example, the solution of equimolar $C_{10}SO_4$–$C_{10}NE$ with $c_T = \mathrm{cmc}_{25\,°C}$ ($\mathrm{cmc}_{25\,°C}$ is the cmc at 25 °C) and the solution of equimolar $C_{10}SO_3$–$C_{10}NE$ with $c_T = \mathrm{cmc}_{25\,°C}$ were kept at 3 °C; the former forms a precipitate, while the latter remains homogeneous. This result implies the Krafft point of $C_{10}SO_4$–$C_{10}NE$ is higher than that of $C_{10}SO_3$–$C_{10}NE$. Therefore, the variation of the Krafft points for $C_{10}SO_4$–$C_{10}NE$ and $C_{10}SO_3$–$C_{10}NE$ is in contrast to that for $C_{10}SO_4$ and $C_{10}SO_3$, i.e., we have the order of Krafft points $C_{10}SO_4 < C_{10}SO_3$, $C_{10}SO_4$–$C_{10}NE > C_{10}SO_3$–$C_{10}NE$.

Forming the aqueous two-phase system

Besides the solubility difference, the catanionic surfactant mixtures of C_nSO_4 and those of C_nSO_3 are quite different in forming aqueous two-phase systems (ATPS), especially in the types of ATPS and the phase-separation speed.

Mixed catanionic surfactant systems will separate into two immiscible aqueous phases at certain compositions and concentrations, which are called ATPS [13, 14]. Forming ATPS is an interesting phenomenon of mixed catanionic surfactant systems. The ATPS formed by catanionic surfactant mixtures is a favorable partitioning system for bioactive materials owing to its special advantages, and thus attracts researchers' attention [13, 14, 15, 16].

The ATPS formed in C_nSO_4–C_nN mixed systems and C_nSO_3–C_nN mixed systems were studied (Table 2). The results showed that the types of ATPS formed in the two kinds of catanionic mixed systems were very different. C_nSO_4–C_nN usually formed ATPS in two narrow regions away from equimolar composition, which was called the first kind of ATPS (denoted as ATPS-I), for example, $C_{12}SO_4$–$C_{12}NE$ formed ATPS-I at a mixing

Table 1 Phase states of equimolar mixed catanionic surfactant systems (25 °C, $c_T = 0.1$ mol l^{-1}). Precipitate (↓), homogeneous solution (+), aqueous two phases (*2L*)

	C_8SO_4	$C_{10}SO_4$	$C_{12}SO_4$	C_8SO_3	$C_{10}SO_3$	$C_{12}SO_3$
C_8NE	+	2L	2L	+	+	+
$C_{10}NE$	↓	↓	↓	+	+	+
$C_{12}NE$	↓	↓	↓	+	2L	2L
$C_{14}NE$	↓	↓	↓	+	2L	↓
$C_{16}NE$	↓	↓	↓	+	2L	↓
$C_{10}NB$	↓	↓	↓	2L	2L	2L
$C_{12}NB$	↓	↓	↓	2L	2L	2L
$C_{14}NB$	↓	↓	↓	2L	2L	

Table 2 Types of aqueous two-phase systems (ATPS) formed in mixed catanionic surfactant systems. ATSP-I (*I*), ATPS-II (*II*), clear homogeneous solution (+)

	C_8SO_4	$C_{10}SO_4$	$C_{12}SO_4$	C_8SO_3	$C_{10}SO_3$	$C_{12}SO_3$
C_8NM	I	I	I	+	+	+
$C_{10}NM$	I	I	I	II	I	I
$C_{12}NM$	I	I	I	I	I	
C_8NE	+	II	II	+	+	+
$C_{10}NE$	I	I	I	+	+	+
$C_{12}NE$	I	I	I	+	II	II
$C_{14}NE$	I			+	II	I
$C_{16}NE$	I			+	II	I
$C_{10}NB$	I	I	I	II	II	II
$C_{12}NB$	I	I	I	II	II	
$C_{14}NB$	I	I	I	II	II	

molar ratio $c^+:c^- = 1.7:1–1.5:1$ and $1:2.2–1:2.3$ (c^+ and c^- are the concentrations of cationic and anionic surfactant, respectively). For C_nSO_3–C_nN, ATPS-I was also formed with the cationic surfactant having a smaller headgroup, such as C_nNM, for example, $C_{12}SO_3$–$C_{10}NM$ formed ATPS-I at $c^+:c^- = 1.7:1–1.5:1$ and $1:1.9–1:2.0$. Conversely, however, with the cationic surfactant having a bigger headgroup, such as C_nNE or C_nNB, C_nSO_3–C_nN formed ATPS in a composition region crossing over the equimolar mixing ratio, which was called the second kind of ATPS (denoted as ATPS-II), for example, $C_{12}SO_3$–$C_{12}NE$ formed ATPS-II at $c^+:c^- = 1.3:1–1:1.3$.

