

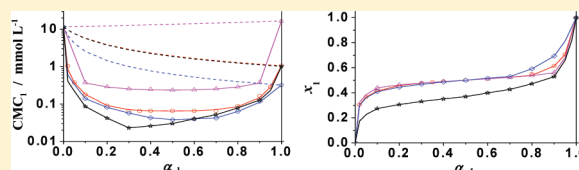
# Mixed Micellization and the Dissociated Margules Model for Cationic/Anionic Surfactant Systems

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## Supporting Information

**ABSTRACT:** The first and the second critical micelle concentration ( $CMC_1$  and  $CMC_2$ ) for three alkyltrimethylammonium bromide ( $C_n$ TAB)/sodium dodecylsulfonate (AS)/ $H_2O$  mixed systems, and  $CMC_1$  for trimethylene-1,3-bis(dodecyldimethylammonium bromide) (12–3–12)/AS/ $H_2O$  mixed system have been measured. The largest negative  $\beta^m$  value means the strongest synergism between 12–3–12 and AS. The  $CMC_1$  and  $CMC_2$  for the  $C_n$ TAB/AS/ $H_2O$  mixed systems decrease with the increase of  $n$ . The equimolar mixed systems give the smallest  $CMC_1$  values, whereas the  $CMC_2$  values decrease with the increase of the composition of the surfactant with higher surface activity in the  $C_n$ TAB/AS/ $H_2O$  mixed systems. For the  $C_{16}$ TAB/AS mixed systems far from equimolar, specific counterion effect on lowering  $CMC_1$  enhances according to the Hofmeister series. There is slightly or no salt effect on the  $CMC_1$  of the other wide composition range of  $C_{16}$ TAB/AS/ $H_2O$  mixed system. The pseudophase separation model coupled with the dissociated Margules model has been proposed and gives satisfactory description of the mixed  $CMC_1$ , the calculated micellar compositions are in well accordance with composition information from the  $\zeta$  potential measurements. The addition of salt into the  $C_{16}$ TAB/AS/ $H_2O$  mixed system, leads to a certain degree of decrease in  $CMC_2$ . In addition to counterion effect, the co-ion effect on  $CMC_2$  of the mixed system was explained using Collins' concept of matching water affinities.



## 1. INTRODUCTION

The first critical micelle concentration ( $CMC_1$ ) at which surfactants tend to self-assemble into spherical micelles and the second critical micelle concentration ( $CMC_2$ ) at which the micelles undergo structural transition from spherical to rodlike micelles, represent fundamental micellar quantities to study the self-aggregation of amphiphilic surfactant molecules in solution. The aggregation and micellization ability of surfactant molecules dependent on the CMC values plays an important role in a wide range of surfactant-based phenomena and applications, such as detergency, painting, coating, cosmetics, tertiary oil recovery, and so forth.

Solution properties of mixed surfactants are more interesting than pure surfactants, from both physicochemical and application points of view. Among the various types of binary surfactant systems, the mixed cationic/anionic surfactants exhibit the largest synergistic effects arising from the strong electrostatic attraction between the oppositely charged headgroups, leading to a reduction of the total amount of surfactant used in a particular application, which in turn reduces both the cost and environmental impact. Thus, mixed micellization of cationic/anionic surfactants has attracted increasing interest over the past 20 years.<sup>1–27</sup> Literature work focuses mostly on the determination of  $CMC_1$ , mixed adsorbed films at the air/aqueous solution interface and the synergism between the cationic and anionic surfactant molecules. To our knowledge, the number of studies involving in  $CMC_2$  data of mixed cationic/anionic surfactant systems is very limited,<sup>19,22,23</sup> the dependence of  $CMC_2$  on composition is still unknown. However, since viscoelastic

fluids based on rodlike micelles have remarkable rheological properties and play an important role in industrial applications, systematic investigation in the  $CMC_2$  of this kind of surfactant systems is significant.

It is well-known that the molecular structure of the surfactants,<sup>3–21</sup> such as the type of headgroups, type of tail chains, chain length, the alkyl chain number and headgroup number, is an important factor influencing the micellization of surfactants. For the mixed cationic/anionic surfactants, chain length symmetry,<sup>28</sup> type of ionic surfactant<sup>13–17,29</sup> and additives<sup>15</sup> etc., are important factors for the formation of micelles.

Dimeric surfactants as a new class of surfactants, which consist of two amphiphilic “monomer” units linked together by spacer groups, have attracted and continue to attract considerable interest in both academic and industrial communities working on surfactants<sup>12–21,30</sup> by virtue of their unusual solution and interfacial properties (such as low critical micelle concentrations, high surface activity, unusual rheology, and self-assembly). The mixed micellization of oppositely charged dimeric/monomeric surfactant systems is one of the interesting research topics.<sup>12–17</sup> However, There are several different consequences about synergism of oppositely charged dimeric/monomeric surfactant systems based on experimental  $CMC_1$  results. For example, in comparison with  $C_{12}$ TAB/SDS system, 12–2–12/SDS and 12–6–12/SDS systems show weaker

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synergism;<sup>13,17</sup> Whereas, in comparison with C<sub>12</sub>TAB/SOS system, 12–2–12/SOS system show stronger synergism.<sup>16</sup> In addition, (C<sub>12</sub>H<sub>25</sub>(CH<sub>3</sub>)<sub>2</sub>N<sup>+</sup>CH<sub>2</sub>CHOHCHOHCH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>N<sup>+</sup>C<sub>12</sub>H<sub>25</sub>)-2Br<sup>−</sup>/C<sub>12</sub>H<sub>25</sub>SO<sub>3</sub>Na system shows no synergism at all.<sup>15</sup> Different interpretations were used to explain the different synergisms.<sup>13–17</sup> To search for the synergism rule of oppositely charged dimeric/monomeric surfactant systems, more experiments are required.

In most of their applications, surfactants are used in the presence of additives. Inorganic salts are the most used additives. The addition of inorganic salts to ionic surfactant solutions has pronounced specific ion effects on micellar properties,<sup>31–34</sup> which is mainly due to a decrease in the value of the apparent area per molecule at the interface (hydrated headgroup)  $a$ , thus is beneficial for the formation of micelles and influences a surfactant critical packing parameter  $p = \nu/(l_{\max} a)$ , where  $\nu$  and  $l_{\max}$  are the volume and length of the hydrophobic part, respectively and are not significantly influenced by the added salts.<sup>35–37</sup>  $p$  can be thought as a measure of the curvature of the micelles, for  $p < 1/3$  spherical micelles and for  $1/3 < p < 1/2$  rodlike micelles are predicted. The specific ion effects on the micellization of single ionic surfactants have been extensively studied and are still an interesting research topic nowadays since CMC<sub>1</sub> of ionic surfactant depends on counterions and follows direct or reversed Hofmeister series.<sup>31–34,38–40</sup> For the investigations of micellization of mixed cationic/anionic surfactants, inorganic salts NaCl and NaBr are the commonly used additives to adjust the ionic strength of the studied systems.<sup>11,18,28,29,41–43</sup> Sometimes, inorganic salt effect was discussed,<sup>3,7,14,15,19,44</sup> indicating that the addition of inorganic salt results in the reduction of the CMC<sub>1</sub> of ionic surfactants, while has little or no effect on the mixed CMC<sub>1</sub> of the cationic/anionic surfactant systems with molar ratios not very far from equimolar composition. Whereas, for those aqueous mixed cationic/anionic surfactants far from equimolar, the addition of salt reduces the mixed CMC<sub>1</sub><sup>3,19</sup> and CMC<sub>2</sub><sup>19</sup> more pronouncedly. However, the investigations about specific ion effects on the micellization or the surface properties of mixed cationic/anionic surfactants, are relatively scarce.<sup>15,45</sup> The micellar compositions of the mixed cationic/anionic surfactants at CMC<sub>1</sub> are nearly equimolar for a wide range of mixing ratios.<sup>43,46–48</sup> This may be the reason why specific ion effect on micellization of mixed cationic/anionic surfactants has been scarcely investigated. Whereas at concentrations much higher than CMC<sub>1</sub>, the micelle or aggregate composition approaches the bulk solution mixing ratio,<sup>46,47</sup> specific ion effect should be taken into consideration. For example, specific alkali cation effects were found to influence strongly the critical salt concentrations, in which rod-like micelles turn to vesicles in aqueous solutions composed of DTAB and an excess of SDS through the addition of salts.<sup>49</sup> The investigation about the influence of added salts on the aqueous two-phase regions of cationic/anionic surfactant systems indicated that the salt effect is mainly dependent on the counterion specificity.<sup>50</sup>

Some theoretical models have been proposed to explain the properties of mixed micelles and the mixed adsorbed films at the air/aqueous solution interfaces. The pseudophase separation approach coupled with a regular solution approximation with a single interaction parameter  $\beta^m$  or  $\beta^s$  proposed by Rubingh<sup>51</sup> and Rosen et al.,<sup>52</sup> is the most widely used theory in the field of nonideal mixed micelles or adsorbed films. Since this theory is applicable to a wide variety of surfactant mixtures,<sup>7–9,11–13,53–55</sup> it enables a direct comparison of the

aggregation process for different types of surfactant mixtures. However, from thermodynamic point of view, the regular solution theory is suitable for systems with symmetric nonideal mixing behaviors.<sup>56</sup> For asymmetric mixed systems,<sup>4,11,44,56,57</sup> the model is insufficient, and usually yields composition-dependent interaction parameter  $\beta^m$ . Two-parameter modifications of regular solution approach have been used previously for characterizing asymmetric mixed surfactant systems.<sup>58–60</sup> Two-parameter van Laar model or Margules model substitutes regular solution theory to calculate the activity coefficients of components and gives improved fits to micellization properties of asymmetric mixed surfactant systems.<sup>61,62</sup> Simple theoretical arguments show that the van Laar model or Margules model is valid for interactions among headgroups which operate over long distances (e.g., electrostatic interactions) or short distances (e.g., contact interactions). Motomura et al.<sup>63</sup> have shown that the process of micelle formation can be treated from the viewpoint of thermodynamics and takes into account dissociation of ionic surfactants. However Motomura's model does not deal with the surfactant interaction parameter, a general comparison with other theories can be attempted on the basis of the component mole fractions in the mixed micelles.<sup>55</sup> The recent research of Turmine et al.<sup>64</sup> also indicated the importance of the dissociation of the ionic surfactant for mixed micellization, and the models they used are Clint model and regular solution theory. Blankschtein et al.<sup>65,66</sup> have developed a molecular thermodynamic theory to quantitatively predict the behavior of mixed surfactant solutions. The theory combines a thermodynamic description of mixed micellar solutions with a molecular model of micellization. Although the theory is more fundamental and of predictive character, it requires a priori information on the structures of both surfactant molecules and mixed micelles, which is not always available,<sup>67</sup> and neglecting the Stern layer of cationic/anionic surfactant mixed micelles results in lower predictions for mixed CMC<sub>1</sub> values and in higher predictions for micelle size.<sup>66</sup> Therefore, there is still a need to develop a theoretical model which takes the dissociation of ionic surfactant and the interaction between surfactants into consideration to account for the mixed micellization of cationic/anionic surfactants.

