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Effect of sodium chloride on interaction between amino sulfonate amphoteric surfactant and octylphenol polyoxyethylene ether (10) in aqueous solution

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ABSTRACT

In aqueous solution containing the NaCl of 0.25 mol/L, the micellization of binary mixtures of sodium dodecyl diamino sulfonate (C12AS) and octylphenol polyoxyethylene ether (10) (OP-10) have been investigated employing both the UV–vis spectroscopy method, using pyrene as a probe, and the tensiometric method. The values of critical micelle concentration (*cmc*) at different molar compositions in the mixture of C12AS/OP-10 were determined by both the UV–vis spectroscopy measurement and the tensiometric measurement. Within the framework of pseudophase separation model, some parameters (including the ideal values of mixed *cmc*, the interaction parameters, components and activity coefficients in mixed micelles, and thermodynamic parameters of micellization) were calculated using various models and treatments, e.g. the regular solution theory, the ideal model from the Lang model, the Rodenas's treatment and the Motomura's treatment, and the mechanism on effect of NaCl on the interacting behavior between two surfactants was discussed. The results show that as compared to the cases in the absence of NaCl, the addition of NaCl enhances non-ideal mixing and synergism between C12AS and OP-10 in all mixed systems, mainly resulting from the decrease of the steric effect of headgroups of two surfactants and the increase of the ionic strength in aqueous solution. Thermodynamic data show that on adding NaCl the micellization for the mixtures of C12AS and OP-10 can proceed spontaneously, and is an enthalpy-driven process owing to the variation of hydrophobic properties in aqueous solution.

Introduction

In practical application, mixtures of surfactants, rather than individual surfactants, are used [1–3]. Some surfactant mixtures exhibit superior properties, such as, lower cost than single unmixed surfactant systems, higher surface/interfacial activities, synergistic properties and so on. In last three decades, many investigations have been reported the solution properties of surfactant and mixed surfactants systems [1,3–6]. Among these mixed systems, the observed synergism can be referred to as nonideal mixing, whereas the antagonism properties can be attributed to the repulsion between their molecules. Based on the regular solution theory (RST), the Rubingh model [3] introduces an important parameter, the interaction parameter (β_{12}), which helps us to predict the attraction or repulsion between the two surfactants. For a nonideal mixed system, another parameter, activity coefficient (f), was also introduced into some models [3,4] and was used to partly describe the difference between the nonideal and ideal mixing of surfactants. Considering the restriction of Rubingh's treatment and the different theoretical background, two new treatments, both the Rodenas's treatment [4] and the Motomura's treatment [7], were developed. In addition, other theoretical treatments or models based on thermodynamics that are similar to Rubingh's model have also been used [8,9]. These treatments can help us to obtain some parameters describing the interacting behavior between molecules in the mixed surfactant systems, and then to understand both the theoretical and practical significance.

A larger number of investigations [4–12] have been reported the interacting behaviors for the mixed surfactant systems in aqueous solutions in the absence of inorganic salts. Nevertheless, in many engineering applications, the inorganic salts always exist

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in the water systems dissolved by the mixed surfactant systems. The addition of inorganic salts is known to modify the properties of surfactant solutions, such as solubility, the interaction parameters of both solute–solute and solute–solvent, the micellar behavior for individual or mixed surfactant systems, and so on. For the ionic surfactants, the added inorganic salt, especially counterion, can compress the thickness of ionic atmosphere for the ionic headgroup of surfactant, consequently resulting in the reduction of electrostatic repulsion between their ionic headgroups, and favoring the formation of micelles [1,2,13,14]. While in nonionic surfactants solution, the addition of inorganic salt does not have drastic effects on the formation of micelle as compared to the ionic surfactants [1,2]. For the mixed surfactant systems, the addition of inorganic salt may result in different micellar behavior [13–15]. At present, many investigations have reported the effect of inorganic salt on the micellar behaviors for the mixtures of ionic-nonionic surfactants [13–15]. However, the micellar behaviors of zwitterionic-nonionic surfactants in aqueous solution containing inorganic salt have rarely been investigated. In this paper, the attempt was made to investigate the micellar behavior between an amino sulfonate amphoteric surfactant, *n*-dodecyl diamine sulfonate (C12AS) developed by our group [11,16], and nonionic surfactant octylphenol polyoxyethylene ether (10), OP-10, in aqueous solution, especially in the presence of sodium chloride. The main purpose of this investigation is to explore the micellar behavior of mixed surfactant systems as well as the composition of mixed micelles in aqueous solution containing sodium chloride of 0.25 mol/L. To obtain the information of the interaction between two surfactants and the compositions of mixed micelles, we are adopting different theories, models and treatments, e.g., regular solution theory (RST), the Lang model [17], the Rodenas's and the Motomura's treatments, and then the results is theoretically discussed.

