

# Interaction between cetyltrimethylammonium bromide and $\beta$ -cyclodextrin: surface tension and interfacial dilational viscoelasticity studies

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**Abstract** The interaction between cetyltrimethylammonium bromide (CTAB) and  $\beta$ -cyclodextrin ( $\beta$ -CD) was studied via surface tension and dilational viscoelasticity methods. The effect of sodium bromide and sodium chloride on the interaction between CTAB and  $\beta$ -CD were studied as well. The surface tension isotherms provided a series of parameters, including apparent critical micelle concentration ( $\text{cmc}^*$ ), surface tension at the  $\text{cmc}^*$  ( $\gamma_{\text{cmc}}$ ), stoichiometry of the complex ( $R$ ), and the efficiency of adsorption ( $pC_{20}$ ). The addition of NaBr and NaCl decreases the  $\text{cmc}^*$  of CTAB/ $\beta$ -CD solution. CTAB molecules enter the cavities of  $\beta$ -CD molecules thus formed both 1:1 and 1:2 inclusion complexes. From the change of  $\gamma_{\text{cmc}}$ , it can be seen that the CTAB/ $\beta$ -CD complexes (1:1) act as short-chain alcohol, which decrease  $\gamma_{\text{cmc}}$ , but the depression of  $\text{cmc}^*$  is too small to be detected.  $R$  first decreases then increases as a function of NaBr and NaCl. Compared to NaCl, NaBr increases  $R$  more efficiently. The presence of NaBr and NaCl increases  $pC_{20}$  of CTAB/ $\beta$ -CD solution. The results obtained from the dila-

tional viscoelasticity measurements at low dilational frequencies (0.005–0.1 Hz) reveal that the dilational modulus passes through a maximum value with increasing concentration of  $\beta$ -CD at a given concentration of CTAB. The addition of both NaBr and NaCl decreases the dilational modulus of a given concentration CTAB/ $\beta$ -CD solution.

**Keywords** Cetyltrimethylammonium bromide ·  $\beta$ -Cyclodextrin · Dilational viscoelasticity · Surface tension

## Introduction

Cyclodextrins are macrocyclic oligosugars most commonly composed of six, seven, or eight glucosidic units bearing the names  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cyclodextrin (CD), respectively [1]. They get a hydrophobic inner cavity and a hydrophilic outside surface. This internal cavity can accommodate a wide range of guest molecules, ranging from polar compounds such as alcohols, acids, amines, and small inorganic anions to apolar compounds such as aliphatic and aromatic hydrocarbons [2–6]. CDs are widely used in the pharmaceutical, cosmetics, and food industries for improving solubility, dissolution rate, stability, and the bioavailability of drugs [1, 7–9].

Surfactants have a well-known amphipathic structure. The capacity to aggregate in solutions is one of the characteristics of surfactants [10]. They are widely used in pharmaceuticals, detergents, drilling muds, and the flotation agents. The extension of surfactant applications to such high-technology areas as electronic printing, magnetic recording, biotechnology, micro-electronics, and viral research has been seen in recent years [11]. In many cases, surfactants and cyclodextrin are both consisted in a

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formulation. The hydrophobic part of surfactant can be included by the hydrophobic cavity of CD, so the properties of the system may be affected. Therefore, the interaction between surfactants and cyclodextrin has attracted significant scientific and technological interest.

The interaction between surfactant and CD has been investigated by various measurements such as cyclic voltametric method [12], UV and visible spectroscopy [13], fluorescence [14], electrochemistry [15], calorimetry [16], phosphorescence [17], kinetic methods [18, 19], surface tension [20–22], conductometry [20], nuclear magnetic resonance (NMR) spectroscopy [23–26] and so on. Each method has advantages and disadvantages, as well as limitations [22]. Surface tension measurement is a traditional, simple, and useful measurement in the study of the interaction between surfactant and cyclodextrin [14, 17, 21, 22, 27–34].

Many technical and natural systems with fluid interfaces, such as foams and emulsions in general, food colloids, coating flows, the air/sea interface, and biological liquids, are to a great extent characterized by surface rheological properties. The surface dilational modulus is a constitutive property of the system and the studies of the dilational modulus also provide information about the equilibrium thermodynamic characteristics of the interfacial layer [35]. The interest in this area has been increased recently [36–44].

The interaction between cetyltrimethylammonium bromide (CTAB) and  $\beta$ -cyclodextrin ( $\beta$ -CD) has been investigated by various methods [12, 15–17, 24]. The results indicated that both 1:1 and 1:2 inclusion complexes can be formed between CTAB and  $\beta$ -CD. The equilibrium constant for 1:1 complexes is greater than the one of 1:2. The interfacial properties of ionic surfactants show strong dependence on the type of counter-ion of the salt added to the surfactant solution [45]. It has been demonstrated [29, 33, 46] that the addition of electrolyte increases the binding constant of surfactant/cyclodextrin.