In the present paper, the CMC<sub>1</sub> and CMC<sub>2</sub> of three oppositely charged monomeric/monomeric surfactant (C<sub>*n*</sub>TAB/AS,  $n = 12, 16, 18$ ) aqueous mixed systems and the CMC<sub>1</sub> of one oppositely charged dimeric/monomeric surfactant (12–3–12/AS) aqueous mixed system at 318.15 K, have been measured to investigate the molecular structure effect of cationic surfactant on the mixed micellization. The inorganic salt (NaCl, NaBr, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub>, KCl) aqueous solutions were used as solvents for the CMC<sub>1</sub> and CMC<sub>2</sub> measurements of C<sub>16</sub>TAB/AS system to investigate the specific counterion effect or co-ion effect on the mixed micellization. The regular solution theory of Rubingh was used to treat the mixed micelles of these systems, and the micellar interaction parameter  $\beta^m$  have been calculated to compare the synergisms and interaction strength between different cationic and anionic surfactant molecules. One main objective of this research is to develop a theoretical model of mixed micellization for cationic/anionic surfactants. For this purpose, the pseudophase separation approach coupled with the dissociated two-parameter Margules model has been proposed. The  $\zeta$  potentials and microstructures of some mixed micelles have been studied by Malvern Zetasizer Nano ZS and negative-stained TEM method, respectively.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Sodium dodecylsulfonate (AS) (purity  $\geq 97\%$ ) was recrystallized as previously.<sup>68,69</sup> 12–3–12 was synthesized and purified according to literature<sup>70</sup> as previously.<sup>69</sup> Dodecyltrimethylammonium bromide ( $C_{12}$ TAB), tetradecyltrimethylammonium bromide ( $C_{14}$ TAB), cetyltrimethylammonium bromide ( $C_{16}$ TAB), stearyltrimethylammonium bromide ( $C_{18}$ TAB), the salts NaCl, NaBr, KCl and  $Na_2SO_4$ , purity  $\geq 99\%$ , were used without further purification. Pyrene (Py), purity  $\geq 90\%$ , was recrystallized three times from ethanol. All the above reagents were dried in a vacuum desiccator at 333.15 K for 24 h before use.  $Na_3PO_4 \cdot 12H_2O$ , purity  $\geq 99\%$ , was used as obtained. Water was redistilled from potassium permanganate solution.

**2.2. Electrical Conductivity Measurements.** A Mettler Toledo SevenMulti Modular Meter System with the conductivity expansion unit was used for the electrical conductivity measurements. The reference temperature is 298.15 K. The temperature of the sample solution was maintained at  $318.15 \pm 0.1$  K by a water flow thermostat. The measurement error is within  $\pm 0.5\%$ .

**2.3. Steady-State Fluorescence Measurements.** Spectrofluorometry with pyrene as fluorescent probe was used to determine  $CMC_1$ . The pyrene concentration in the surfactant solutions was  $5 \times 10^{-7}$  mol·L<sup>-1</sup>. The fluorescence spectra of pyrene solubilized in the investigated solutions were recorded using a Hitachi F-4500 spectrofluorometer in the range of 360–450 nm at an excitation wavelength of 335 nm. The measurement error of micropolarity (i.e., pyrene polarity ratio  $I_1/I_3$ ) is  $\pm 0.02$ .

**2.4. Electron Microscopy Measurements.** Negatively stained electron micrographs were obtained using a JEOL-1230 electron microscope operating at 100 kV. A drop of the sample was first spread on a 200-mesh copper grid coated with a carbon film; another drop of the staining solution (1.0 wt % of aqueous uranyl acetate solution) was then added. The excess solution was sucked away by filter paper. The sample was then air-dried before the TEM observation.

**2.5.  $\zeta$  Potential Measurements.**  $\zeta$  potential measurements (using a laser–Doppler Velocimetry technique) were made on a temperature controlled Malvern Zetasizer Nano ZS at  $318.15 \pm 0.01$  K. The instrument uses a laser at a wavelength of 632.8 nm and detects the scattered light at an angle of  $173^\circ$ . The nominal accuracy on  $\zeta$  potential is to  $\pm 1.0$  mV. The  $\zeta$  potential was taken as the mean value of three to six measurements.

## 3. MODEL

The pseudophase separation model for the formation of nonideal binary mixed micelles shows that at the  $CMC_1$  ( $C_{12}^m$ ) of a mixed surfactant system, there exists a simple relation between  $C_{12}^m$  and the  $CMC_1$  ( $C_i^m$ ) of each pure surfactant  $i$ :

$$\alpha_i C_{12}^m = x_i \gamma_i C_i^m \quad (i = 1, 2) \quad (1)$$

In which,  $\alpha_i$  and  $x_i$  are the mole fractions of the surfactant  $i$  in the total mixed solute and in the mixed micelles, respectively, and  $\gamma_i$  is the activity coefficient of the surfactant  $i$  in the mixed micelles. The mole fractions obey the constraints:

$$\alpha_1 + \alpha_2 = 1 \quad (2)$$

$$x_1 + x_2 = 1 \quad (3)$$

The combination of eqs 1–3 gives a generalized relationship for  $C_{12}^m$  with  $C_i^m$ :

$$\frac{1}{C_{12}^m} = \frac{\alpha_1}{\gamma_1 C_1^m} + \frac{\alpha_2}{\gamma_2 C_2^m} \quad (4)$$

If  $\gamma_1$  and  $\gamma_2$  equal to 1, the Clint condition of ideality is then recovered.

**3.1. Rubingh's Model.** Using the regular solution approximation developed by Rubingh,<sup>51</sup> the activity coefficient  $\gamma_i$  can be expressed as:

$$\ln \gamma_1 = \beta^m (1 - x_1)^2 \quad (5)$$

$$\ln \gamma_2 = \beta^m x_1^2 \quad (6)$$

$\beta^m$  is a constant related to net pairwise interactions in the mixed micelle of the form:

$$\beta^m = L(W_{11} + W_{22} - 2W_{12})/RT \quad (7)$$

In which  $W_{11}$ ,  $W_{12}$ , and  $W_{22}$  are pairwise interaction energies between surfactant molecules in micelle,  $L$  is Avogadro's number. Synergism in mixed micelle formation exists when the  $C_{12}^m$  of a mixture is less than that of individual surfactants among the mixture. The conditions for synergism to exist in the mixture<sup>71</sup> are as follows:

(a)  $\beta^m$  must be negative and (b)  $|\beta^m| > |\ln(C_1^m/C_2^m)|$ .

$x_1$  and  $\beta^m$  can be calculated using the following equations:

$$\frac{x_1^2 \ln(\alpha_1 C_{12}^m / C_1^m x_1)}{(1 - x_1)^2 \ln[(1 - \alpha_1) C_{12}^m / C_2^m (1 - x_1)]} = 1 \quad (8)$$

$$\beta^m = \frac{\ln[\alpha_1 C_{12}^m / C_1^m x_1]}{(1 - x_1)^2} \quad (9)$$

Equation 8 was solved iteratively to obtain the value of  $x_1$ . Then substitution the value of  $x_1$  into eq 9 gives the value of  $\beta^m$ .

**3.2. The Dissociation of Ionic Surfactant.** According to the approach of Turmine et al.,<sup>64</sup> the possible dissociation of ionic surfactant must be considered when treating the mixed micellization. For the mixtures formed by cationic surfactant 1 and anionic surfactant 2, we suppose that surfactant 1 generates  $r_1$  particles, and surfactant 2 generates  $r_2$  particles. Mole fractions of particles  $x_{1,r_1}$  and  $x_{1,r_2}$  constituting the micelles are linked to the stoichiometric mole fractions  $x_1$  and  $x_2$  of micelles according to:

$$x_{1,r_1} = \frac{r_1 n_1^m}{r_1 n_1^m + r_2 n_2^m} = \frac{r_1 x_1}{r_1 x_1 + r_2 x_2} = \frac{r_1 x_1}{r_2 + x_1(r_1 - r_2)} \quad (10)$$

$$x_{2,r_2} = \frac{r_2 n_2^m}{r_1 n_1^m + r_2 n_2^m} = \frac{r_2 x_2}{r_1 x_1 + r_2 x_2} = \frac{r_2(1 - x_1)}{r_2 + x_1(r_1 - r_2)} \quad (11)$$

In this case, the micelles are supposed to be constituted by  $n_1^m$  of 1 and  $n_2^m$  of 2, and water does not participate in the micelles. AS and  $C_n$ TAB as simple 1–1 electrolytes, if they are supposed not to be dissociated in the micelle, then  $r_i = 1$ ; if they are supposed to be totally dissociated, then  $r_i = 2$ ; i.e.,  $1 \leq r_i \leq 2$ . For the dimeric cationic surfactant 12–3–12, as a 2–1 electrolyte, the value of  $r_1$  is between 1 and 3.

