Measurement of the interaction enthalpy for mixed micelles of dodecyltrimethylammonium bromide and 1-dodecyl-3-methylimidazolium bromide

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A B S T R A C T

In order to clarify the nature of the inter-micellar interactions, we developed an approach to obtain the intermicellar interaction enthalpy through measuring the mixing heats of dodecyltrimethylammonium bromide (DTAB)/1-dodecyl-3-methylimidazolium bromide (C_{12}mimBr) mixed micelles by using flow-mixing calorimetry. It was found that the inter-micellar interaction enthalpies for this system were negative, representing the attractive enthalpy interactions between the mixed micelle droplets. These results are contradictory to those reported in the literature and interpreted by the predominant attractive dehydration effect of counterion. Static light scattering experiment revealed that the repulsive nature of the interaction characterized by the Gibss free energy should be dominated by the entropy interaction.
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Introduction

Recently, considerable research efforts were devoted to the mixed surfactant aqueous solutions because of their theoretical interests and practical applications [1,2]. Surfactants aggregate spontaneously in aqueous solutions at certain conditions to form micelles or mixed micelles and their properties and stabilities were widely studied [3–16], which are closely linked to the inter-micellar interactions [17–19]. The inter-micellar interactions of single ionic surfactant systems have been studied mostly by using small angle neutron-scattering (SANS) [20–23], light scattering [17,24,25], rotating disk electrode (RDE) [26,27]. However, the study of interactions between mixed micelles has not been reported yet. The inter-micellar interaction parameters for single ionic surfactant systems acquired from above measurements closely correlate to the second virial coefficient, which has a character of Gibbs free energy [28,29]. However, it was commonly accepted that these inter-micellar interactions between ionic micelles are apparently repulsive due to energy potentials [17,20,22–25], which results from the competition between the repulsive Coulombic potential and the attractive van der Waal's potential, since the Coulombic repulsion is much stronger than the van der Waal's attraction [17,20,23–25]. It is well known that the effect of entropy in aqueous solutions is often significant and possibly dominant in some cases and the change of the Gibbs free energy is the sum of effects of entropy and enthalpy $\Delta G = \Delta H - T\Delta S$; therefore the interaction enthalpy and the Gibbs free energy of interaction may have opposite signs, for instance, the interaction enthalpy may be attractive while the Gibbs free energy of interaction is repulsive. It has also been pointed that besides the Coulombic potential and the van der Waal's potential, there exists an additional potential termed as the water mediated interaction [22,23,30], which is possibly crucial in the micelle aqueous solutions and required to be further explored.

In order to clarify the nature of the inter-micellar interactions, direct measurement of the inter-micellar interaction enthalpy is highly required. The interaction enthalpies can be directly determined through measuring the dilution enthalpies of dilute micelle solutions by calorimetry; however, the demicellization enthalpy in the dilution process is usually significant and must be properly eliminated. This possibly is a reason that the measurement of the interaction enthalpy between the micelles has not been found.

In this paper, based on a proper experimental design and the corresponding data analysis to eliminate the demicellization enthalpies, the heats of mixing for a series of aqueous solutions

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of mixed surfactants of dodecyltrimethylammonium bromide (DTAB) and 1-dodecyl-3-methylimidazolium bromide (C_{12}mimBr) are measured at different compositions and 298.15 K by using flow-mixing calorimetry. The inter-micellar interaction enthalpies of the mixed micelles are then calculated; which together with the result of static light scattering are used to clarify the nature of inter-micellar interactions for DTAB/C_{12}mimBr mixed micelle system.

Materials and methods

Chemicals

The 1-dodecyl-3-methylimidazolium bromide (C_{12}mimBr, ≥99% mass fraction) and the dodecyltrimethylammonium bromide (DTAB) (≥99% mass fraction) were purchased from Cheng Jie Chemical Co., Ltd. (Shanghai, China) and Aladdin Chem. Co., Ltd. (Shanghai, China), respectively; their structures are shown in Fig. 1. Both of surfactants were dried under vacuum at about 5 kPa for 48 h before use. The mass fractions of water remaining in the dried samples were analyzed by the coulometric Karl-Fischer titration and found to be about 1×10^{-4}. The various surfactant compositions of solutions were characterized by the DTAB mole fractions in the total mixed surfactants (α_1) and the DTAB mole fractions in the mixed micelles (x_1).

Static light scattering (SLS)

A Brookhaven BI200SM goniometer and BI9000 digital correlator were used to perform the static light scattering measurements at 298.15 ± 0.1 K. The measurement angle was fixed at 90°. The light source is an argon-ion laser with a wavelength of 488 nm. Surfactant solutions were filtered with Millipore 0.22 μm filters to remove dust before taking measurements. The derivative of n with respect to the concentration C dn/dC was measured by a differential refractometer (BI-DNDC, Brookhaven Instruments Corporation).

