



# Specific ion effects of chloride vis-à-vis acetate, propionate and butyrate counterions on the cetylpyridinium headgroup at the micelle–solution and air–solution interfaces



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## ABSTRACT

Aliphatic carboxylate anions due to their varying kosmotropy and hydrophobicity are expected to compete with chloride ion for binding at interfaces. Such competition leads to the specific ion effect (SIE) and investigating the SIE at micelle/solution and air/solution interfaces has a bearing on the selectivity of ions at biological interfaces. In this paper, critical micelle concentration (cmc) values of aqueous cetylpyridinium chloride solution in the presence of acetate, propionate and butyrate anions were determined by surface tension and conductance methods. Hydrodynamic radii of the cetylpyridinium micelles were measured by using the dynamic light scattering technique. The dependence of cmc on the added salt concentration is explained in the light of the modified Corrin–Harkins (CH) equation. Non-linearity of the plots of the modified CH equation is shown to be due to exchange of carboxylate and chloride ions at the micellar interface. The surface excess values of CPC in the presence of carboxylate anions are also calculated in the light of the Gibbs adsorption isotherm. The main finding of this study is that a new method has been demonstrated for determining selectivity coefficient (it quantifies the SIE) on the basis of the modified CH equation.

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## 1. Introduction

Ions play a vital role in biology as they influence and regulate many biological phenomena. The preference of one ion over another for binding at biological interfaces is broadly termed as the specific ion effect (SIE). On the basis of SIE, ions are arranged in series and the Hofmeister series is one such well-known arrangement. Experimental and theoretical efforts are still going on to understand the basis of the SIE [1–22]. Micelles are used as models to mimic biological membranes and therefore investigating the effect of ions on the aggregation and adsorption phenomena of ionic surfactants provides results that are useful to understand SIE. Additionally, studying the effect of ions on the micellization and morphology of aggregates of ionic surfactants gives us information much needed in tuning the surfactant properties.

Varade et al. [23] reported that on adding NaCl and NaBr to aqueous cetylpyridinium chloride (CPC) solution, critical micelle concentration (cmc) decreased and micellar size increased, but these effects were more pronounced in the case of NaBr. Less amount of NaBr produced larger micellar growth unlike NaCl. Therefore, the nature of condensation of  $\text{Cl}^-$  and  $\text{Br}^-$  on to the micelle surface was reported to be different

[23]. Similarly, the addition of NaBr to an aqueous solution of cetylpyridinium bromide (CPB) of fixed concentration causes a large increase in micellar size, whereas the addition of NaCl did not produce a noticeable increase in micellar size [24]. Similar observations were reported on adding KBr and KCl to cetyltrimethylammonium bromide (CTAB) [25]. Miller et al. [26] reported that the microstructures of ditetradecyldimethylammonium aggregates transformed from multilamellar liposomes to unilamellar vesicles + microtubules and then to spherical micelles when the bromide-to-acetate ( $\text{Ac}^-$ ) counterion ratio was changed from large values to zero. Anacker and Underwood [27] reported that the cmc and aggregation number of decyltrimethylammonium bromide (DeTAB) decreased when a fixed amount of  $\text{CH}_3(\text{CH}_2)_n\text{COONa}$  (0.5 M,  $M = \text{mol kg}^{-1}$ ) was added. As  $n$  increased from 0 to 5, the cmc of DeTAB decreased, but the aggregation number remained constant for  $n = 0$  to 3 [27].

The following points motivated us to undertake the present study: (1) Despite studies on the effects of mixed counterions like  $\text{Cl}^-/\text{Br}^-$  and  $\text{Br}^-/\text{Ac}^-$  on the aggregation and aggregate microstructures of cationic surfactants [23–27], the effect of chloride and aliphatic carboxylate mixed counterions on the aggregation and adsorption of CPC has not been investigated. (2) SIE depends on the nature of the binding ion and the target. Therefore, studying SIE using different sets of ions with a fixed ionic surfactant as the target or a fixed set of ions with surfactants of varying types of headgroups and chain lengths as targets will provide information that are useful for understanding SIE better.

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(3) Investigation of SIE using surfactants involves mixed counterions. The thermodynamics of binding of mixed counterions to an ionic surfactant in the line of Corrin–Harkins (CH) approach has been reported recently [28–30]. Based on this thermodynamic approach, it is possible to develop a method for determining the selectivity coefficient of a set of two counterions exhibiting SIE.