According to the approach of Turmine et al.,<sup>64</sup> for  $C_n$ TAB/AS/ $H_2O$  mixed systems, the relation between  $C_{12}^m$  and  $C_1^m$ ,  $C_2^m$  is

$$x_{1,r_1} = \frac{1}{\gamma_{1,r_1}} \left( \frac{\alpha_1 C_{12}^m}{C_1^m} \right)^{2/r_1} \quad (12a)$$



$$x_{2,r_2} = \frac{1}{\gamma_{2,r_2}} \left[ \frac{(1 - \alpha_1)C_{12}^m}{C_2^m} \right]^{2/r_2} \quad (12b)$$

$$1 = x_{1,r_1} + x_{2,r_2} = \frac{1}{\gamma_{1,r_1}} \left( \frac{\alpha_1 C_{12}^m}{C_1^m} \right)^{2/r_1} + \frac{1}{\gamma_{2,r_2}} \left[ \frac{(1 - \alpha_1)C_{12}^m}{C_2^m} \right]^{2/r_2} \quad (12c)$$

For the  $C_n$ TAB/AS/salt aqueous mixed systems, the relation between  $C_{12}^m$  and  $C_1^m$ ,  $C_2^m$  is as follow:

$$x_{1,r_1} = \frac{1}{\gamma_{1,r_1}} \left( \frac{\alpha_1 C_{12}^m}{C_1^m} \right)^{1/r_1} \quad (13a)$$

$$x_{2,r_2} = \frac{1}{\gamma_{2,r_2}} \left[ \frac{(1 - \alpha_1)C_{12}^m}{C_2^m} \right]^{1/r_2} \quad (13b)$$

$$1 = x_{1,r_1} + x_{2,r_2} = \frac{1}{\gamma_{1,r_1}} \left( \frac{\alpha_1 C_{12}^m}{C_1^m} \right)^{1/r_1} + \frac{1}{\gamma_{2,r_2}} \left[ \frac{(1 - \alpha_1)C_{12}^m}{C_2^m} \right]^{1/r_2} \quad (13c)$$

For the  $C_n$ TAB/AS mixed systems, at equimolar composition, strong electrostatic attraction between the oppositely charged headgroups means the totally release of the counterions of the surfactants, therefore, we suppose  $r_1 = r_2 = 2$ .

For the 12–3–12/AS/H<sub>2</sub>O mixed system, the relation between  $C_{12}^m$  and  $C_1^m$ ,  $C_2^m$  is as follow:

$$x_{1,r_1} = \frac{1}{\gamma_{1,r_1}} \left( \frac{\alpha_1 C_{12}^m}{C_1^m} \right)^{3/r_1} \quad (14a)$$

$$x_{2,r_2} = \frac{1}{\gamma_{2,r_2}} \left[ \frac{(1 - \alpha_1)C_{12}^m}{C_2^m} \right]^{2/r_2} \quad (14b)$$

$$1 = x_{1,r_1} + x_{2,r_2} = \frac{1}{\gamma_{1,r_1}} \left( \frac{\alpha_1 C_{12}^m}{C_1^m} \right)^{3/r_1} + \frac{1}{\gamma_{2,r_2}} \left[ \frac{(1 - \alpha_1)C_{12}^m}{C_2^m} \right]^{2/r_2} \quad (14c)$$

At  $\alpha_1 = 1/3$ , for the oppositely charged headgroups, the amount of positive charge equals the amount of the negative charge, i.e.  $\alpha_1 = 1/3$  is the equimolar composition, there are strong electrostatic attraction, we suppose  $r_1 = 3$  and  $r_2 = 2$ , and  $x_1 = 1/3$ .

The derivation of eqs 12a–14c was given in the Supporting Information.

### 3.3. The Dissociated Two-Parameter Margules Model.

According to the two-parameter Margules model,<sup>62</sup> the activity coefficient  $\gamma_i$  can be expressed as a function of  $x_i$  and the parameters  $A_{12}$  and  $A_{21}$ :

$$\ln \gamma_1 = [A_{12} + 2(A_{21} - A_{12})x_1](1 - x_1)^2 \quad (15)$$

$$\ln \gamma_2 = [A_{21} + 2(A_{12} - A_{21})(1 - x_1)]x_1^2 \quad (16)$$

If  $A_{12} = A_{21} = \beta^m$ , then eqs 15 and 16 recover to eqs 5 and 6.

The possible dissociation in the oppositely charged surfactant mixed systems should be taken into consideration, then eqs 15 and 16 should be rewritten as

$$\ln \gamma_{1,r_1} = [A_{12} + 2(A_{21} - A_{12})x_{1,r_1}](1 - x_{1,r_1})^2 \quad (17)$$

$$\ln \gamma_{2,r_2} = [A_{21} + 2(A_{12} - A_{21})(1 - x_{1,r_1})]x_{1,r_1}^2 \quad (18)$$

Then for the above oppositely charged surfactant mixed systems,  $A_{12}$  and  $A_{21}$  were iteratively evaluated with eqs 10, 11, 17, 18, and eqs 12a–12c (or eqs 13a–13c, or eqs 14a–14c) from the experimental data of  $C_1^m$ ,  $C_2^m$ , and  $C_{12}^m$  at equimolar composition with the calculated  $\beta^m$  as their initial values. Since the micellar composition  $x_1$  is nearly equimolar at  $CMC_1$  in wide range of overall surfactant compositions  $\alpha_1$  due to strong electrostatic attraction between the oppositely charged headgroups.<sup>48,72</sup> We suppose that  $x_1$  is equimolar when  $\alpha_1$  is equimolar. At other compositions, the values of  $r_1$ ,  $r_2$ ,  $x_1$ , and  $C_{12}^m$  were correlated using the above-mentioned equations. The values of  $x_{1,r_1}$  and  $x_{2,r_2}$  calculated by eqs 10 and 11 are their initial values, and then they are substituted into eqs 17 and 18 to calculate  $\gamma_{1,r_1}$  and  $\gamma_{2,r_2}$ , finally the values of  $x_{1,r_1}$  and  $x_{2,r_2}$  calculated by eqs 12a–12c (or eqs 13a–13c, or eqs 14a–14c) are their iterative values. The correlated values of  $r_1$ ,  $r_2$ ,  $x_1$ , and  $C_{12}^m$  satisfy the following conditions: there is the smallest error between the correlated value and experimental value of  $C_{12}^m$ , meanwhile the difference between the iterative value and the initial value of  $x_{i,r_i}$  is less than  $1 \times 10^{-5}$ .

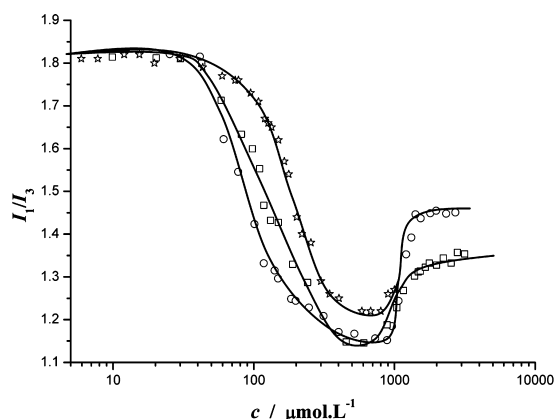
## 4. RESULTS AND DISCUSSION

**4.1.  $CMC_1$  and  $CMC_2$  of the Individual Ionic Surfactant Aqueous Systems.** For the surfactants  $C_{12}$ TAB,  $C_{14}$ TAB,  $C_{16}$ TAB,  $C_{18}$ TAB, 12–3–12, and AS, the variation of the electrical conductivity  $\kappa$  with concentration  $c$  was represented by Figure S1 (Supporting Information). The concentrations corresponding to the first break point and to the second break point are  $CMC_1$  and  $CMC_2$ , respectively. The  $CMC_1$  and  $CMC_2$  values were determined to within  $\pm 3\%$ . For  $C_{12}$ TAB,  $C_{14}$ TAB and 12–3–12, there is only one break point in the  $\kappa$  vs  $c$  plot, indicating that their micelles remain spherical even at fairly high concentration, in accordance with literature work.<sup>73,74</sup> For 12–3–12, at concentrations close to  $CMC_1$ , only spherical micelles form, even at  $100.0 \text{ mmol} \cdot \text{L}^{-1}$ , large amount of spheroidal micelles and small amount of rodlike micelles coexist (Figure S2, Supporting Information).

Steady-state fluorescence method was also used to determine  $CMC_1$ . Figure S3, Supporting Information, shows the pyrene polarity ratio  $I_1/I_3$  as a function of  $c$  at 318.15 K.  $CMC_1$  was taken as the intercept of the extrapolations of the rapidly varying part of the plot and of the nearly horizontal part of the plot at high concentration. The  $CMC_1$  values were determined to within  $\pm 5.5\%$ .

The  $CMC_1$  and  $CMC_2$  data at 318.15 K obtained from the above two methods are given by Table S1 (Supporting Information). Some literature data are also given. Our experimental results are well in accordance with the literature data.

**4.2.  $CMC_1$  of the Oppositely Charged Surfactants Aqueous Mixtures.** The  $CMC_1$  of  $C_n$ TAB/AS/H<sub>2</sub>O ( $n = 12, 16$  and  $18$ ) and 12–3–12/AS/H<sub>2</sub>O mixed systems at 318.15 K have been measured by steady-state fluorescence method. For most of the mixed systems with different compositions, the variation of  $I_1/I_3$  with  $c$  is similar to that in Figure S3, Supporting Information. However, for the  $C_{16}$ TAB/AS/H<sub>2</sub>O system and 12–3–12/AS/H<sub>2</sub>O system with  $\alpha_1 = 0.9$ , at low concentration, the variation of  $I_1/I_3$  with  $c$  is similar to that in Figure S3, Supporting Information; at  $c > CMC_1$ , two  $I_1/I_3$  plateaus were observed (Figure 1). For the  $C_{16}$ TAB/AS/H<sub>2</sub>O system with  $\alpha_1 = 0.95$ , the situation is similar to that for the two



□ and ☆:  $C_{16}$ TAB/AS/ $H_2O$  system with  $\alpha_1 = 0.90$  and  $0.95$ , respectively;  
○: 12-3-12/AS/ $H_2O$  system with  $\alpha_1 = 0.9$ ;

**Figure 1.** Variation of the pyrene intensity ratio  $I_1/I_3$  with the total surfactant concentration  $c$  for  $C_{16}$ TAB/AS/ $H_2O$  system and 12-3-12/AS/ $H_2O$  system at 318.15 K.

systems with  $\alpha_1 = 0.9$ , since  $c$  is not large enough, the second plateau is not formed.