The interaction between CTAB and  $\beta$ -CD was investigated using the methods of surface tension and dilational interfacial rheology. In this paper, the effect of NaBr and NaCl on the air/solution interface properties was studied systematically to reveal new sights into the adsorption of CTAB/ $\beta$ -CD complexes. The effects on the properties of concentration of  $\beta$ -CD were studied as well. Dilational interfacial rheology, which is a useful method in the study of surfactant, was introduced into the area of the interaction between surfactant and cyclodextrin. The interfacial dilational rheological property of CTAB in the presence of  $\beta$ -CD is described, so does the effect of NaBr and NaCl on the CTAB/ $\beta$ -CD solution. It is expected that these results would guide the design of formulations consist both ionic-surfactant and cyclodextrin.

## Experimental details

### Materials

CTAB (>99%) were purchased from Sigma. Sodium halides, NaCl (A.R.) and NaBr (A.R.) were purchased from Tianjin Experimental Reagent Co., Ltd., and used without further purification.  $\beta$ -CD (C.P.) was purchased from Shanghai Chemical Agents Company. The sample was recrystallized three times and dried under vacuum at 80°C for at least 24 h before use. Triply distilled water was used in all experiments.

### Methods

#### Sample preparation

Stock solutions were prepared by dissolving appropriate amounts of  $\beta$ -CD, NaCl, and NaBr in water, which is 10 mM, 0.5 M, and 0.5 M, respectively. A series of sample solutions were then prepared at natural pH by mixing different amounts of the stock solutions to obtain desired concentrations. For example, 10 ml  $\beta$ -CD and 20 ml NaBr stock solution was mixed and diluted to 100 ml to get a solution containing 1 mM  $\beta$ -CD and 0.1 M NaBr. These solutions were then used as solvent to prepare CTAB solutions.

#### Surface tension measurements

The surface tension measurements of CTAB aqueous solutions with and without  $\beta$ -CD in the presence of NaCl or NaBr were performed on a K12 processor tensiometer (Germany, Kruss Co.; the precise degree of measurement is  $0.01 \text{ mN}\cdot\text{m}^{-1}$ ) using the Wilhelmy plate at  $25\pm 0.1^\circ\text{C}$ . The detailed procedure of measurement has been reported earlier [47].

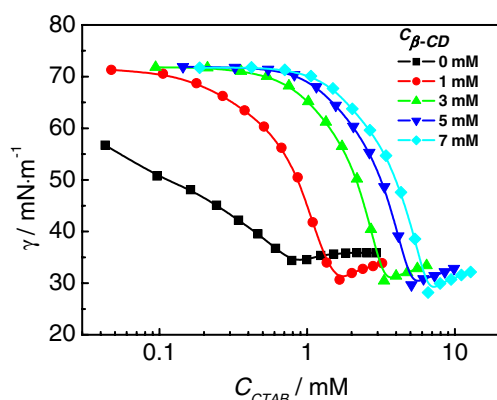
#### Interfacial dilational viscoelasticity measurements

In this method, the surface is subjected to small periodic sinusoidal compressions and expansions by means of two oscillating barriers at a given frequency ( $\omega$ ) and amplitude. The dilational modulus  $\varepsilon$  is generally defined as the ratio of a small change in surface tension ( $\gamma$ ) to the change in surface area ( $A$ ).

$$\varepsilon = \frac{d\gamma}{d\ln A} \quad (1)$$

Equation 1 is valid in the linear regime [48].

The interfacial dilational viscoelasticity meter JMP2000A (Powereach Ltd., Shanghai, China) was used to measure the parameters of dilational viscoelasticity of systems with



**Fig. 1** Surface tension results as a function of CTAB concentration in the absence and in the presence of  $\beta$ -CD

various component. The construction of JMP2000A apparatus and detailed method of measurement have been described previously [36] (see [Supplementary Materials](#)).

## Results and discussion

### Surface tension of the systems

#### *Effect of $\beta$ -CD on the surface activity of CTAB*

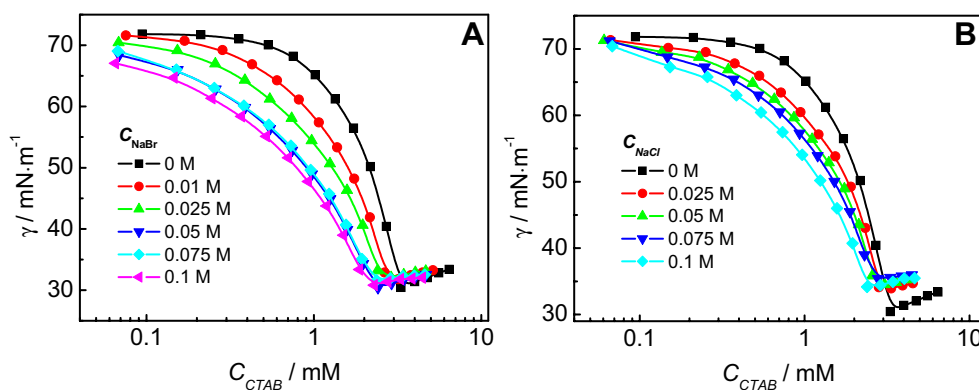
Figure 1 displays the variations in the surface tension for CTAB in the presence of different concentrations of  $\beta$ -CD. For the concentration of CTAB below its cmc, the surface tension values ( $\gamma$ ) are higher in the presence of  $\beta$ -CD than in the absence of  $\beta$ -CD. It is notable that the  $\gamma$  values are comparable to that of water if the concentration of CTAB is low enough, which implies that neither the  $\beta$ -CD nor the CTAB/ $\beta$ -CD complexes have surface activity alone [46]. The cmc of CTAB is 0.76 mM, which agrees well with reported values [49, 50]. The apparent critical micelle concentration ( $\text{cmc}^*$ ) moves to a higher CTAB concentration in the presence of  $\beta$ -CD. These results indicate that the surface activity of CTAB decreases while the surfactant molecules are included in the cavities of  $\beta$ -CD [27].