The following is a sketch of the two kinds of ATPS, by which we can differentiate them better. A marked difference between them lies in the composition of the mixed surfactants. For ATPS-I, the mixed surfactants are nonequimolar, while for ATPS-II, the composition of the mixed surfactants can be nonequimolar or equimolar. Adjacent to the region of ATPS-I, on one side is the region of precipitate or turbid solution, and on the other side is the region of clear homogeneous solution. Distinctly, however, on both sides of the region of ATPS-II are clear homogeneous solutions. Nevertheless, the two kinds of ATPS are related to each other. If the region of precipitate or turbid solution in the catanionic surfactant mixed system forming ATPS-I decreases gradually until the two regions of ATPS-I join up, then the region of ATPS-II will form eventually.

In addition, the phase-separation speed of the ATPS of C_nSO_4–C_nN mixtures and that of C_nSO_3–C_nN mixtures are also very different. The phase-separation speed of the latter is much faster than that of the former. Usually the ATPS of C_nSO_3–C_nN will separate into two phases in several minutes, while that of C_nSO_4–C_nN needs several minutes to hours, or tens of hours.

The distinction between C_nSO_4–C_nN mixtures and C_nSO_3–C_nN mixtures in forming ATPS will be of avail in the choice of a suitable aqueous two-phase partition system for different materials. As already mentioned, the compositions of the mixed surfactants in ATPS-I and ATPS-II are different. It has been shown [14] that the partition coefficient of proteins in ATPS depends on the composition of the mixed surfactants. So we can choose ATPS with different surfactant compositions, for example, equimolar or nonequimolar, for different proteins. On the other hand, a fast phase-separation speed is very important for the partitioning process, especially for the partitioning of biomaterials. For this purpose, the ATPS of C_nSO_3–C_nN should be more practical than that of C_nSO_4–C_nN.

Aggregate distribution

Besides the macrographic differences, C_nSO_4–C_nN and C_nSO_3–C_nN have a great difference in their aggregate distribution and size. The distribution and size of aggregates in $C_{10}SO_4$–$C_{10}NE$ and $C_{10}SO_3$–$C_{10}NE$ equimolar mixed systems were measured by DLS (Figs. 1, 2). In Figs. 1 and 2, R_h is the hydrodynamic radius of the aggregates, and $f(R_h)$ is the weight of the scattering light intensity of the aggregates with R_h. In precise terms, $f(R_h)$ represents the z-average weight of the scattering light intensity of the aggregates with R_h.

The aggregates in $C_{10}SO_4$–$C_{10}NE$ system are polydispersing (Fig. 1), and on increasing the total surfactant concentration from 2.0 to 4.0 mmol l^{-1}, the number of aggregates with hydrodynamic radius of about several tens of nanometers decreases, while that of the aggregates with hydrodynamic radius of about 400 nm increases. (In fact, some floccules formed in $C_{10}SO_4$–$C_{10}NE$ when c_T exceeds 3.0 mmol l^{-1}, and the sample at $c_T = 4.0$ mmol l^{-1} was measured by DLS after centrifuging.) That is to say, the aggregates in the $C_{10}SO_4$–$C_{10}NE$ system grow rapidly with increasing c_T, and will rapidly become large enough to separate as precipitates from the solution when c_T exceeds 3.0 mmol l^{-1}. In contrast, the aggregates in the $C_{10}SO_3$—$C_{10}NE$ system are narrowly distributed (Fig. 2), and the radii of the aggregates are within