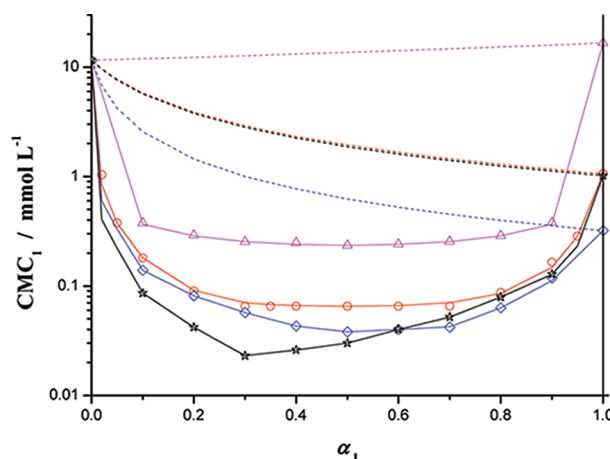
Figure 2 shows the  $CMC_1$  of the above four mixed systems at different compositions. The  $C_{14}$ TAB/AS/ $H_2O$  system has not been studied due to the formation of precipitate over wide composition range. The experimental values of the mixed  $CMC_1$  are much lower than those predicted from Clint model based on ideal mixing, indicating strong synergism. The mixed systems around equimolar ratio, i.e.,  $C_n$ TAB/AS/ $H_2O$  systems around  $\alpha_1 = 0.5$  and 12-3-12/AS/ $H_2O$  system around  $\alpha_1 = 1/3$ , give the lowest  $CMC_1$ .

For the  $C_n$ TAB/AS/ $H_2O$  systems with the same  $\alpha_1$ , the values of  $CMC_1$  decrease with the increase of  $n$ , indicating chain length effect. The increase of the hydrophobicity of the alkyl chain for the  $C_n$ TAB/AS/ $H_2O$  systems with the increase

of  $n$  is beneficial for the formation of micelles, thus results in the decrease of  $CMC_1$ .

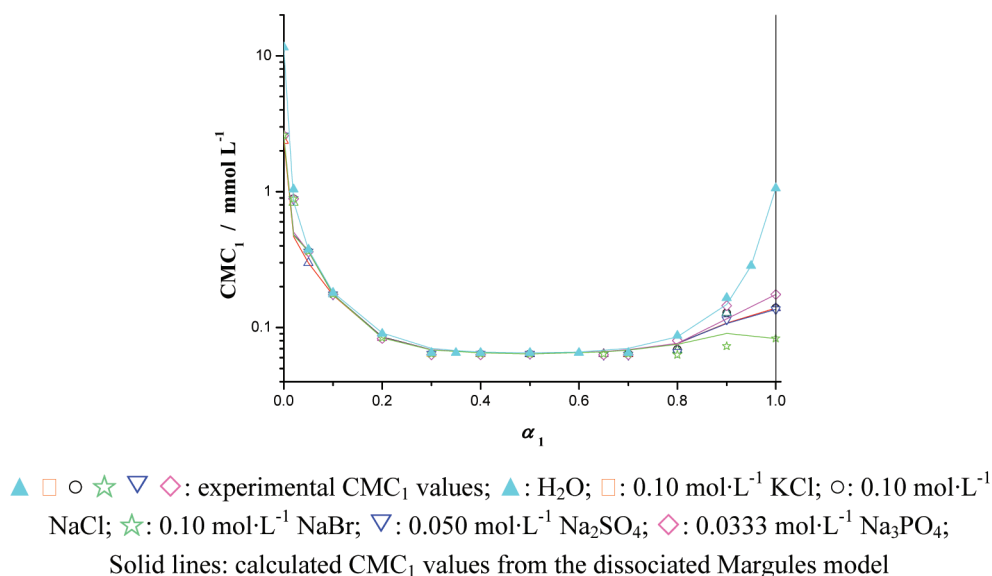
Although the  $CMC_1$  of 12-3-12 is close to that of  $C_{16}$ TAB, the  $CMC_1$  values of 12-3-12/AS/ $H_2O$  system are lower than those of  $C_{16}$ TAB/AS/ $H_2O$  system with the same  $\alpha_1$ . Higher alkyl chain density and higher charge density of its headgroups in 12-3-12 due to short spacer effect,<sup>14,16</sup> and chain length symmetry between 12-3-12 and AS, lead to stronger attraction between 12-3-12 and AS than that between  $C_{16}$ TAB and AS, and give rise to lower values of  $CMC_1$  for 12-3-12/AS/ $H_2O$  system. It is interesting to note that although the  $CMC_1$  of  $C_{18}$ TAB is smaller than that of 12-3-12, the  $CMC_1$  values of 12-3-12/AS/ $H_2O$  system are lower than those of  $C_{18}$ TAB/AS/ $H_2O$  system with the same  $\alpha_1$  when  $\alpha_1 \leq 0.5$ . Addition small amount of 12-3-12 into AS results in much larger decrease of  $CMC_1$  than that addition small amount AS into 12-3-12.

**4.3. Salt Effect on the  $CMC_1$  of  $C_{16}$ TAB/AS/ $H_2O$  System.** First, 0.10 mol·L<sup>-1</sup> KCl, NaCl, and NaBr aqueous solutions, 0.050 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> (i.e., 0.10 mol·L<sup>-1</sup>  $1/2$ Na<sub>2</sub>SO<sub>4</sub>), and 0.0333 mol·L<sup>-1</sup> Na<sub>3</sub>PO<sub>4</sub> (i.e., 0.10 mol·L<sup>-1</sup>  $1/3$ Na<sub>3</sub>PO<sub>4</sub>) aqueous solutions were used to investigate the salt effect and specific ion effect on  $CMC_1$  of  $C_{16}$ TAB/AS/ $H_2O$  system. The concentrations of Na<sup>+</sup> in these sodium salt solutions are equal to each other, which is convenient for us to compare the specific ion effect of Br<sup>-</sup>, Cl<sup>-</sup>,  $1/2$ SO<sub>4</sub><sup>2-</sup>, and  $1/3$ PO<sub>4</sub><sup>3-</sup> on mixed  $CMC_1$ ; the concentrations of Cl<sup>-</sup> in the two 0.10 mol·L<sup>-1</sup> chloride salt solutions are equal to each other, which is convenient for us to compare the specific ion effect of Na<sup>+</sup> and K<sup>+</sup> on mixed  $CMC_1$ . Figure 3 and Table S2 (Supporting Information) show the  $CMC_1$  values of  $C_{16}$ TAB/AS/salt aqueous mixed systems. For  $C_{16}$ TAB/AS/salt aqueous mixed systems with  $\alpha_1 = 0.3$  to  $0.7$ , the values of  $CMC_1$  are almost constant for the above different salts and almost equal to the values of  $CMC_1$  in the absence of salt. That means the addition of salt has almost no effect on the mixed  $CMC_1$ <sup>7</sup> when the salt concentration is not large.

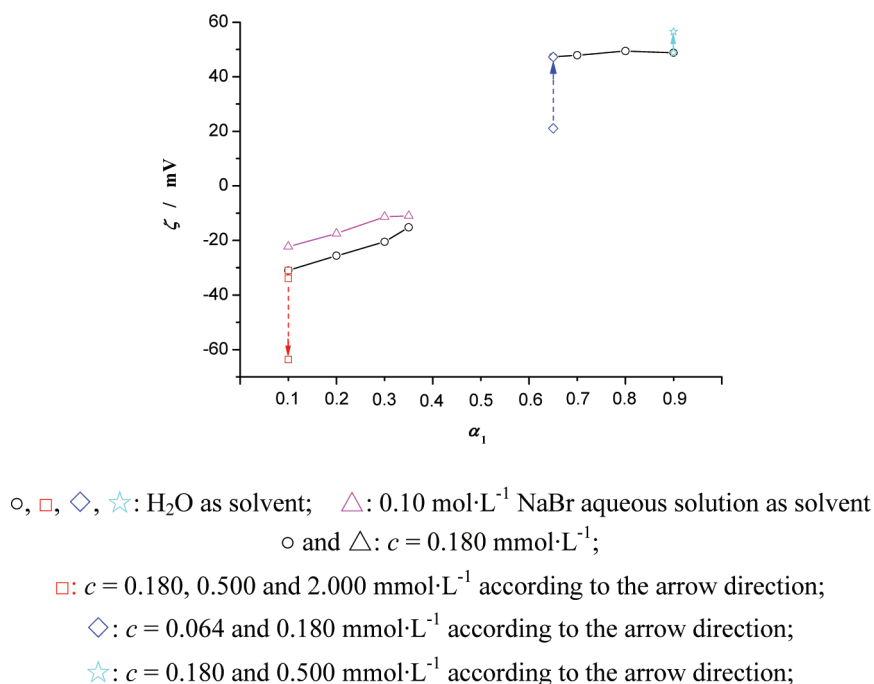


◇, ○, △, ☆: experimental  $CMC_1$  values; ◇:  $C_{18}$ TAB/AS/ $H_2O$  system;  
○:  $C_{16}$ TAB/AS/ $H_2O$  system; △:  $C_{12}$ TAB/AS/ $H_2O$  system; ☆: 12-3-12/AS/ $H_2O$  system  
Dashed lines: predicted  $CMC_1$  values from Clint model;  
Solid lines: calculated  $CMC_1$  values from the dissociated Margules model

**Figure 2.** Variation of  $CMC_1$  with the composition  $\alpha_1$  for the cationic/anionic surfactant mixed systems at 318.15 K.



**Figure 3.** Variation of CMC<sub>1</sub> with the composition  $\alpha_1$  for the C<sub>16</sub>TAB/AS/salt aqueous mixed systems at 318.15 K.



**Figure 4.**  $\zeta$  potential of C<sub>16</sub>TAB/AS mixed system with water or 0.10 mol·L<sup>-1</sup> NaBr aqueous solution as solvent at 318.15 K.