Accordingly, we have investigated in this paper the aggregation and adsorption characteristics of CPC in the presence of  $\text{CH}_3(\text{CH}_2)_n\text{COO}^-$  with  $n = 0$  ( $\text{Ac}^-$ ), 1 (propionate,  $\text{Pr}^-$ ) and 2 (butyrate,  $\text{Bu}^-$ ). We could actually develop a new approach for determining selectivity coefficient on the basis of the modified CH equation. Selectivity coefficient is an important parameter as it quantifies SIE.

## 2. Materials and methods

CPC (Aldrich, >99.0%), sodium acetate (NaAc, Sisco), sodium propionate (NaPr, Sigma), sodium butyrate (NaBu, E-Merck) and sodium chloride (E-Merck) were used as received without further purification. Milli-Q grade water was used for preparing solutions for surface tension, conductivity and DLS measurements. Density of solutions was measured using an Anton Parr DMA 5000 density meter. A Haake DC 10 circulation bath was used for maintaining the temperature and all experimental measurements were made at 25 °C. Surface tension was measured using a K11 Krüss tensiometer and a Wilhelmy plate. Electrical conductance was measured using a B905 Wayne Kerr Automatic Precision Bridge and a dip type conductivity cell. Reproducibility of the measurements was checked by repeating the experiments. Surface tension and specific conductivity values were reproducible within  $\pm 1.0 \text{ mN m}^{-1}$  and  $\pm 0.5 \text{ mS m}^{-1}$ , respectively.

Dynamic light scattering (DLS) measurements were made with a Malvern Zetasizer Nano ZS instrument operating at 633 nm (4 mW He Ne laser is used) and 90° scattering angle. Samples were filtered through a 0.22  $\mu\text{m}$  membrane filter prior to measurements. The scattering intensity data were processed using the instrumental software to obtain the hydrodynamic diameter ( $d_H$ ) of the aggregates in each sample. During DLS measurements the temperature was maintained at 25 °C by the built-in temperature control unit (peltier) of the instrument.

## 3. Results and discussion

### 3.1. Cmc and its dependence on counterion

The cmc values of CPC as a function of varying amounts of salt were determined from the surface tension ( $\gamma$ ) and specific conductivity ( $\kappa$ ) data. The experimental values of surface tension and conductivity are presented in Figs. S1–S6 (Supplementary material). From the  $\kappa$  data, cmc could be determined as a function of salt concentration ( $c_e$ ) only up to  $c_e \leq 0.01 \text{ M}$ , because the variation of  $\kappa$  with CPC concentration becomes insignificant when  $c_e > 0.01 \text{ M}$  owing to high background conductivity. The cmc values are listed in Table S1 and these values from the two methods are comparable within  $\pm 0.1 \text{ mM}$ . The dependence of cmc on  $c_e$  is shown in Fig. 1. In Fig. 1, for comparison purpose, the cmc values of CPC in the presence of NaCl [31] (cmc values above 0.02 M NaCl were determined in this work) and NaBr (cmc values were determined by the surface tension method and the experimental values of  $\gamma$  are shown in Fig. S7) are also shown. With respect to the relative values of cmc of CPC, the anions can be arranged in the order  $\text{Ac}^- > \text{Cl}^- \sim \text{Pr}^- > \text{Bu}^- > \text{Br}^-$  and thus Fig. 1 clearly depicts SIE on the cmc of CPC. It may be noted that at some concentration range ( $0.001 \text{ M} < c_e < 0.02 \text{ M}$ ) the cmc of CPC in the presence of NaCl is lower than that in the presence of NaPr. With respect to the reported [27] cmc values of DeTAB in the presence of different salts, the arrangement of the anions follow the order  $\text{Ac}^- > \text{Pr}^- > \text{Bu}^- > \text{Br}^-$ , which is in agreement with our present observation. The reported [32] cmc values of dodecyltrimethylammonium bromide (DTAB)/acetate (DTAAc)/propionate (DTAPr)/butyrate (DTABu) also follow the order