The  $\text{cmc}^*$  increases as the concentration of  $\beta$ -CD increases (see [Supplementary materials Figure S1](#)). This result proves the formation of inclusion complexes between the CTAB molecules and the  $\beta$ -CD cavities present in solution, so the  $\text{cmc}^*$  appears at a higher CTAB concentration. The surface tension value at  $\text{cmc}^*$  ( $\gamma_{\text{cmc}}$ ) is lower in the present of  $\beta$ -CD than that in the absence of  $\beta$ -CD, similar result were reported in reference [20]. The highest  $\gamma_{\text{cmc}}$  is obtained in the absence of  $\beta$ -CD, while the lowest  $\gamma_{\text{cmc}}$  is obtained in the presence of 7 mM  $\beta$ -CD. It may be due to the CTAB/ $\beta$ -CD complexes adsorb on the air/solution interface and increase the density of the hydrophobic chains in the interface.

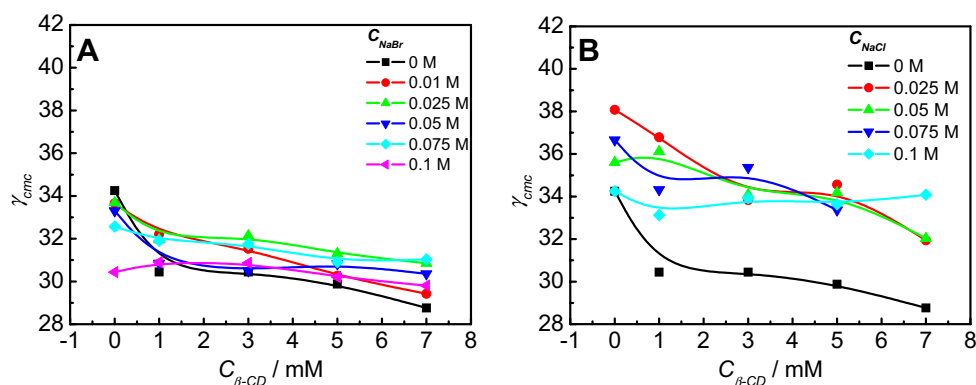
#### *Effect of NaBr and NaCl on the interaction between CTAB and $\beta$ -CD*

The effects of NaBr and NaCl on the surface tension of the CTAB/ $\beta$ -CD solutions are summarized in supplementary materials Figure S2. Figure 2 illustrates the case when [NaBr] and [NaCl] is 3 mM. Surface tension of CTAB decreases significantly in the presence of NaBr and NaCl, as has been reported in refs [51–54]. As shown in Fig. 2a, for a given concentration of CTAB and  $\beta$ -CD, the presence of NaBr decreases the surface tension of CTAB/ $\beta$ -CD solution as well. The  $\text{cmc}^*$  moves to a lower CTAB concentration (supplementary materials Figure S3). The addition of NaCl has a similar effect (Fig. 2b). But the  $\gamma_{\text{cmc}}$  in NaCl solution moves to a higher value, compared to that in NaBr solution. These characters are similar to the effect of KBr and KCl on the CTAB solution [45, 55]. The reason can be explained by the difference in the polarizability of  $\text{Br}^-$  and  $\text{Cl}^-$ . The polarizability of  $\text{Br}^-$  is higher than that of  $\text{Cl}^-$ . Due to strong interaction with the electric field at the air/solution interface,  $\text{Br}^-$  tends to be accumulate in the surface layer [45, 56–59], so it can decrease the thickness of the ionic atmosphere surrounding the ionic head groups efficiently. Therefore, the presence of  $\text{Br}^-$  leads to a lower  $\gamma_{\text{cmc}}$ . But  $\text{Br}^-$  accumulation in the adsorbed layer is mainly due to electrostatic attraction and can easily be replaced by

**Fig. 2** Surface tension isotherms of different solutions as a function of CTAB concentration in the presence of **a** 3 mM  $\beta$ -CD and NaBr, **b** 3 mM  $\beta$ -CD and NaCl