For C<sub>16</sub>TAB/AS mixed systems with AS in large excess, when  $\alpha_1$  is very small (such as  $\alpha_1 = 0.02$  and  $0.05$ ), the salt effect on the CMC<sub>1</sub> is similar to the case of AS, the CMC<sub>1</sub> values decrease in the following sequence:  $1/3 \text{ Na}_3\text{PO}_4 \approx 1/2 \text{ Na}_2\text{SO}_4 \approx \text{NaBr} \approx \text{NaCl} > \text{KCl}$ . However, when  $\alpha_1 = 0.1$  and  $0.2$ , the salt effect of the sodium salt and KCl on the CMC<sub>1</sub> of the mixed systems is equivalent, their CMC<sub>1</sub> values are equal to each other and slightly smaller than those of the mixed systems with pure water as solvent. For C<sub>16</sub>TAB/AS mixed systems with C<sub>16</sub>TAB in large excess (such as  $\alpha_1 = 0.8$  and  $0.9$ ), the salt effect on CMC<sub>1</sub> is similar to the case of C<sub>16</sub>TAB, the CMC<sub>1</sub> values decrease in the following sequence:  $1/3 \text{ Na}_3\text{PO}_4 > \text{NaCl} \approx \text{KCl} \geq 1/2 \text{ Na}_2\text{SO}_4 > \text{NaBr}$ . These results illustrate that specific counterion effect plays important role on CMC<sub>1</sub> of C<sub>16</sub>TAB/AS

mixed systems far from equimolar, specific co-ion effect was negligible.

According to Collins' concept of matching water affinities,<sup>37,75,76</sup> the tendency of oppositely charged small ions spontaneously associating as inner sphere ion pairs in aqueous solution is related to matching absolute free energies of ion hydration. This is supposed to be due to the fact that the strength of interaction between the ions and the water molecules is correlated to the strength with which the ion interacts with other ions. Kunz et al.<sup>37</sup> propose a way to classify headgroups in a Hofmeister-like series with the ordering from kosmotropic (structure making) to chaotropic (structure breaking): carboxylate, monovalent phosphate, sulfate and sulfonate in sequence; similarly, alkylammonium headgroup can be classified

as a chaotrope. As far as specific headgroups are involved in colloidal and biological systems, they all can be explained by combining the Hofmeister series for both ions and headgroups with the concept of matching water affinities. Following Collins' concept, chaotropes can form direct ion pairs with other chaotropes, much as kosmotropes with other kosmotropes, but chaotropes can not come into close contact with kosmotropes. Therefore, the counterion effect on  $\text{CMC}_1$  of ionic surfactants can differ much depending on the kosmotropic or chaotropic properties of the specific ions as well as surfactant headgroups. Both the headgroups of AS and  $\text{C}_{16}\text{TAB}$  are chaotropic, then they should come in close contact with chaotropic counterions like  $\text{K}^+$  and  $\text{Br}^-$ , respectively. Such ion pairs will be much less hydrated than separate ions and headgroups. This smaller hydration is reflected in smaller effective headgroup areas  $a$  corresponding to stronger aggregation ability and thus leading to lower  $\text{CMC}_1$ . Therefore, the affinity of anions toward cationic micelles strengthens according to the Hofmeister series:  $1/3\text{PO}_4^{3-} < \text{Cl}^- \leq 1/2\text{SO}_4^{2-} < \text{Br}^-$ ,<sup>77,78</sup> the counterion binding of cations to anionic micelles increases according to the Hofmeister series:  $\text{Na}^+ < \text{K}^+$ .<sup>79</sup> In comparison with cationic surfactants, the effect of the nature of the counterions in the case of anionic surfactants is much less dramatic.<sup>80</sup> That is why for the  $\text{C}_{16}\text{TAB}/\text{AS}$  mixed systems with AS in very large excess, the counterion effect on  $\text{CMC}_1$  increases according to the Hofmeister series:  $\text{Na}^+ < \text{K}^+$ , whereas for the mixed systems with  $\alpha_1 = 0.10$  and  $0.20$ , the counterion effect of  $\text{Na}^+$  or  $\text{K}^+$  on  $\text{CMC}_1$  is equivalent. For the mixed systems with  $\text{C}_{16}\text{TAB}$  in large excess, the counterion effect on  $\text{CMC}_1$  increases according to the Hofmeister series:  $1/3\text{PO}_4^{3-} < \text{Cl}^- < 1/2\text{SO}_4^{2-} < \text{Br}^-$ . Meanwhile, the stronger counterion effect of the inorganic anions on the mixed micelles than that of the inorganic cations leads to the increase of the asymmetry of the  $\text{CMC}_1$  vs  $\alpha_1$  curves with the addition of inorganic salt.

The experimental results in Table S2 (Supporting Information) indicate that the salt effect of NaBr on the  $\text{CMC}_1$  of  $\text{C}_{16}\text{TAB}/\text{AS}$  mixed systems increases with the increase of the salt concentration, as the concentration of NaBr increases to  $0.50 \text{ mol}\cdot\text{L}^{-1}$ , the  $\text{CMC}_1$  values of the mixed systems in the whole composition range decrease further.

In order to explain the influence of salt concentration on  $\text{CMC}_1$ ,  $\zeta$  potentials of  $\text{C}_{16}\text{TAB}/\text{AS}$  mixed systems have been measured, and the results were given by Figure 4. Eight samples with different  $\alpha_1$  were prepared by  $0.180 \text{ mmol}\cdot\text{L}^{-1}$   $\text{C}_{16}\text{TAB}/\text{AS}/\text{H}_2\text{O}$  mixed system,  $\text{CMC}_1 = 0.180 \text{ mmol}\cdot\text{L}^{-1}$  for the sample with  $\alpha_1 = 0.1$  and  $\text{CMC}_1 < 0.180 \text{ mmol}\cdot\text{L}^{-1}$  for the other samples. The mixed systems with  $\alpha_1$  close to  $0.5$  have not been considered due to the formation of flocs or precipitates. The  $\zeta$  potentials for the mixed systems with AS in excess are negative, illustrating that the formed spherical micelles are negatively charged and with AS in excess; and the  $\zeta$  potentials for the mixed systems with  $\text{C}_{16}\text{TAB}$  in excess are positive, illustrating that the formed spherical micelles are positively charged and with  $\text{C}_{16}\text{TAB}$  in excess.

The absolute values of  $\zeta$  for spherical micelles increase with the increase of  $c$ . For example, for the  $\text{C}_{16}\text{TAB}/\text{AS}/\text{H}_2\text{O}$  mixed system with  $\alpha_1 = 0.65$ ,  $\zeta = 21.1 \text{ mV}$  at  $c = \text{CMC}_1 = 0.064 \text{ mmol}\cdot\text{L}^{-1}$ , and  $\zeta = 47.3 \text{ mV}$  at  $c = 0.180 \text{ mmol}\cdot\text{L}^{-1}$ , respectively. These results suggest that at low concentrations near  $\text{CMC}_1$ , the micellar composition approaches equimolar, the surface charge density of micelles is low; as  $c$  increases, the micellar composition changes from nearly equimolar to the bulk solution mixing ratio at high concentrations,<sup>46,81</sup> the

surface charge density for spherical micelles increases with the increase of  $c$ . Therefore, we can deduce that the absolute values of  $\zeta$  for the  $\text{C}_{16}\text{TAB}/\text{AS}/\text{H}_2\text{O}$  mixed systems with  $\alpha_1 = 0.2$  to  $0.9$  at  $\text{CMC}_1$  are smaller than those at  $0.180 \text{ mmol}\cdot\text{L}^{-1}$ , especially for those mixed systems with  $\alpha_1 = 0.3$  to  $0.7$  at  $\text{CMC}_1$ , the absolute values of  $\zeta$  are low. It means that the micellar compositions for these mixed systems are close to equimolar, meanwhile,  $\alpha_1$  is less than  $0.5$  when  $\alpha_1$  is less than  $0.5$ , and vice versa.

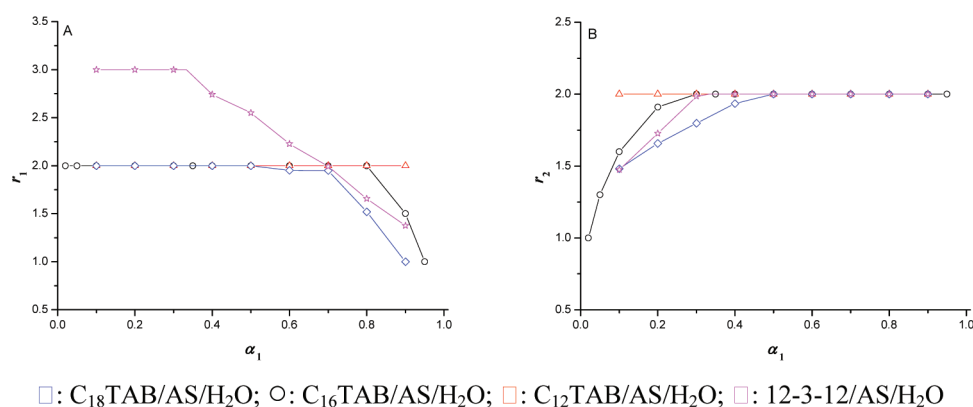
The addition of NaBr into the  $\text{C}_{16}\text{TAB}/\text{AS}$  mixed systems results in higher counterion binding with the micelles and decreases the charge density of the micelles, thus reduces their  $\zeta$  potentials. The micellar composition approaches equimolar as  $\alpha_1$  approaching  $0.5$ , the salt effect is weak, thus the decrease extent of  $\zeta$  becomes smaller. That is why  $\text{CMC}_1$  of the  $\text{C}_{16}\text{TAB}/\text{AS}$  mixed systems with  $\alpha_1 = 0.3$  to  $0.7$  keeps as constant when the concentration of NaBr is  $0.10 \text{ mol}\cdot\text{L}^{-1}$ . Whereas the salt effect of  $0.50 \text{ mol}\cdot\text{L}^{-1}$  NaBr becomes stronger and leads to the decrease of  $\text{CMC}_1$  further.

