

The Ionic Exchange Coefficients of Surfactant Counterions at the Solid/Liquid Interface. I. The Ionic Exchange Coefficients of F⁻ and Cl⁻ on Adsorbed Cetyltrimethylammonium Bromide at the Silica/Water Interface

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The adsorption of surfactants at solid/liquid interfaces is fundamentally important for many technical applications, in most of which the surfactants consist of mixtures. Adsorption of ionic surfactants at solid/liquid interfaces in the presence of electrolytes is particularly interesting in both applied and academic research. However, little is known of the ionic exchange between electrolytes and the adsorbed counterions of ionic surfactants at the solid/liquid interface.

The adsorption mechanisms of ionic surfactants at polar surfaces can be described in the following way. The surface-active ions are initially adsorbed by electrostatic attraction on the oppositely charged sites at the surface, after which surface aggregates are formed (i.e. hemimicelles) through hydrophobic interaction between the hydrocarbon chains of the surface-active ions.^{1–7} Obviously, some of the counterions of the surfactants would be attracted to the surface of oppositely charged hemimicelles through electrostatic attraction,^{3,4} and in the presence of electrolytes, an ionic exchange reaction will occur between these counterions and the similarly charged ions from the added electrolytes.

Recently, based on a two-step adsorption mechanism and the mass-action treatment, experimental results have been interpreted successfully.^{1–7} However, the effects of the counterions are still not clear. Further investigations of the exchange of surfactant counterions on solid/liquid interfaces may offer a new insight into this.

Theoretical

Dealing with the adsorption of ionic surfactants, e.g. cetyltrimethylammonium bromide (CTABr) from aqueous

solution in the presence of an electrolyte, e.g. NaCl, onto a solid adsorbent, at equilibrium we have reaction (1), and the ionic exchange coefficient as given in eqn. (2), where



$$K_{\text{Cl}^-/\text{Br}^-} = (a_{\text{CTACl(ads)}} a_{\text{Br}^-}) / (a_{\text{CTABr(ads)}} a_{\text{Cl}^-}) \quad (2)$$

$a_{\text{CTACl(ads)}}$ and $a_{\text{CTABr(ads)}}$ are the activities of adsorbed ion pairs of CTA^+Cl^- and CTA^+Br^- , and a_{Br^-} and a_{Cl^-} represent the activities of Br^- and Cl^- in bulk solution, respectively. In a dilute solution as in our case, $a_{\text{Br}^-} = C_{\text{Br}^-}$ and $a_{\text{Cl}^-} = C_{\text{Cl}^-}$, where C_{Br^-} and C_{Cl^-} are the concentrations of Br^- and Cl^- in bulk solution, respectively. For an adsorbent with low charge density, in our case silica, the adsorption quantities of ion pairs, Γ_{CTABr} and Γ_{CTACl} , can be used instead of $a_{\text{CTABr(ads)}}$ and $a_{\text{CTACl(ads)}}$, respectively. Thus eqn. (2) becomes eqn. (3), where B is the binding constant

$$K_{\text{Cl}^-/\text{Br}^-} = (\Gamma_{\text{CTACl}} C_{\text{Br}^-}) / (\Gamma_{\text{CTABr}} C_{\text{Cl}^-}) \equiv B_{\text{CTACl}} / B_{\text{CTABr}} \quad (3)$$

between the adsorbed CTA^+ and the corresponding counterions. From the value of K we may compare the magnitudes of binding constants for different counterions in the same surfactant–adsorbent system.

Results and discussion

From eqn. (3) one could calculate the ionic exchange coefficient if both counterion concentrations could be measured. However, generally there are difficulties in making these measurements (e.g. by using ion-selective electrodes) because of the mutual disturbance between different counterions. It is possible to avoid this difficulty by keeping one of the counterion concentrations much higher than the

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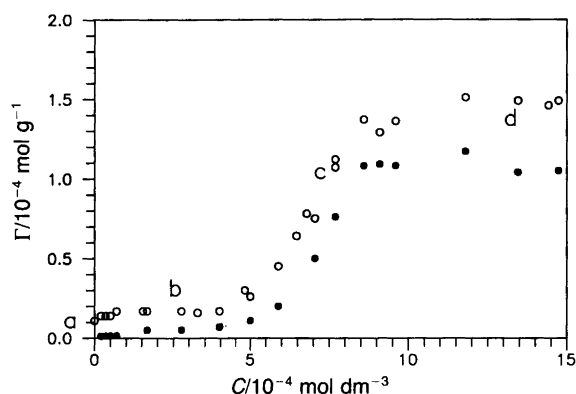


Fig. 1. (○) Adsorption isotherm of CTA^+ from aqueous solution on silica gel; (●) corresponding adsorption of Br^- . C is the concentration of CTA^+ .

other. This can be illustrated in the following way. Fig. 1 shows the adsorption isotherm of CTABr and Fig. 2 is a schematic representation of various stages in the adsorption of CTA^+ and Br^- on silica.^{3,4} Tables 1 and 2 show the results for the systems CTABr – 0.01 mol dm⁻³ NaCl and CTABr – 0.01 mol dm⁻³ NaF on silica.³ The concentration of bromide ion was determined by using a bromide-ion selective electrode (ORION Research, model 94-35) with a saturated calomel electrode having a double liquid junction as the reference electrode and with sodium nitrate to maintain the ionic strength. The calibration curve and the samples were measured at the 25.0±0.1°C simultaneously in order to maintain the conditions of the standard solution and the samples as constant as possible.³