**Fig. 3** Dependence of  $\gamma_{\text{cmc}}$  of CTAB on the concentration of  $\beta$ -CD in the presence of different concentration of **a** NaBr, **b** NaCl

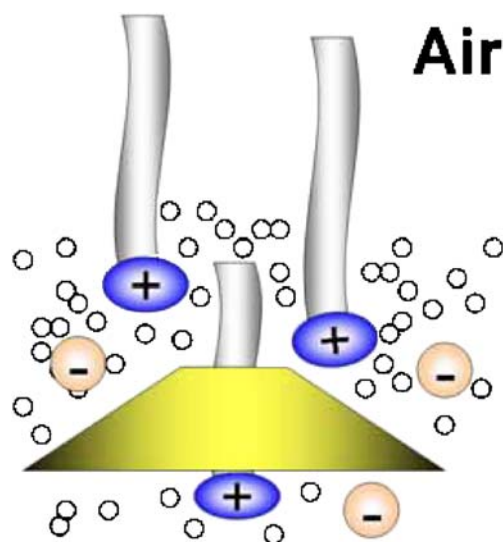


$\text{Cl}^-$  ions when excess of NaCl is added to the CTAB solution [45]. So  $\gamma_{\text{cmc}}$  of CTAB in NaCl solution moves to a higher value compared to NaBr.

The dependence of  $\gamma_{\text{cmc}}$  of CTAB on the concentration of  $\beta$ -CD in the presence of NaBr and NaCl is summarized in Fig. 3. Without electrolytes, the  $\gamma_{\text{cmc}}$  of CTAB decreases sharply in the presence of 1 mM  $\beta$ -CD (Fig. 3a), then decreases as a function of  $[\beta\text{-CD}]$ . In 0.01 M NaBr, the  $\gamma_{\text{cmc}}$  of CTAB also decreases as a function of  $\beta$ -CD, although the values are larger than that in the absence of NaBr. At higher NaBr concentration, the  $\gamma_{\text{cmc}}$  of CTAB decreases slightly as a function the concentration of  $\beta$ -CD and is similar to the value in the presence of the same amount of NaBr without  $\beta$ -CD. We can see that the addition of electrolytes first increase the  $\gamma_{\text{cmc}}$ , then decrease the  $\gamma_{\text{cmc}}$ . These results may due to two reasons. Firstly,  $\beta$ -CD can include the CTAB to form complexes. It has been reported [24, 60] that  $\beta$ -CD cavity can accommodate eight to ten  $\text{CH}_2$  groups in a bended conformation, so there are six to eight  $\text{CH}_2$  moieties outside the cavity for the 1:1 CTAB/ $\beta$ -CD complexes. The CTAB/ $\beta$ -CD complexes may act as multi-hydroxyl alcohol molecules. Since the cross-sectional area of an aliphatic chain-oriented perpendicular to the interface is about  $20 \text{ \AA}^2$  and the occupied area per molecule at the surface at surface saturation for CTAB molecules is  $43\text{--}61 \text{ \AA}^2$  [11, 53] (depending on the amount of electrolytes in the solution), it is apparent that the hydrophobic chains of CTAB adsorbed at the surface are in the loosely packed arrangement normal to the surface at saturation adsorption. So the CTAB/ $\beta$ -CD complexes adsorb on the air/solution interface by hydrophobic interaction, and increase density of the hydrophobic chains in the interface and therefore the  $\gamma_{\text{cmc}}$  decreases (Scheme 1). The interaction between CTAB/ $\beta$ -CD complex and the head group of surfactant is ion–dipole interaction [61]. Secondly, the addition of NaBr increases the adsorption of both  $\text{CTA}^+$  and  $\text{Br}^-$  in the surface layer; in other words, the presence of NaBr decreases the degree of ionization and the repulsion between CTAB molecules in the surface, thus increases the adsorption of CTAB which decreases the

$\gamma_{\text{cmc}}$ . The decrease of  $\gamma_{\text{cmc}}$  is a competition of the two factors. At lower NaBr concentration, the surfactant molecules still packed in a loose way, so the CTAB/ $\beta$ -CD complexes can adsorb on the surface. But the  $\gamma_{\text{cmc}}$  is higher than that in the absence of NaBr, especially in 1 mM  $\beta$ -CD. The  $\gamma_{\text{cmc}}$  decreases as a function the concentration of  $\beta$ -CD which conforms there is competition between the two factors. As the NaBr concentration increases, the surfactant molecules packed in a closer way, only a few CTAB/ $\beta$ -CD complexes can absorb on the air/solution interface, so the difference between the  $\gamma_{\text{cmc}}$  in the presence of  $\beta$ -CD and the one in the absence of  $\beta$ -CD is small. The  $\gamma_{\text{cmc}}$  of CTAB first increases in the presence of NaCl, then decreases as a function of NaCl. The effect of  $\beta$ -CD on the  $\gamma_{\text{cmc}}$  of CTAB/NaCl solution is similar to the one in CTAB/NaBr solution. At lower NaCl concentration, the presence of  $\beta$ -CD sharply decreases the  $\gamma_{\text{cmc}}$ , although at higher NaCl concentration,  $\beta$ -CD has little effect on the  $\gamma_{\text{cmc}}$ .