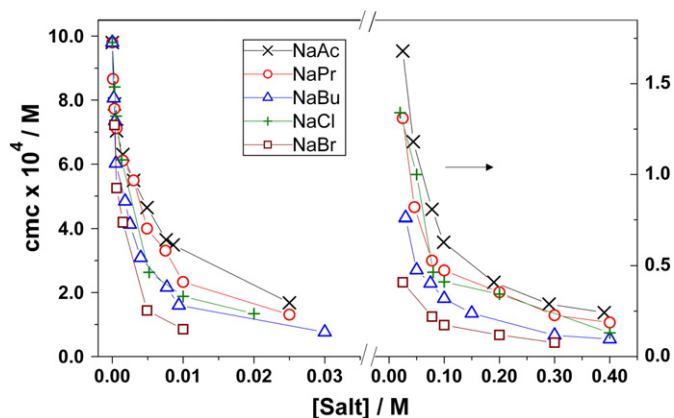


Fig. 1. Cmc (from surface tension) of CPC in the presence of salts in an aqueous medium at 25 °C. Cmc data in the presence of NaCl (up to 0.02 M) are from reference [31].

$\text{Ac}^- > \text{Pr}^- > \text{Bu}^- > \text{Br}^-$ . From the reported [33–35] cmc values it has also been noticed that cetyltrimethylammonium acetate (CTAAc) has higher cmc than cetyltrimethylammonium chloride (CTACl). Thus, the arrangement of the anions on the basis of cmc follows the order  $\text{Ac}^- > \text{Cl}^- \sim \text{Pr}^- > \text{Bu}^- > \text{Br}^-$  irrespective of the length of hydrocarbon chain of cationic surfactant, and the SIE of each of these ions towards pyridinium and trimethylammonium headgroups is almost similar. The arrangement of  $\text{Ac}^-$ ,  $\text{Cl}^-$  and  $\text{Br}^-$  in the Hofmeister series is in the same order as shown above on the basis of cmc [2]. Collins' model [36,37], known as the 'concept of matching water affinities', has been used [2,12] to explain the SIE of counterions at micellar interfaces containing surfactant headgroups. According to this concept, ions are classified as kosmotropes and chaotropes, and interaction between similar ions is stronger. Accordingly, ions interact more strongly if both are kosmotropes or chaotropes than if one is kosmotrope and the other is chaotrope. Kosmotrope ions have higher charge density and are more hydrophilic, whereas chaotrope ions have lower charge density and are weakly hydrated. Pyridinium and trimethylammonium headgroups behave as chaotropes due to a large surface area and low charge density [2,38]. In the present case,  $\text{Ac}^-$  is more kosmotropic than  $\text{Cl}^-$  and hence binds weakly with chaotropic pyridinium headgroup, due to which the cmc of CPC in the presence of NaAc is higher than that in the presence of NaCl. As pointed out above, the cmc of CPC in the presence of NaAc, NaPr and NaBu follows the trend  $\text{Ac}^- > \text{Pr}^- > \text{Bu}^-$ . However, one would expect the binding of these three carboxylate ions to the pyridinium headgroup to weaken continuously as  $\text{Ac}^-$  is replaced by  $\text{Pr}^-$  and thereafter by  $\text{Bu}^-$ , because the kosmotropy of  $\text{CH}_3(\text{CH}_2)_n\text{COO}^-$  ions is reported to increase up to  $n = 5$  [39]. Therefore, on the basis of the kosmotropy, the cmc of CPC in the presence of the three carboxylate ions is expected to follow the trend  $\text{Bu}^- > \text{Pr}^- > \text{Ac}^-$ , which is opposite to the observed trend. Further, these carboxylate ions become progressively stronger conjugate bases with an increase in hydrocarbon chain length which is apparent from the  $\text{pK}_a$  values of the corresponding acids (4.75, 4.87 and 4.82 for acetic, propionic and butyric acids, respectively). The carboxylate ions can undergo hydrolysis producing thereby acid and hydroxyl ions, which would affect the cmc values. But it has been reported [34] that the cmc value of CTAAc in the presence of NaAc did not change on adding acetic acid and similar observation was also made in the case of DTAAc on adding NaAc and acetic acid + NaAc [32]. Thus, the effect of hydrolysis and hydrolysis products of carboxylate ion on the cmc of CPC is negligible. Therefore, the decrease in cmc of CPC due to increasing chain length of the carboxylate ion must be predominantly due to the enhanced hydrophobic interaction of counterion with the micelle.  $\text{Pr}^-$  and  $\text{Bu}^-$  ions are expected to penetrate into the micellar interior, which would bring the carboxylate group nearer

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