Flow-mixing calorimetry

The interaction enthalpy of micelles was studied by a flow-mixing calorimeter (Thermal Activity Monitor 2277, Thermometric AB, Järfäfla, Sweden) at 298.15 ± 0.02 K. To prevent the dissociation of the micelles, a series of micelle solutions or mixed micelle solutions with somewhat higher concentrations were mixed with a dilute one (about 1.5 times of its corresponding critical micelle concentration) in sequence by pumping them into the flow-mixing vessel in a calorimeter using a 403U-VM250 RPM dual channel pump to measure the heats of the mixing. In each of mixings, the concentrated solution and the dilute solution have the same value of α_1. This procedure was carried out for a series of mixed surfactant systems with various α_1 (Scheme 1).
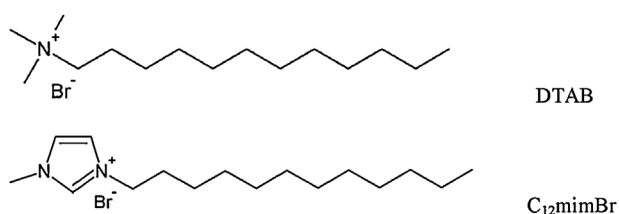

Fig. 1. Chemical structure of DTAB and C_{12}mimBr.

Results and discussion

Static light scattering

Static light scattering is usually used to determine the weight-averaged molar masse of micelle and the second virial coefficient, the latter represents the interaction between micelles. The Debye equation [31] gives the relation of the Rayleigh ratio at the 90° scattering angle (ΔR_{90}) and the surfactant concentration constructing the micelles ($C - \text{cmc}$) with the unit of 1 kg surfactant per unit solution volume (kg dm^{-3}):

$$\frac{K(C - \text{cmc})}{\Delta R_{90}} = \frac{1}{M_w} + 2B_2(C - \text{cmc}) \tag{1}$$

where K is the optical constant and can be calculated by $K = 4\pi^2 n^2 (\text{d}n/\text{d}C)^2/(N_A \lambda^4)$ with n, dn/dC,N_A and λ being the solvent refractive index, the differential refractive index increment, the Avogadro number, and the wavelength of the incident light in vacuo, respectively; B_2 is the second virial coefficient with the unit of mol dm^3 kg^{-2}, M_W is the weight-averaged molar masse of the micelle. A series of Rayleigh ratios ΔR_{90} at various surfactant concentrations ($C - \text{cmc}$) at 298 K were measured, which are listed in Table S1.

Eq. (1) can be rewritten as

$$\frac{KM_S^2}{\Delta R_{90}}(C - \text{cmc})_S = \frac{1}{N} + 2B_S(C - \text{cmc})_S \tag{2}$$

where $B_S = B_2 M_S^2$ is the second virial coefficient with the unit of kg mol^{-1}, N is the aggregation number of micelles, M_s is the average molar mass of mixed surfactants calculated by $M_S = \alpha_1 M_1 + (1 - \alpha_1)M_2$ (M_1 and M_2 are the molar masses of DTAB and C_{12}mimBr, respectively), $(C - \text{cmc})_s$ is the surfactant concentration constructing the micelles with the unit of 1 mol surfactant per unit solution mass (mol kg^{-1}), and can be calculated by $(C - \text{cmc})_s \approx (C - \text{cmc})/ (\rho M_s)$, ρ is the density of the solution, which was approximately taken as 1 kg dm^{-3} at the experimental conditions in this work.

A plot of $KM_S^2(C - \text{cmc})_S/\Delta R_{90}$ versus $(C - \text{cmc})_s$ yields a straight line, as shown in Fig. 2 for various α_1. The intercepts of these lines are the reciprocals of aggregation numbers of micelles N and the slopes are the second virial coefficients B_S, which were obtained by linear least-square fits. The second virial coefficients of micelles B_m with the unit of kg mol^{-1} were calculated by

$$B_m = B_S N^2 \tag{3}$$

The values of N and B_m are listed in Table 1.

As found in Table 1, the aggregation numbers of DTAB and C_{12}mimBr are 53 ± 7 and 53 ± 10, respectively; which are consistent with the results reported in references (N_{DTAB} = 48, N_{C12mimBr} = 46) [32,33]. All the values of the second virial coefficients are positive, suggesting that repulsive intermicellar interaction is dominant [31]. As shown in Table 1, the uncertainties in determinations of N and B_m are significantly large; however, it is clear that the values of the second virial coefficient and the aggregation number have maximums at α_1 = 0.6 as illustrated in Fig. 3a, indicating that the larger repulsion between the micelles results from the larger size of the micelles. These observations accorded with the commonly accepted fact that the larger reversed micelles have larger interactions between them [34–36].

Flow-mixing calorimetry

With an assumption that the micelle concentrations of the surfactant solutions prepared for measurements of the heats of mixing in this work are sufficiently dilute, the enthalpy of the