Since CTAB/ $\beta$ -CD complexes can adsorb on the air/solution interface, they should also take part in the



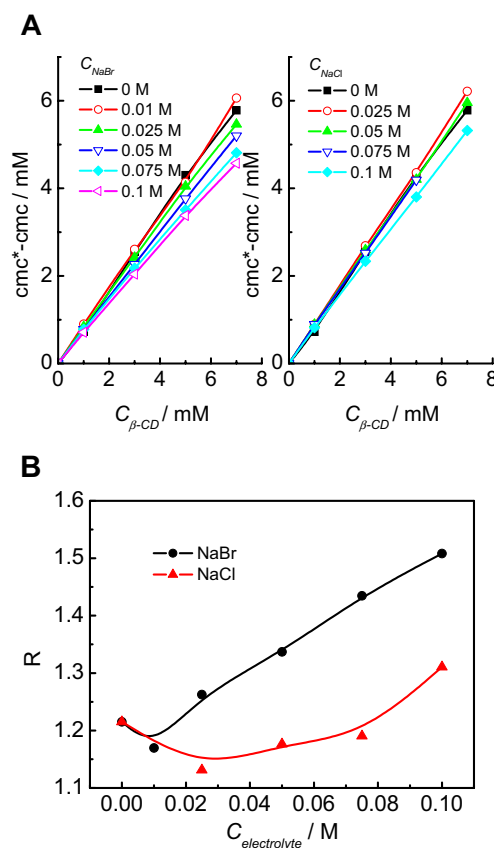
**Scheme 1** Schematic representation of the CTAB/ $\beta$ -CD complex adsorb on the air/solution interface

micellization. There are many dissertations about whether  $\beta$ -CD and surfactant/ $\beta$ -CD complexes interact with micelle. Some authors [12, 14, 62] found the evidence of cyclodextrin–micelle interactions, while others [13, 63, 64] found that the interaction does not exist. According to Junquera [64], the aggregation number of CTAB is unchanged upon the addition of  $\beta$ -CD, this may be due to that CTAB/ $\beta$ -CD complexes can be seen as short-chain alcohol, the decrease of the cmc is very small [61], thus

$$\text{cmc}^* - \text{cmc} = \frac{[\beta - \text{CD}]}{R} \quad (2)$$

A plot of  $\text{cmc}^* - \text{cmc}$  versus  $[\beta\text{-CD}]$  should give a straight line and the reciprocal of the slope is stoichiometry of the complex,  $R$ , defined as the ratio  $[\beta\text{-CD}]_{\text{complex}}/[\text{saa}]_{\text{complex}}$ .

The  $\text{cmc}^* - \text{cmc}$  versus  $[\beta\text{-CD}]$  in the presence of different concentration of NaBr and NaCl is summarized in Fig. 4a. It can be seen that both NaBr and NaCl change the slope and NaBr exhibits more remarkable effect. CTAB and  $\beta$ -CD can form 1:1 and 1:2 complexes [24, 65]. The stoichiometries,  $R$ , derived from Fig. 4a, are shown in



**Fig. 4** The relationship between **a**  $\text{cmc}^* - \text{cmc}$  and the concentration of  $\beta$ -CD in the presence of NaBr and NaCl, **b** stoichiometry  $R$  and the concentration of NaBr and NaCl

Fig. 4b. In the presence of NaBr,  $R$  decreases to 1.17 (0.01 M NaBr) first, and then linearly increases to 1.51 (0.1 M NaBr). In other words, the proportion of 1:2 CTAB/ $\beta$ -CD complexes has a minimum value. It has been reported that hydrophobicity plays a crucial role in the formation of complex [66, 67]. The addition of salt can enhance the hydrophobicity, thus both the interaction between surfactant molecules and the interaction between surfactant and  $\beta$ -CD molecules increases. From Eq. 2, it can be seen  $R$  related to  $\text{cmc}^* - \text{cmc}$ . The change of cmc relates to the interaction between CTAB/CTAB molecules, while the alteration of  $\text{cmc}^*$  consists both the interaction between CTAB/CTAB molecules and CTAB/ $\beta$ -CD molecules. As mentioned in “Effect of NaBr and NaCl on the interaction between CTAB and  $\beta$ -CD”, the addition of electrolytes decreases both cmc and  $\text{cmc}^*$ . Therefore, if the addition of electrolyte affects the interaction between CTAB molecules more effectively, the extent of the decreasing of the cmc is larger, and  $R$  decreases; but if the change of the interaction between surfactant and  $\beta$ -CD molecules is more effective, and the extent of the formation of the 1:2 CTAB/ $\beta$ -CD complexes increases, so the decrease of  $\text{cmc}^*$  is more apparent, thus  $R$  increases. In the presence of lower NaBr concentration (0.01 M),  $R$  decreases a little, this may be attributed to the interaction between CTAB molecules are more effective than the enhancement of the interaction between CTAB and  $\beta$ -CD, so the CTAB molecules tend to form micelles. As the concentration of NaBr increasing, the interaction between CTAB and  $\beta$ -CD molecules is more effective which increases the  $R$  value. The presence of NaCl affects  $R$  in a similar way. The difference between NaBr and NaCl can be ascribed to the degree of binding of the counterion of CTAB and cetyltrimethylammonium chloride, which is 0.84 [68] and 0.63 [49], respectively.