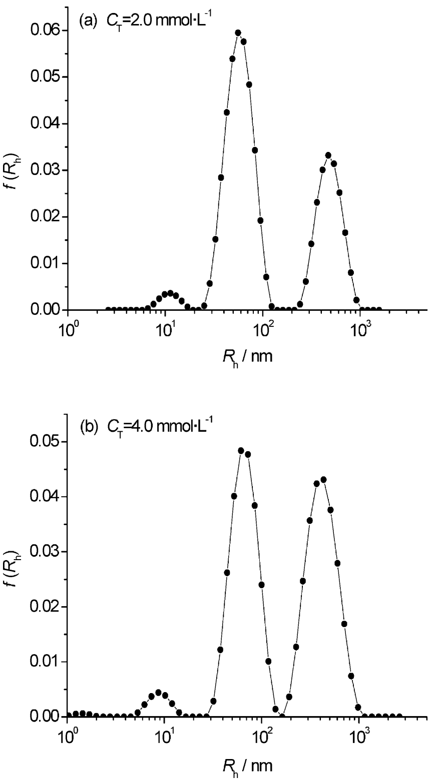
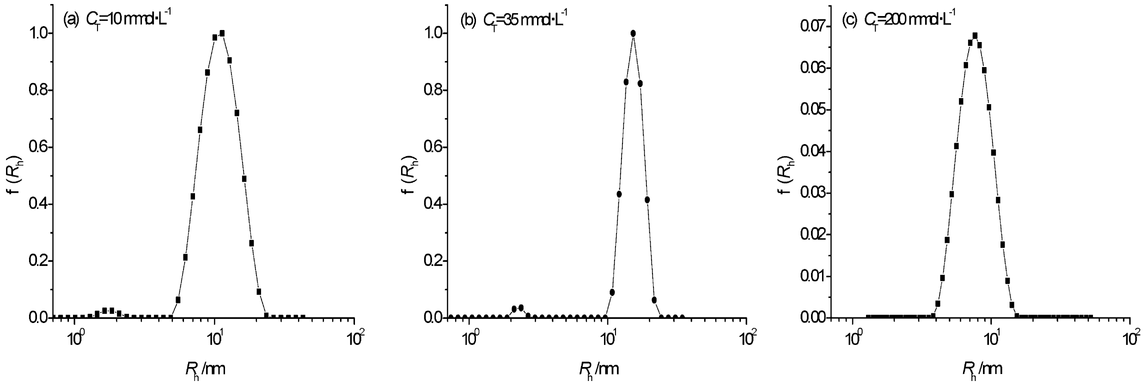


Fig. 1 The distribution of aggregates in the $C_{10}SO_4$–$C_{10}NE$ equimolar mixed system (25 °C): **a** $c_T = 2.0$ mmol l^{-1}, **b** $c_T = 4.0$ mmol l^{-1}

20 nm. With increasing c_T, the aggregate radii increase at first and then decrease after reaching a maximum at about 35 mmol l^{-1}, but their radii are always small (Fig. 3). Therefore, the $C_{10}SO_3$–$C_{10}NE$ mixed system can still form a clear homogeneous solution even when c_T increases to 0.2 mol l^{-1}.

Fig. 2 The distribution of aggregates in the $C_{10}SO_3$–$C_{10}NE$ equimolar mixed system (25 °C): **a** $c_T = 10$ mmol l^{-1}, **b** $c_T = 35$ mmol l^{-1}, **c** $c_T = 200$ mmol l^{-1}



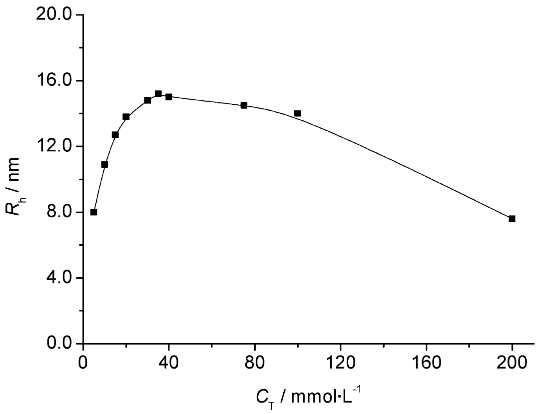


Fig. 3 The variation of aggregate radii, R_h, with the total surfactant concentration, c_T, in the $C_{10}SO_3$–$C_{10}NE$ equimolar mixed system (25 °C)

Intermolecular interaction

The differences in the solution properties and phase behavior of C_nSO_4–C_nN and C_nSO_3–C_nN can be attributed to the difference in the interactions between surfactant molecules. We measured the γ versus $\log c_T$ curves of equimolar $C_{10}SO_4$–$C_{10}NE$ and equimolar $C_{10}SO_3$–$C_{10}NE$, and calculated the molecular interaction parameter, β, and the composition of the cationic surfactant in the mixed micelles, x_{m1}, by regular solution theory [17]:

$$\beta = \frac{\ln \frac{x_1 \mathrm{cmc_T}}{x_{m1}\mathrm{cmc}_1^0}}{(1 - x_{m1})^2} = \frac{\ln \frac{(1-x_1)\mathrm{cmc_T}}{(1-x_{m1})\mathrm{cmc}_2^0}}{x_{m1}^2}, \qquad (1)$$

where x_1 and x_{m1} are the mole fractions of surfactant 1 (e.g., cationic surfactants) in bulk solution and mixed micelles, respectively. cmc_i^0 and $\mathrm{cmc_T}$ (expressed by the total surfactant concentration) are the cmcs of pure surfactant i and binary surfactant mixtures, respectively.