**4.4. The Synergism and Nonideality of Mixed Micelles.** Regular solution approximation of Rubingh<sup>51</sup> for nonideal mixed systems was used to determine the micellar interaction parameter  $\beta^m$ . The calculated  $\beta^m$  for the  $\text{C}_n\text{TAB}/\text{AS}/\text{H}_2\text{O}$  systems and  $12-3-12/\text{AS}/\text{H}_2\text{O}$  system are shown in Table S3 (Supporting Information). Large negative values of  $\beta^m$  have been obtained, meanwhile  $|\beta^m| > |\ln(C_1^m/C_2^m)|$ , which mean strong attraction and strong synergism between the oppositely charged surfactants, suggest that there is synergism in the surface tension reduction efficiency. For the  $\text{C}_n\text{TAB}/\text{AS}/\text{H}_2\text{O}$  systems, symmetry of the hydrocarbon chains between the oppositely charged surfactants means stronger hydrophobic interactions, thus larger negative value of  $\beta^m$  (average value about  $-16.2$ ) is obtained for  $\text{C}_{12}\text{TAB}/\text{AS}/\text{H}_2\text{O}$  system. In comparison with  $\text{C}_{12}\text{TAB}/\text{AS}/\text{H}_2\text{O}$  system, larger negative value of  $\beta^m$  (average value about  $-22.4$ ) is obtained for  $12-3-12/\text{AS}/\text{H}_2\text{O}$  system. The result suggests that stronger synergism and stronger attraction exist between  $12-3-12$  and AS, which is consistent with the consequences of literature work.<sup>14,16</sup>

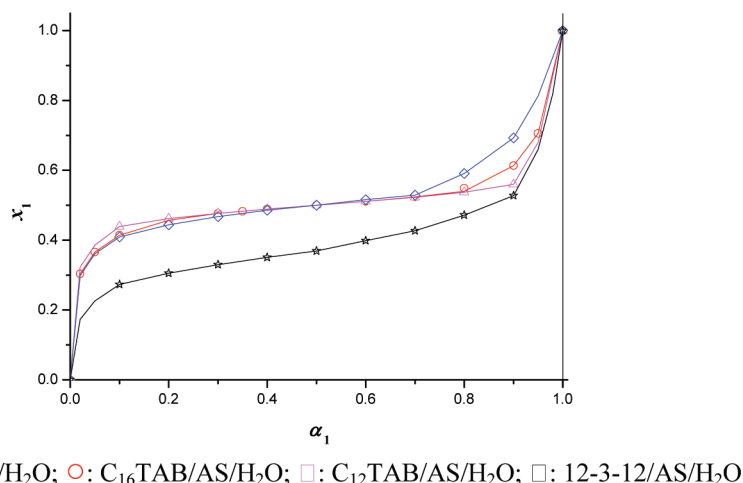
In comparison with the results in Table S3, Supporting Information, the calculated  $\beta^m$  values for  $\text{C}_{16}\text{TAB}/\text{AS}/\text{salt}$  aqueous mixed systems shown in Table S4 (Supporting Information), illustrate that the addition of salt reduces the negative values of  $\beta^m$ , it is related to the fact that the increase of the counterion amount leads to more efficient screening of the electrostatic attraction between the oppositely charged headgroups. The decrease of the absolute values of  $\zeta$  with the addition of NaBr in Figure 4 verified that the increase of the counterion binding degree of the mixed micelles in the process. The increase of salt concentration reduces the absolute values of  $\beta^m$  further as predicted.

The calculated  $\beta^m$  values are reasonable and can be used to interpret the interaction strength between  $\text{C}_n\text{TAB}$  and AS and that between  $12-3-12$  and AS, and the salt effect on interaction between  $\text{C}_{16}\text{TAB}$  and AS. However,  $\beta^m$  are not constant with respect to composition. Meanwhile, the calculated micellar compositions may be unreasonable. For example, for  $\text{C}_{16}\text{TAB}/\text{AS}/\text{H}_2\text{O}$  mixed system with  $\alpha_1 = 0.1$ , at  $\text{CMC}_1 = 0.180 \text{ mmol}\cdot\text{L}^{-1}$ , the calculated micellar composition  $x_1 = 0.507$ , however,  $\zeta = -31.0 \text{ mV}$  indicating  $x_1 < 0.5$ . It means that regular solution approximation of Rubingh has





**Figure 5.** Variation of  $r_1$  and  $r_2$  with the composition  $\alpha_1$  for the aqueous oppositely charged surfactant mixed systems.



**Figure 6.** Micellar compositions  $x_1$  for the oppositely charged surfactant mixtures.

**Table 1. Parameters  $A_{12}$  and  $A_{21}$  of the Dissociated Margules Model for the Aqueous Mixed Oppositely Charged Surfactant Systems**

systems	$A_{12}$	$A_{21}$
C <sub>18</sub> TAB/AS/H <sub>2</sub> O	−22.861	−8.523
C <sub>16</sub> TAB/AS/H <sub>2</sub> O	−20.713	−11.167
C <sub>12</sub> TAB/AS/H <sub>2</sub> O	−15.573	−17.030
12–3–12/AS/H <sub>2</sub> O	−30.293	−9.553

limitation in modeling the mixed micellization of cationic/anionic surfactants.

**4.5. The Application of the Dissociated Margules Model.** The pseudophase separation model coupled with the dissociated two-parameter Margules model (abbreviated as the dissociated Margules model) was used to calculate the nonideal mixed CMC<sub>1</sub> of the binary oppositely charged surfactant mixtures. The solid lines in Figure 2 are the correlation results with the dissociated Margules model for C<sub>n</sub>TAB/AS/H<sub>2</sub>O and 12–3–12/AS/H<sub>2</sub>O mixed systems and give satisfactory description of the mixed CMC<sub>1</sub>. The model parameters  $A_{12}$  and  $A_{21}$  are shown in Table 1, the variation of  $r_1$  and  $r_2$  with composition  $\alpha_1$  is given by Figure 5. The calculated micellar compositions  $x_1$  in the whole composition range are represented by Figure 6.

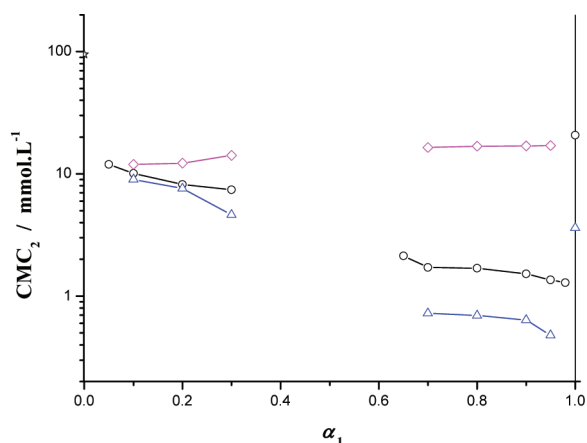
Table 1 indicates that for these mixed systems, both the model parameters  $A_{12}$  and  $A_{21}$  are negative, similar to  $\beta^m$ .

Margules model we used can be taken as a special case of Wohl's three-suffix equation when  $q_1 = q_2$ .<sup>82,83</sup> Parameters  $q_1$  and  $q_2$  are effective molar volumes of component 1 and 2.  $A_{12}$  and  $A_{21}$  are related to interaction parameters  $a_{12}$ ,  $a_{122}$  and  $a_{112}$  ( $a_{ii} = 0$ ,  $a_{iii} = 0$ ,  $i = 1$  or  $2$ ) as follows:

$$A_{12} = q_1(2a_{12} + 3a_{122}), \quad A_{21} = q_2(2a_{12} + 3a_{112}) \quad (19)$$

Parameter  $a_{12}$  is a constant characteristic of the interaction between molecule 1 and molecule 2; parameter  $a_{112}$  is a constant characteristic of the interaction between three molecules, two of component 1 and one of component 2, and so on. The two-suffix Margules model is obtained by neglecting three-body interactions  $a_{122}$  and  $a_{112}$ , and it is equivalent to Rubingh's regular solution theory, i.e.,  $A_{12} = A_{21} = \beta^m$ . Although the assumption  $q_1 = q_2$  suggests that Margules model should be used only for mixtures whose components have similar molar volumes; it is nevertheless used frequently for all sorts of liquid mixtures, regardless of the relative sizes of the different molecules. Considering the fact that different components usually have different molar volumes in cationic/anionic surfactant mixtures, meanwhile the three-body interaction parameter  $a_{122}$  is different from  $a_{112}$ , that is why  $A_{12}$  and  $A_{21}$  are different from each other, and they are different from  $\beta^m$  (Table S3 in Supporting Information), too. Equation 19 tells us that larger effective molar volume or stronger two-body or three-body attractive interaction causes more negative Margules model





◇: C<sub>12</sub>TAB/AS/H<sub>2</sub>O system; ○: C<sub>16</sub>TAB/AS/H<sub>2</sub>O system; △: C<sub>18</sub>TAB/AS/H<sub>2</sub>O system

**Figure 7.** Variation of CMC<sub>2</sub> with  $\alpha_1$  for the C<sub>*n*</sub>TAB/AS/H<sub>2</sub>O systems at 318.15 K.

parameter. For C<sub>*n*</sub>TAB/AS/H<sub>2</sub>O mixed systems, more negative  $A_{12}$  with the increase of *n* is mainly dependent on the increase of effective molar volume of C<sub>*n*</sub>TAB; less negative  $A_{21}$  with the increase of *n* arises from the weakening of the two-body and three-body attractive interactions due to chain length asymmetry. In comparison with its monomer C<sub>12</sub>TAB, when dimeric surfactant 12–3–12 mixed with AS,  $A_{12}$  is almost two times larger, the main reason is that the effective molar volume of the dimer is almost two times larger than that of its monomer; however,  $A_{21}$  is less negative, the main reason is that the three-body attractive interaction  $a_{112}$  is much weaker in 12–3–12/AS/H<sub>2</sub>O mixed system due to the large excess of positive charge. At equimolar composition, the value of  $(r_1A_{12} + r_2A_{21})/(r_1 + r_2)$  is equivalent with the value of  $\beta^m$ , illustrating that this value can be used as a measure of the excess interaction between the two different surfactants in mixed micelles.