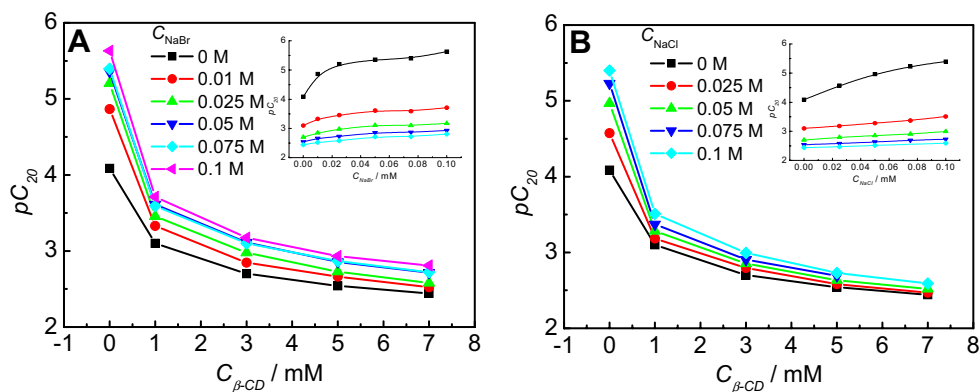
The efficiency of adsorption can be measured by the negative logarithm of the concentration of surfactant in the bulk phase required to produce a  $20 \text{ mN}\cdot\text{m}^{-1}$  reduction in the surface or interfacial tension of the solvent,  $pC_{20}$

$$-\log C_{(-\Delta\gamma=20)} \equiv pC_{20} \quad (3)$$

where  $C$  is the surfactant concentration. Observation of  $\gamma - \log C$  plots reveals that when the surface tension of the pure solvent has been decreased about  $20 \text{ mN}\cdot\text{m}^{-1}$  by adsorption of the surfactant, the surface (excess) concentration of the surfactant is close to its saturation value. The ideal measure of efficiency of adsorption would be some function of the minimum concentration of surfactant in the bulk phase necessary to produce maximum adsorption at the air/solution interface. The larger the value of  $pC_{20}$ , the more efficiently the surfactant is adsorbed at the interface and the more efficiently it reduces surface or interfacial tension [11].



**Fig. 5** The  $pC_{20}$  of CTAB as a function of  $\beta$ -CD in the presence of **a** NaBr, **b** NaCl. The inset is  $pC_{20}$  as a function of added electrolyte, the symbols present the same sequence of  $\beta$ -CD concentration, 0, 1, 3, 5, 7 mM



The  $pC_{20}$  of CTAB as a function of  $\beta$ -CD in the presence of NaBr and NaCl is shown in Fig. 5. For a given NaBr and NaCl concentration, the addition of  $\beta$ -CD decreases the  $pC_{20}$  of CTAB and the  $pC_{20}$  decreases as a function of  $\beta$ -CD. The presence of  $\beta$ -CD decreases the efficiency of adsorption of CTAB. It is understandable that CTAB molecules are included in the  $\beta$ -CD cavities and this part of CTAB molecules contribute to the efficiency of adsorption as short-chain alcohol as mentioned above. At this [CTAB], most  $\beta$ -CD form complexes with CTAB, so the higher the  $\beta$ -CD concentration, the more effective CTAB/ $\beta$ -CD complexes are adsorbed on the air/solution interface. Therefore the slope of the  $pC_{20}$  decreases. The insets of Fig. 5 show that for a given concentration of  $\beta$ -CD, the addition of NaBr and NaCl slightly increases  $pC_{20}$ . But the increasing of the concentration of  $\beta$ -CD decreases the effect of electrolytes on the  $pC_{20}$ . That is because the NaBr and NaCl increase the adsorption of CTAB in the surface layer and the interaction between CTAB and  $\beta$ -CD molecules. Compare the insets of Fig. 5a and b,  $pC_{20}$  increases sharply then increases slightly in NaBr, while increases slightly in NaCl in the absence of  $\beta$ -CD. That is because the  $\text{Cl}^-$  needs to replace  $\text{Br}^-$  from the air/solution interface. In the presence of  $\beta$ -CD, the addition of NaBr and NaCl increases  $pC_{20}$  in a slight way. There are many “alcohol” molecules adsorbed on the air/solution interface