The results (Table 3) showed that the cmc and γ_{cmc} of $C_{10}SO_4$–$C_{10}NE$ were less than those of $C_{10}SO_3$–$C_{10}NE$, while β of the former was much more negative than that

Table 3 Critical micelle concentration expressed by the total surfactant concentration (*cmc*), γ_{cmc}, the composition of the cationic surfactant in mixed micelles, x_{m1}, and the molecular interaction parameter, β, of equimolar mixed catanionic surfactant systems ([NaBr] = 0.1 mol l^{-1}, 25 °C)

Mixed systems	cmc/mM	γ_{cmc}/mN m^{-1}	x_{m1}	β
$C_{10}SO_4$–C_{10}NE	1.3	24.9	0.47	−11.5
$C_{10}SO_3$-C_{10}NE	3.2	26.9	0.43	−7.2

of the latter, indicating that the intermolecular interactions of the former were much stronger than those of the latter. It was the difference in the intermolecular interactions that made the two kinds of catanionic mixed systems quite different.

The difference in the molecular interactions between catanionic mixtures of alkyl sulfate and those of alkyl sulfonate originated from the difference in the molecular charge distribution between alkyl sulfate and alkyl sulfonate. For ionic surfactants, the entire charge is often considered to be a point charge at the headgroup. Recently, however, Huibers [18] has estimated the charge distribution in common ionic surfactant molecules using quantum chemical methods, and the results showed that in reality the headgroup charge is partially distributed to the rest of the molecule, with significant charge on the α-methylene group and a partial charge on the remaining alkyl tail.

The charge on the α-methylene group is as large as –0.40 for alkyl sulfonate, owing to the highly polar C–S bond, whereas it is lower and of the opposite sign (+0.18) for alkyl sulfate [18]. As a result, the hydration shell of the polar head extends over a larger part of the alkyl chain in alkyl sulfonate, which "shortens" its hydrophobic tail with respect to that of the equivalent alkyl sulfate. On the other hand, the alkyl chain of alkyl sulfate has a little negative charge, whereas that of alkyl sulfonate has a little positive charge [18]. Additionally, the alkyl chain of alkyl quaternary ammonium is usually charged positively [18]. Therefore, the two factors made the intermolecular interactions of alkyl sulfonate and alkyl quaternary ammonium weaker than that of alkyl sulfate and alkyl quaternary ammonium.

Discussion

Owing to the strong attractive intermolecular interactions, C_nSO_4–C_nN mixtures are prone to forming large aggregates and thus are easy to precipitate in aqueous solutions. So the mixtures are much less soluble and have higher Krafft points than the single components, which is the usual behavior of catanionic surfactant mixtures. Conversely, the attractive molecular interactions of C_nSO_3–C_nN mixtures are not strong enough to make their aqueous solutions precipitate or phase-separate; meanwhile, the moderate attractive interactions will promote the formation of mixed aggregates, into which alkyl sulfonate will be "dissolved". Thus, a clear homogeneous solution is formed, and it appears that the catanionic mixtures are much more soluble and have lower Krafft points than the single components. On the other hand, as C_nSO_4–C_nN mixed systems usually formed precipitates at compositions close to equimolar, they will generally form ATPS-I if they can. In contrast, C_nSO_3–C_nN mixed systems will form ATPS-II when the intermolecular interactions are not weak enough to form homogeneous solutions and also not strong enough to form precipitates.

Conclusion

In this work, the properties of catanionic mixtures containing alkyl sulfate and alkyl sulfonate were studied and compared. The results showed that the organic moiety of the surfactant headgroup has a great effect on the properties and phase behavior of catanionic mixed system, and the headgroup works by influencing the interactions between surfactant molecules. Although the chemical difference between alkyl sulfate and alkyl sulfonate is just one oxygen atom, their catanionic surfactant mixtures are quite different in solution properties, phase behavior and aggregate properties, which can all be attributed to the distinction between their intermolecular interactions. So in applications of mixed-surfactant systems, we can tailor their properties and behavior by adjusting the organic compositions of the headgroups.

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