Experimental

Materials and solutions

C12AS developed by our group [11,16] has a purity of over 96% (the rest is the water of about 4%), measured with Vario EL III Automatic Elementary Analyser made by Germany Elementar Co. OP-10 is a chemical pure reagent, and sodium chloride (NaCl) is an analytical reagent. Both OP-10 and NaCl from Sinopharm Chemical Reagent Co., Ltd. have the purities of over 99%. Pyrene with a purity of 98% is purchased from American Aldrich Chemical Reagent Co. The chemical structure formulas of C12AS and OP-10 are depicted in Fig. 1. C12AS and OP-10 were used as supplied. NaCl and pyrene were recrystallized three times using deionized triple distilled (DTD) water before use.

Solutions of C12AS, OP-10, and their mixtures were prepared respectively by DTD water containing the NaCl of 0.25 mol/L. It should be noted that the purities of C12AS and OP-10 were considered for calculating the concentrations and the mole fractions of binary mixtures. The pH values of mixed surfactant solutions were found to be close to 6.2 within the range of isoelectric point for C12AS.

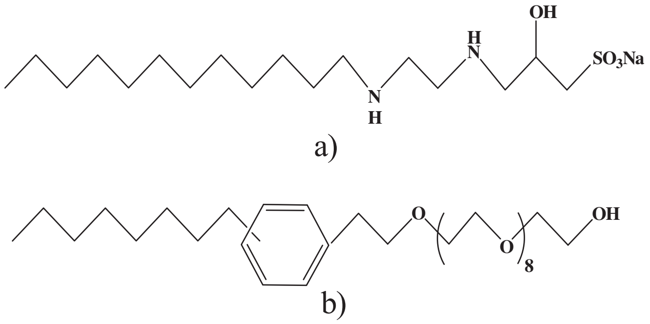

Fig. 1. Chemical structure formulas of compounds: (a) C12AS; (b) OP-10.

Instrumentation

Before the analysis of UV–vis spectrum all solutions added the stock solution of pyrene in the conical flasks sealed with rubber plug were allowed to stand in water bath of 25 ± 0.2 °C for over 50 min, where the preparation of the stock solution of pyrene refer to the document [18]. Absorbance measurements were taken in a UV-2450 UV–vis spectrophotometer made by Shimadzu using 5 mL quartz cuvettes at 25 ± 0.2 °C. The spectra were recorded in the 220–400 nm wavelength range, in the intermediate scanning speed, and in the sample interval of 0.5 nm. In addition, the surface tensions of mixed surfactant solutions were measured in a JK99B automatic tensiometer made in China, using Wilhelmy plate method at 25 ± 0.2 °C.

Determination of critical micelle concentration by UV–vis spectroscopy and tensiometry

The determination of critical micelle concentration (*cmc*) for the above surfactant systems was carried out through the UV–vis spectroscopy method, using pyrene as a probe. The data of absorbance in UV-spectrum are mean values from several measurements. The curves of absorbance value versus surfactant concentration were used for the determination of *cmc*. The inflection point in the curve was taken as the *cmc* of surfactant or mixed surfactant systems in the corresponding pyrene solution. The values of *cmc* were also determined by the inflection point in the curve of surface tension versus the logarithm of molar concentration.

Results and discussion

Micellization of C12AS, OP-10 and their mixtures in aqueous NaCl solution

Simple absorbance spectra in the UV–vis spectrum with varying surfactant concentration give some useful information about the formation of micelles in solution. With increasing surfactant concentration in aqueous solution, the intensity of peak at a specific wavelength increases, and then the *cmc* value can be obtained from the inflection point of the curve in the plot of the intensity of peak versus concentration [18]. Fig. 2a shows the variation of the ratio of absorbance of pyrene at about 275 nm and molar concentration of surfactant (c), A/c, with the logarithm of c, $\log c$. It is obviously found in Fig. 2a that originally the value of A/c decreases regularly with $\log c$, and then the value of A/c hardly continues to decrease after the $\log c$ increases to a specific value, implying the formation of mixed micelle. In addition, the curves of surface tension versus the logarithm of c, $\log c$, were plotted in Fig. 2b. The tendency for the variation of surface tension with $\log c$ in Fig. 2b is similar to that in Fig. 2a. The experimental values of single or mixed *cmc* in aqueous NaCl solutions determined by both the UV–vis spectroscopy method, using pyrene as a probe, and the tensiometric method are listed in Table 1. As shown in Table 1, the *cmc* values obtained by the UV–vis spectroscopy method are mainly consistent with obtained by the tensiometric method, indicating the validity of two methods in this investigation. It is found in Table 1 that the *cmc* value of individual OP-10 in aqueous solution in the presence of NaCl is slightly less than 0.330×10^{-3} mol/L in the absence of NaCl [1,18], which may be