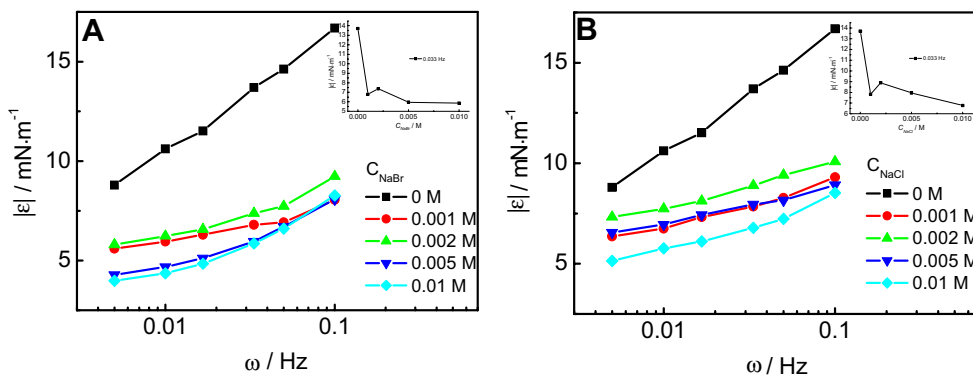
without electrolytes, so the addition of electrolytes exhibits minor effect on the  $pC_{20}$ .

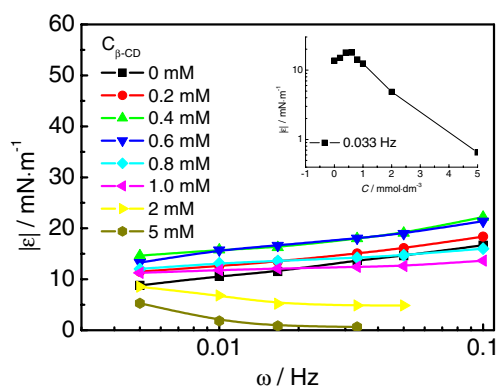
#### Surface viscoelasticity of the systems

##### *The effect of NaBr and NaCl on the dilational viscoelastic behaviors of CTAB*

CTAB molecules can move inside the monolayer, so the surface diffusion can affect viscoelastic parameters. Dilational viscoelasticity of 0.4 mM CTAB solutions with different electrolyte concentrations as a function of dilational frequency is depicted in Fig. 6. It can be seen that the dilational modulus of CTAB adsorbed layers shows an increasing trend with frequency, as we have reported [43]. This could be due to the closer time-scale of surfactant diffusion with surface dilation. The presence of electrolyte decreases the dilational modulus of CTAB. From Eq. 1, we can see that for a given change rate of area, low dilational modulus corresponds to a small change of surface tension. The depression of dilational modulus is mainly due to the decrease in the thickness of the ionic atmosphere surrounding the ionic head groups in the presence of the additional electrolyte and the consequent decreased electrical repulsion between them in the air/solution interface [11]. Therefore, the CTAB molecules can adsorb more efficiently

**Fig. 6** Dilational viscoelasticity of 0.4 mM CTAB with different electrolyte concentrations as a function of dilational frequency, **a** NaBr, **b** NaCl. The insets are dilational modulus as a function of electrolyte concentration at 0.033 Hz





**Fig. 7** Dilational surface elasticity as a function of dilational frequency of CTAB at different  $\beta$ -CD concentrations. The CTAB concentration is 0.4 mM, the symbols represent the concentration of  $\beta$ -CD in mM. The inset is dilational modulus as a function of  $\beta$ -CD concentration at 0.033 Hz

on the interface to decrease the change of surface tension lead by the change of area.

#### *The effect of $\beta$ -CD on the dilational viscoelastic behaviors of CTAB*

As shown in Fig. 7, the dilational rheological properties of CTAB are affected significantly by the addition of  $\beta$ -CD. The dilational modulus (Fig. 7a) increases gradually with the dilational frequency increasing in lower  $\beta$ -CD concentration ( $<1.0$  mM) and has a contrary trend in higher  $\beta$ -CD concentration. At higher  $\beta$ -CD concentration, the dilational modulus is too small to get a reasonable one at high frequencies.

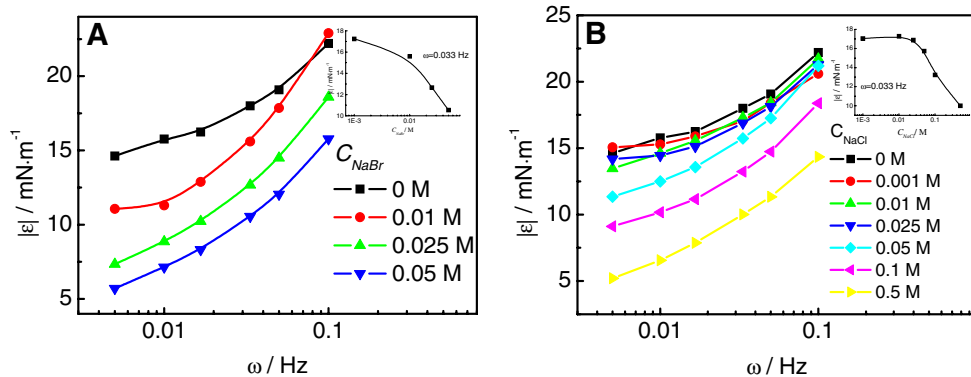
From the inset of Fig. 7, we can see that the dilational modulus passes through a maximum value and a minimum one as the  $\beta$ -CD concentration increases. When the frequency is 0.033 Hz, the maximum value occurs between 0.4 and 0.6 mM  $\beta$ -CD, while the minimum occurs at 5 mM  $\beta$ -CD. The self-diffusion coefficient of CTAB/ $\beta$ -CD is similar to the one of  $\beta$ -CD, which is smaller than CTAB