For the near symmetric C<sub>12</sub>TAB/AS/H<sub>2</sub>O mixed system, the two surfactants C<sub>12</sub>TAB and AS have the same alkyl chain and similar surface activities, their interaction is beneficial for the totally dissociation of surfactants, both  $r_1$  and  $r_2$  are chosen as 2 in the composition range of  $0.1 \leq \alpha_1 \leq 0.9$ . For the three asymmetric oppositely charged surfactant systems, the surfactant with low content or near equimolar composition dissociated totally, whereas the surfactant in excess dissociated only partly, the more excess the surfactant *i*, the lower  $r_i$ . These results are in well accordance with the investigation of Zana et al.<sup>84</sup>

The results shown in Figure 6 suggest that  $x_1$  increases rapidly with the increase of  $\alpha_1$  when composition is far from equimolar, and it increase slowly in the range of  $0.1 < \alpha_1 < 0.9$ . For the C<sub>*n*</sub>TAB/AS/H<sub>2</sub>O mixed systems, the micellar composition  $x_1$  is less than 0.5 when  $\alpha_1$  is less than 0.5, and vice versa. The increase of chain length asymmetry results in slight increase of the difference between the calculated  $x_1$  values and equimolar composition. For the symmetric C<sub>12</sub>TAB/AS/H<sub>2</sub>O mixed system, the calculated  $x_1$  values are very close to equimolar in the range of  $0.1 \leq \alpha_1 \leq 0.9$ . For the C<sub>16</sub>TAB/AS/H<sub>2</sub>O mixed systems, the calculated  $x_1$  values are in well agreement with composition information from the experimental results of  $\zeta$  potentials. For 12–3–12/AS/H<sub>2</sub>O mixed system, the equimolar composition is  $\alpha_1 = 1/3$ , the calculated  $x_1$  values are close to  $1/3$  in the range of  $0.1 \leq \alpha_1 \leq 0.7$ .

The dissociated Margules model was also used to calculate the CMC<sub>1</sub> of C<sub>16</sub>TAB/AS/salt aqueous mixed system in the

whole range of composition. The solid lines in Figure 3 are the correlated CMC<sub>1</sub> values for C<sub>16</sub>TAB/AS mixed systems with inorganic sodium or potassium salt aqueous solution as solvents and are in quite good agreement with the experimental results.

The model parameters  $A_{12}$  and  $A_{21}$  for these systems are shown in Table S5 (Supporting Information). In comparison with the results in Table 1, the addition of salt reduces the negative values of  $A_{12}$  and  $A_{21}$  obviously, corresponding to the weakening of the electrostatic attraction between the oppositely charged headgroups due to the strengthening of counterion binding. For the C<sub>16</sub>TAB/AS/0.10 mol·L<sup>−1</sup> NaBr aqueous mixed system, the sign of parameter  $A_{21}$  even changes from negative to positive, it illustrates that the asymmetry of the mixed CMC<sub>1</sub> vs  $\alpha_1$  increases, the corresponding calculated error increases slightly either.

Figure S4 (Supporting Information) shows the variation of  $r_1$  and  $r_2$  with the composition  $\alpha_1$  of C<sub>16</sub>TAB/AS aqueous mixed systems in the absence of or in the presence of inorganic salt. The results indicate that for the mixed systems with surfactant *i* in large excess, the addition of salt leads to the decrease of  $r_i$ , indicating that addition of salt is unbeneficial for the dissociation of surfactant *i* due to higher counterion binding degrees with the mixed micelles.

Figure S5 (Supporting Information) shows the variation of  $x_1$  with the composition  $\alpha_1$  for the C<sub>*n*</sub>TAB/AS/salt aqueous mixed systems. The results illustrate that the addition of inorganic salt leads to larger deviation of  $x_1$  with 0.5 for those mixed systems with nonequimolar compositions. Higher counterion binding degree weakens the electrostatic attraction between the oppositely charged headgroups in the mixed micelles due to electrostatic screening and results in the larger deviation of  $x_1$  with 0.5. The counterion effect on  $x_1$  is similar to that on the mixed CMC<sub>1</sub>. For those mixed systems in the composition range  $0.3 \leq \alpha_1 \leq 0.7$ , the deviation of  $x_1$  with 0.5 is very small due to the strong electrostatic attraction between the oppositely charged headgroups. For the C<sub>16</sub>TAB/AS mixed systems far from equimolar composition, counterion effect of Na<sup>+</sup> or K<sup>+</sup> on  $x_1$  are almost equal to each other, counterion effect of the anions on  $x_1$  follows the Hofmeister series:  $1/3\text{PO}_4^{3-} < 1/2\text{SO}_4^{2-} \approx \text{Cl}^- < \text{Br}^-$ .

**4.6. CMC<sub>2</sub> of the Oppositely Charged Surfactants Aqueous Mixtures.** Figure S6 (Supporting Information) shows the variation of electrical conductivity  $\kappa$  with *c* for the C<sub>16</sub>TAB/AS/H<sub>2</sub>O system. Different from the case for the

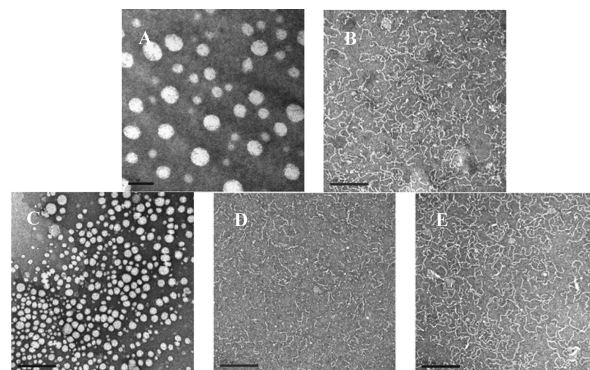
individual surfactant aqueous systems, the concentrations corresponding to the breaks refer to as  $CMC_2$  other than  $CMC_1$  similar to the investigation of Zana et al.<sup>19</sup>

Figure 7 shows the  $CMC_2$  of the three  $C_n$ TAB/AS/ $H_2O$  systems at different  $\alpha_1$ . For systems with  $\alpha_1$  close to 0.5,  $CMC_2$  has not been measured due to the formation of flocs or precipitations. Experimental results indicate that the addition of small amount of ionic surfactant into oppositely charged surfactant systems leads to an obvious decrease of the value of  $CMC_2$  showing strong synergism. For the  $C_n$ TAB/AS/ $H_2O$  mixed systems, there is obvious chain length effect on  $CMC_2$  either.

The results in Figure 7 indicate that  $CMC_2$  decreases with the increase of the composition of surfactant with higher surface activity in the mixed systems, and for the studied  $C_n$ TAB/AS/ $H_2O$  mixed systems with AS or  $C_n$ TAB in excess, the variation of  $CMC_2$  with  $\alpha_1$  is small. This case is quite different from that of  $CMC_1$  with  $\alpha_1$ . The results in Figure 2 illustrate that the curves of  $CMC_1$  vs  $\alpha_1$  are near symmetric around equimolar composition in the composition range  $0.1 \leq \alpha_1 \leq 0.9$ ,  $CMC_1$  decreases remarkably as  $\alpha_1$  approaches 0.5 in the far from equimolar composition range, and the variation of  $CMC_1$  with  $\alpha_1$  is very small in composition range  $0.3 \leq \alpha_1 \leq 0.7$ . The above phenomena are associated with the micellar composition. The micellar compositions at  $CMC_1$  change remarkably in the far from equimolar composition range and are close to equimolar in composition range  $0.3 \leq \alpha_1 \leq 0.7$ , near equimolar micellar composition means strong electrostatic attraction between oppositely charged headgroups, thus corresponds to smaller  $CMC_1$ ; far from equimolar micellar composition means partial charge neutralization of oppositely charged headgroups and the existence of electrostatic repulsion between the excess same charged headgroups, thus corresponds to larger  $CMC_1$ , remarkable micellar composition change imply remarkable  $CMC_1$  change. The micellar compositions  $x_1$  at  $CMC_2$  are more close to the bulk compositions  $\alpha_1$ , therefore, the variation of  $x_1$  with  $\alpha_1$  is relatively uniform. In comparison with spherical micelles, the counterion binding degree of rodlike micelles is larger. The larger difference between  $x_1$  and 0.5 leads to higher counterion binding, thus is beneficial for the formation of micelles due to electrostatic screening. In addition, for  $C_{16}$ TAB/AS/ $H_2O$  and  $C_{18}$ TAB/AS/ $H_2O$  mixed systems, larger  $\alpha_1$  means the increase of the composition of surfactant with longer tail chain in the rodlike micelles, thus corresponds to stronger hydrophobic interactions, which is also a beneficial factor for the formation of rodlike micelles. For  $C_{16}$ TAB/AS/ $H_2O$  and  $C_{18}$ TAB/AS/ $H_2O$  mixed systems with AS in excess, the increase of  $\alpha_1$  means stronger electrostatic attraction between oppositely charged headgroups, stronger hydrophobic interactions and lower counterion binding, the former two factors are favorable and the latter one factor is unfavorable for the formation of rodlike micelles, the overall results is that  $CMC_2$  decreases with the increase of  $\alpha_1$ . For  $C_{16}$ TAB/AS/ $H_2O$  and  $C_{18}$ TAB/AS/ $H_2O$  mixed systems with  $C_n$ TAB in excess, the increase of  $\alpha_1$  means weaker electrostatic attraction between oppositely charged headgroups, stronger hydrophobic interactions and higher counterion binding, the former one factor is unfavorable and the latter two factors are favorable for the formation of rodlike micelles, the overall results is that  $CMC_2$  decreases slightly with the increase of  $\alpha_1$ . Stronger hydrophobic interactions of the tail chains is the reason that  $CMC_2$  of  $C_{16}$ TAB/AS/ $H_2O$  and  $C_{18}$ TAB/AS/ $H_2O$  mixed systems with  $\alpha_1 > 0.5$  is obviously smaller than that with  $\alpha_1 <$

0.5. For  $C_{12}$ TAB/AS/ $H_2O$  mixed system, hydrophobic interactions of the tail chains is irrespective with composition, the  $CMC_2$  values in the whole studied composition range are more close to each other.

The experimental results of  $CMC_1$  and  $CMC_2$  for the  $C_{16}$ TAB/AS/ $H_2O$  system were verified by Negative-stained TEM micrographs (Figure 8). Spherical micelles or rodlike



A and B:  $\alpha_1 = 0.7$ , A:  $c = 0.150 \text{ mmol} \cdot \text{L}^{-1}$  (bar: 50 nm); B:  $c = 1.800 \text{ mmol} \cdot \text{L}^{-1}$  (bar: 200 nm); C, D and E:  $\alpha_1 = 0.8$ ,  $c = 0.150, 1.500, 2.100 \text{ mmol} \cdot \text{L}^{-1}$ , respectively, (bar: 200 nm)

Figure 8. TEM micrographs of some  $C_{16}$ TAB/AS/ $H_2O$  systems.

micelles form when  $c$  is slightly larger than  $CMC_1$  or  $CMC_2$ , respectively. Spherical micelles coexist with rodlike micelles (Figure 8D) when  $c$  is slightly smaller than  $CMC_2$ .