Using these data, it is possible to evaluate $K_{\text{CTACl}/\text{CTABr}}$ as well as $K_{\text{CTAF}/\text{CTABr}}$ without difficulty. Huang *et al.*³ have measured Γ_{CTA^+} , C_{CTA^+} , Γ_{Br^-} and C_{Br^-} . Assuming $\Gamma_{\text{CTABr}} = \Gamma_{\text{Br}^-}$, $\Gamma_{\text{CTACl}} = \Gamma_{\text{Cl}^-}$ and $\Gamma_{\text{CTACl}} = \Gamma_{\text{CTA}^+} - \Gamma_{\text{CTA}^{+\infty,1st}} - \Gamma_{\text{Br}^-}$, where $\Gamma_{\text{CTA}^{+\infty,1st}}$ represents the adsorption isotherm of CTA^+ at the first plateau of the adsorption isotherm of

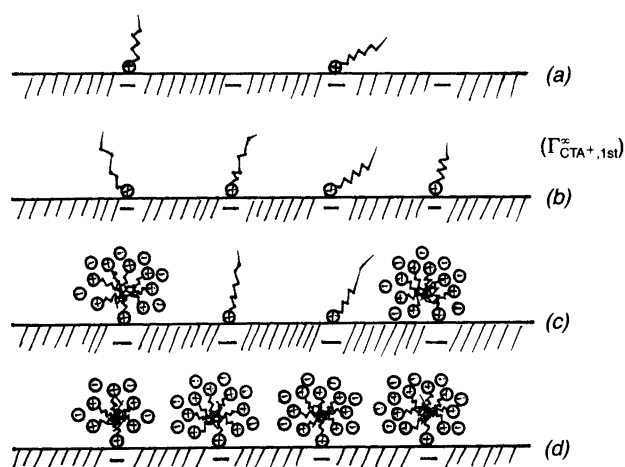


Fig. 2. Schematic representation of various stages in the adsorption of CTA^+ and Br^- on silica gel.

Table 1. $K_{\text{CTACl}/\text{CTABr}}$ for the system CTABr–0.01 mol dm⁻³ NaCl–silica^a ($\Gamma_{\text{CTA}^{+\infty,1st}} = 0.018$ mmol g⁻¹).

C_{CTA^+}	Γ_{CTA^+}	C_{Br^-}	Γ_{Br^-}	Γ_{Cl^-}	$K_{\text{CTACl}/\text{CTABr}}$
1.9	0.082	4.89	0.006	0.058	(0.47)
2.1	1.110	5.92	0.012	0.080	0.40
2.42	1.121	6.98	0.016	0.087	0.38
3.15	1.178	9.20	0.035	0.125	0.33
4.14	1.182	11.1	0.036	0.128	0.40
					(av. 0.40)

^a C is in units of 10⁻⁴ mol dm⁻³; Γ is in mmol g⁻¹.

CTA^+ on silica (Figs. 1 and 2) resulting from electrostatic attraction or ion exchange adsorption.¹⁻⁷ Since the concentration of electrolyte added (0.01 mol dm⁻³) is much higher than that of CTABr in the adsorption experiments, no significant change in the electrolyte concentration could be detected during the adsorption experiments. Thus, if one assumes that the concentration of added electrolyte is unchanged (approximately) during the adsorption reaction, then eqn. (3) can be used to calculate $K_{\text{CTACl}/\text{CTABr}}$ values. Furthermore, we can calculate $K_{\text{CTAF}/\text{CTABr}}$ values with a similar procedure. The results are shown in Tables 1 and 2, respectively.

Although the value of $K_{\text{CTACl}/\text{CTABr}}$ in Table 1 is nearly constant, Table 2 indicates that the value of $K_{\text{CTAF}/\text{CTABr}}$ tends to decrease with increasing concentration of CTA^+ . This may be related to the special properties of F^- ions. Among the three acids HCl, HBr and HF, only HF is a weak acid (its dissociation constant at 25°C is 3.53×10⁻⁴), and thus NaF is a basic salt. Therefore the concentrations of F^- in a solution of constant concentration of NaF would decrease with decreasing pH. On the other hand, the higher the equilibrium concentration of CTABr, the lower its pH in solution. This means that when the concentration of CTABr increases, the concentration of F^- should decrease.

Table 2. $K_{\text{CTAF}/\text{CTABr}}$ for the system CTABr–0.01 mol dm⁻³ NaF–silica^a ($\Gamma_{\text{CTA}^{+\infty,1st}} = 0.018$ mmol g⁻¹).

C_{CTA^+}	Γ_{CTA^+}	C_{Br^-}	Γ_{Br^-}	Γ_{F^-}	$K_{\text{CTAF}/\text{CTABr}}$
1.81	0.087	5.48	0.007	0.062	(0.49)
1.82	0.106	6.15	0.009	0.089	(0.61)
2.55	0.106	8.49	0.029	0.127	0.37
2.91	0.347	17.3	0.131	0.198	0.26
2.92	0.264	11.9	0.074	0.172	0.28
3.07	0.253	10.9	0.062	0.173	0.30
3.75	0.317	13.3	0.078	0.221	0.38
4.12	0.383	17.3	0.157	0.208	0.23
4.50	0.363	12.4	0.169	0.176	0.13
8.63	0.400	17.7	0.197	0.185	0.17
					(av. 0.32)

^a C is in units of 10⁻⁴ mol dm⁻³; Γ is in mmol g⁻¹.

SHORT COMMUNICATION

In conclusion, the data indicate that generally the order of the binding coefficients of halide ions on adsorbed CTA⁺ ions is Br⁻ > Cl⁻ > F⁻, in agreement with that on micelles of the same series of compounds in the bulk phase.⁸ It should be noted that direct measurements of both counterions in solution are still most important, and we are now undertaking such a study.

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