[24]. When the concentration of  $\beta$ -CD is less than 0.6 mM, CTAB molecules form complexes with  $\beta$ -CD, which decreases the concentration of surfactant in the bulk, and therefore there is less CTAB molecules to decrease the change of surface tension lead by the change of area. When the concentration of  $\beta$ -CD is in the range of 0.6 mM and 5 mM, the amount of  $\beta$ -CD is more than that of CTAB, so there are only a few free CTAB molecules in the solution, and the amount decreases as the concentration of  $\beta$ -CD increasing. At this range, the decreasing of dilational modulus is not because of the mechanism in the previous range. At this concentration range, the surface tension of  $\beta$ -CD is very insensitive to the change of area (which is not shown here). So the high dilational modulus may be due to the adsorption of CTAB/ $\beta$ -CD complexes and the displacement of the complexes by  $\beta$ -CD leads to the decrease of dilational modulus. It has been reported that both surfactant/ $\alpha$ -CD and  $\alpha$ -CD can self-assemble at the solution/air interface [69]. When the concentration of  $\beta$ -CD is larger than 1.0 mM, the dilational modulus lost the characteristic of CTAB, the dilational modulus decreases gradually with the dilational frequency, and at high frequencies, and the dilational modulus is too small to be detected. This may be due to that the CTAB molecules no longer stay on the surface because the CTAB molecules form complexes with  $\beta$ -CD.

#### *Effect of NaBr and NaCl on dilational viscoelastic behaviors of CTAB/ $\beta$ -CD solutions*

The effects of NaBr and NaCl on the dilational viscoelastic behaviors of CTAB/ $\beta$ -CD solutions are summarized in Fig. 8. It can be seen from Fig. 8a that the dilational modulus of CTAB/ $\beta$ -CD solutions decreases as a function of NaBr concentration. This could be the same reason described in “The effect of NaBr and NaCl on the dilational viscoelastic behaviors of CTAB”, the effect of NaBr on the CTAB system. In the case of NaCl, The dilational modulus first decreases slowly, and then decreases sharply. This may

**Fig. 8** Interfacial dilational viscoelasticity as a function of dilational frequency of CTAB/ $\beta$ -CD at different electrolyte concentrations. **a** NaBr, **b** NaCl. The CTAB and  $\beta$ -CD concentrations are 0.4 mM, respectively. The symbols represent the concentration of NaBr in M. The insets are dilational modulus as a function of electrolyte concentration at 0.033 Hz



be due to the difference in the polarizability of  $\text{Br}^-$  and  $\text{Cl}^-$ , as mentioned in “Effect of NaBr and NaCl on the interaction between CTAB and  $\beta$ -CD”. The addition of NaCl will decrease dilational modulus as a function of NaCl concentration, until the concentration of  $\text{Cl}^-$  is large enough to replace  $\text{Br}^-$  from the surface.

## Conclusion

The interaction between CTAB and  $\beta$ -CD were investigated via surface tension and dilational viscoelasticity methods. From the surface tension measurement, it can be seen that both 1:1 and 1:2 CTAB/ $\beta$ -CD complexes present in the solution and 1:1 CTAB/ $\beta$ -CD complexes can decrease the  $\gamma_{\text{cmc}}$  by adsorbing on the interface like short-chain alcohol. Stoichiometry of the complex,  $R$ , decreases first by the addition of low concentration NaBr and NaCl, and then increases as a function of electrolyte concentration, which shows that the concentration of 1:2 complexes first decreases then increases. The adsorption efficiency ( $pC_{20}$ ) is lower in the presence of  $\beta$ -CD, because the formation of CTAB/ $\beta$ -CD complexes. As  $\beta$ -CD concentration increasing, the slope of  $pC_{20}$ –[ $\beta$ -CD] decreases, because the CTAB/ $\beta$ -CD complexes adsorb on the air/solution interface. The addition of electrolyte increases  $pC_{20}$  and NaCl is not as efficient as NaBr.

The dilational modulus derived from dilational viscoelasticity methods shows that the dilational viscoelasticity is dependent on  $\beta$ -CD concentration and there is a maximum value as a function of [ $\beta$ -CD]. When the [ $\beta$ -CD] is high enough, the dilational modulus–frequency plot lost the characteristic of CTAB. The addition of electrolyte can decrease both the dilational modulus of CTAB and the solution of CTAB and  $\beta$ -CD (mole ratio is 1:1) but more NaCl is needed to lower the dilational modulus in the same extent.

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