For the  $C_{16}$ TAB/AS/ $H_2O$  mixed system, the experimental results of  $CMC_1$  and  $CMC_2$  in Figures 2 and 7 indicate that the difference between  $CMC_2$  and  $CMC_1$  decreases with the increase of  $\alpha_1$ . When  $\alpha_1 = 0.9$  and  $0.95$ , the difference between  $CMC_2$  and  $CMC_1$  is quite small. The two plateaus of  $I_1/I_3$  after micelle formation in Figure 1 correspond to spherical micelle formation and rodlike micelle formation, respectively. When pyrene is incorporated into a micelle, its solubilization site is in the palisade layer<sup>85,86</sup> which is essentially made up of ionic headgroups, counterions, water molecules, and  $\alpha$ - and  $\beta$ -methylene groups of surfactant alkyl chain.<sup>87</sup> For mixed micelles, the micellar composition and degree of counterion binding depend on the total surfactant concentration. When  $\alpha_1 = 0.9$  and  $0.95$ , for spherical micelles, the charge neutralization of the oppositely charged headgroups arising from micellar compositions more close to equimolar other than the bulk compositions, leads to lower micropolarity of the palisade layer; whereas for the rodlike micelles, large excess of trimethylammonium ions (although the counterion binding will partially neutralize the trimethylammonium ions) arising from micellar compositions more close to the bulk compositions, leads to higher micropolarity of the palisade layer. That is why the second plateau corresponding to the formation of rodlike micelles is higher than the first plateau corresponding to the formation of spherical micelles.

**4.7. Salt Effect on the  $CMC_2$  of  $C_{16}$ TAB/AS/ $H_2O$  System.** Table 2 gives the values of  $CMC_2$  for  $C_{16}$ TAB/AS/salt aqueous mixed systems. The mixed systems with  $0.2 < \alpha_1 < 0.7$  have not been investigated due to flocs and precipitations formed easily. The addition of salt into  $C_{16}$ TAB/AS/ $H_2O$  mixed systems, leads to significant decrease of  $CMC_2$ . This is mainly due to a decrease in the value of area per hydrated headgroup  $a$  with the addition of salt, which does not significantly influence  $\nu$  and  $l_{\text{max}}$ , thus leads to an increase of the

Table 2. CMC<sub>2</sub> (Unit: mmol L<sup>-1</sup>) of C<sub>16</sub>TAB/AS/Salt Aqueous Mixed System at 318.15 K

$\alpha_1$	0.010 mol·L <sup>-1</sup> NaBr	0.050 mol·L <sup>-1</sup> NaBr	0.10 mol·L <sup>-1</sup> NaBr	0.10 mol·L <sup>-1</sup> NaCl	0.10 mol·L <sup>-1</sup> KCl	0.050 mol·L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub>	0.0333 mol·L <sup>-1</sup> Na <sub>3</sub> PO <sub>4</sub>
0			8.64	8.84	6.02	8.50	8.15
0.05	6.75	3.70	2.44	2.86	2.57	2.40	2.29
0.1	6.53	3.66	2.40	2.65	1.88	2.30	2.25
0.2	6.26	3.28	2.31	2.60	1.33	1.79	1.10
0.7	1.05	1.08	1.05	1.17	0.77	1.03	1.12
0.8	0.98	1.00	0.84	1.09	0.78	0.82	1.05
0.9	0.94	0.98	0.82	0.88	0.75	0.89	1.08
0.95	1.05	0.90	0.81	0.86	0.73	0.73	0.89
1			0.79	0.83	0.85	0.64	0.99

critical packing parameter  $p$  and is beneficial for the formation of rodlike micelles. Rodlike micelles form easily in the mixed systems with  $\alpha_1 \geq 0.7$ , all the CMC<sub>2</sub> values are about 1 mmol·L<sup>-1</sup>. The values of CMC<sub>2</sub> for C<sub>16</sub>TAB/AS mixed systems with  $\alpha_1 \leq 0.2$  are larger than those with  $\alpha_1 \geq 0.7$ , and decrease with the increase of  $\alpha_1$ .

The salt effect on CMC<sub>2</sub> for the mixed systems with  $\alpha_1 \leq 0.2$  strengthens according to the following order: NaCl < KCl. Rodlike micelles formed in the mixed systems with AS in excess are negatively charged, in comparison with Na<sup>+</sup>, K<sup>+</sup> counterions are more chaotropic and stronger counterion binding with the rodlike micelles, that is why the salt effect of KCl on CMC<sub>2</sub> for the mixed systems with  $\alpha_1 \leq 0.2$  is stronger than that of NaCl. Analogous to the case of salt concentration effect on CMC<sub>1</sub>, the values of CMC<sub>2</sub> for the mixed systems with  $\alpha_1 \leq 0.2$  decrease with the increase of the concentration of NaBr aqueous solution.

In addition to Na<sup>+</sup> and K<sup>+</sup> counterions, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, Br<sup>-</sup>, and Cl<sup>-</sup> co-ions also play a role on the CMC<sub>2</sub> of C<sub>16</sub>TAB/AS mixed systems with  $\alpha_1 \leq 0.2$ . The sodium salt effect strengthens according to the following sequence: NaCl < NaBr <  $\frac{1}{2}$ Na<sub>2</sub>SO<sub>4</sub> <  $\frac{1}{3}$ Na<sub>3</sub>PO<sub>4</sub>. Studying the sphere-to-rod transition of TTAB micelles, Imae and Ikeda<sup>88</sup> suggested that in comparison with KBr, NaBr screens the headgroup repulsion more efficiently and may be attributed to specific co-ion effects.

According to Collins,<sup>75,76</sup> the Jones–Dole viscosity  $B$  coefficients for the Na<sup>+</sup> (0.086), PO<sub>4</sub><sup>3-</sup> (0.590), SO<sub>4</sub><sup>2-</sup> (0.208), Cl<sup>-</sup> (−0.007), and Br<sup>-</sup> (−0.032) are measures of the water affinity of these ions. The difference in Jones–Dole viscosity  $B$  coefficients of two ions is a measure of their mismatch in water affinity. Those oppositely charged ions with matching water affinity will most readily form inner sphere ion pairs. Therefore, Cl<sup>-</sup> has the greatest tendency to bind to Na<sup>+</sup>, followed by Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup> in sequence. For the sodium salts aqueous solutions with the concentration of Na<sup>+</sup> = 0.10 mol·L<sup>-1</sup>, the binding of Na<sup>+</sup> with the inorganic anions will weaken its counterion binding with the rodlike micelles and thus is unbeneficial for the formation of rodlike micelles; therefore, the values of CMC<sub>2</sub> decrease according to the following co-ion series: Cl<sup>-</sup> > Br<sup>-</sup> >  $\frac{1}{2}$ SO<sub>4</sub><sup>2-</sup> >  $\frac{1}{3}$ PO<sub>4</sub><sup>3-</sup>.

## 5. CONCLUSIONS

The mix of cationic and anionic surfactants leads to an obvious decrease in both CMC<sub>1</sub> and CMC<sub>2</sub> indicating strong synergism, and strong spherical and rodlike micelle self-assembly ability. There are several points related to the applications of cationic/anionic surfactants which need to pay attention:

- (1) The relationship between CMC<sub>1</sub> and  $\alpha_1$  is significantly different from that between CMC<sub>2</sub> and  $\alpha_1$ , which means that for a broad range of surfactant-based applications,

composition of mixed cationic/anionic surfactants is a key factor should be taken into consideration according to application purpose. If the applications are related to surface activity, the relationship between CMC<sub>1</sub> and  $\alpha_1$  should be taken into account. If the applications are related to viscoelastic fluids, the relationship between CMC<sub>2</sub> and  $\alpha_1$  should be taken into account.

- (2) Addition of a small amount of ionic surfactant with higher surface activity to an oppositely charged surfactant with lower surface activity results in much larger decrease of CMC<sub>1</sub> than the reversed addition process. In comparison with its monomeric analogues C<sub>*n*</sub>TAB ( $n = 12, 16, 18$ ), the dimeric surfactant 12–3–12 is more effective in reducing CMC<sub>1</sub> when it is added into the oppositely charged surfactant AS. The information is important for the effective use of ionic surfactants, especially the dimeric ionic surfactants.
- (3) For the mixed cationic/anionic surfactants, the partially or totally charge neutralization of oppositely charged headgroups is an unfavorable factor for salt effect. However, it is worthwhile to point out that for mixed cationic/anionic surfactants with compositions far from equimolar, or with compositions not too far from equimolar but with higher total surfactant concentrations, the salt effect and the specific ion effect should be taken into consideration. The above investigation results suggest that for mixed cationic/anionic surfactants especially at high total surfactant concentration, inorganic salt is an important factor influencing the formation of micelles or aggregates; thus, aqueous mixed cationic/anionic surfactant systems in the presence of inorganic salt have wide application prospects.

The proposed dissociated Margules model in which the dissociation of ionic surfactants has been taken into consideration, gives satisfactory description of the mixed CMC<sub>1</sub> and micellar compositions of oppositely charged surfactant systems. The model provides  $(r_1A_{12} + r_2A_{21})/(r_1 + r_2)$  instead of  $\beta^m$  as a measure of the interaction and synergism between the oppositely charged surfactants in the mixed micelles. The dissociated Margules model provides a practical approach to model mixed micellization of cationic/anionic surfactant systems and of other binary surfactant systems containing ionic surfactant, and it is helpful to improve the understanding of the mixed micellization.

## ■ ASSOCIATED CONTENT

### Supporting Information

Figures about variation of electrical conductivity  $\kappa$  with concentration  $c$ , variation of  $I_1/I_3$  with  $c$ , variation of  $r_1$  and  $r_2$  or  $x_1$  with composition  $\alpha_1$  for single surfactants or some



cationic/anionic surfactant systems, and electrical micrographs of 12–3–12 aqueous solutions, tables about CMC<sub>1</sub> and CMC<sub>2</sub>,  $\beta^m$ , and parameters  $A_{12}$  and  $A_{21}$  of the Margules model for single surfactants or some cationic/anionic surfactant systems, and the equation derivation of the dissociated Margules model. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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