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Effect of Counterionic Species on the Adsorption of Tetradecyltrimethylammonium Ion at the Polarized Nitrobenzene-Water Interface

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The effect of counterions, F^-, Cl^-, and Br^- on the adsorption of the hexadecyltrimethylammonium ion ($HTMA^+$) at the polarized nitrobenzene-water interface has been studied by measuring electrocapillary curves. The interfacial tension in the negative branch of the electrocapillary curve, where the interface is polarized such that the potential in the aqueous phase is negative with respect to that in the nitrobenzene phase, was lowered due to the specific adsorption of $HTMA^+$ ion at the interface. The magnitude of interfacial tension depression in the negative branch became larger in the order F^-, Cl^-, and Br^-, indicating a specific counterion binding at the interface in this order. The adsorption free energy of the $HTMA^+$ ion, ΔG^0_a, for the adsorption of $HTMA^+$ ion at the interface from the nitrobenzene phase was found to depend markedly on the anionic species present in the aqueous side of the interface. This ΔG^0_a values can be taken as a quantitative measure of the counterion specificity at the interface. The meaning of the fact that the change in the shape of the electrocapillary curves depends on the counterion species is discussed in detail in terms of the thermodynamics of the oil-water interface.

The counterion specificity in interfacial chemistry and colloid chemistry has long been recognized. For example, the critical micelle concentration of cationic surfactants with different counterionic species decreases, while its micelle size increases, in accordance with the Hofmeister series of counterions.[1] A similar counterion specificity has been observed in a wide variety of surface phenomena, including surface pressure-area curves at air-water interfaces,[2] flocculation of colloidal particles,[3] and the rate of a chemical reaction at the interface.[4] However, only a few attempts have been made to quantitatively estimate the counterion specificity on the surface activity of surfactants.[5–7] Particular attention has recently been focused on the counterion binding at micelle surfaces in relation to micellar catalysis.[8] In these studies, the micelle was treated as a pseudophase and the relative affinity of counterions to the micelle surface has been estimated in terms of the ion-exchange constants of counterions.[8] In the previous paper we reported on the adsorption behavior of hexadecyltrimethylammonium ion at the polarized nitrobenzene–water interface, where an electrical double layer structure can be studied in the well defined electrical conditions of the interface.[9] This type of an interface provides us with a useful means to study the effect of counterion specificity to the surface properties of ionic surfactants. The present paper deals with the effect of counterion species on the adsorption of hexadecyltrimethylammonium ion ($HTMA^+$) at the polarized nitrobenzene-water interface. The advantage of this approach is that the counterion specificity can be quantitatively estimated through the adsorption free energy, which is obtainable as a function of the potential drop across the interface. Furthermore, in this approach the surfactant and its counterion to be studied reside in separate phases; they interact with each other only at the interface. This makes the interpretation of the experimental data much simpler, since the effect of the counterionic species in the bulk phase, e.g., salting out effect which may exists when both of them are in the same phase, needs not be considered.

Experimental

The interfacial tension of the nitrobenzene–water interface was measured with the drop time method using a dropwise ascending electrolyte solution electrode.[10] This electrode was also used to record current vs. potential curves using a four-electrode potentiostat with a positive feedback circuit for iR compensation. Details of the measurements and the method of calculation to convert the drop time into the interfacial tension value have been described previously.[10] All measurements were made at 25.00±0.05 °C. Methods for the preparation of hexadecyltrimethylammonium tetraphenylborate(HTMATPB), tetrapentylammonium tetraphenylborate(TPnATPB), and lithium tetraphenylborate (LiTPB) have been described elsewhere.[9,11] Lithium bromide and lithium fluoride were of Spurpur grade(Merck). Nitrobenzene was distilled under reduced pressure and then treated with active alumina. Triply distilled water was used to prepare the aqueous solutions.

Results and Discussion

The electrochemical cells used in the present study are represented by:

I	II	III	IV	V
		1 mM	1 mM	(0.1−x)M TPnATPB
Ag	AgCl	LiCl	LiTPB	x M HTMATPB
		(W)	(W)	(NB)

VI	VII	VIII	IX	
satd. LiF (W)	satd. KCl (W)	AgCl	Ag	(I)

and

I	II	III	IV	V	VI	VII	VIII	
Ag	AgCl	1 mM LiCl (W)	1 mM LiTPB (W)	(0.1−x)MTPnATPB x M HTMATPB (NB)	0.5 M LiBr (W)	AgBr	Ag	(II)

where M=mol dm^{-3}. The saturated solution of LiF whose concentration is 0.499 mol dm^{-3} at 25 °C[12] was used for the aqueous phase in Cell (I). The concentration of HTMATPB was varied from 0 to 0.1 mol dm^{-3} while keeping the total concentration of TPnATPB and HTMATPB in the nitrobenzene phase constant at 0.1 mol dm^{-3}. This mixed electrolyte method[13] has been conveniently used for obtaining a specifically adsorbed amount of HTMA$^+$ ion from the electrocapillary curves.[9]

The potential of the right-hand side of the Cells (I) and (II) with respect to the left is indicated as E^{W-}_{O-}, where the super- and subscripts indicate that the reference electrodes in the aqueous phase and the nitrobenzene phase are reversible to the anion (Cl$^-$) and the anion (TPB$^-$), respectively.[9] Figures 1a and 1b show the current vs. potential curves recorded for Cells (I) and (II). The polarized potential ranges for Cell (I) in the presence and the absence of HTMATPB

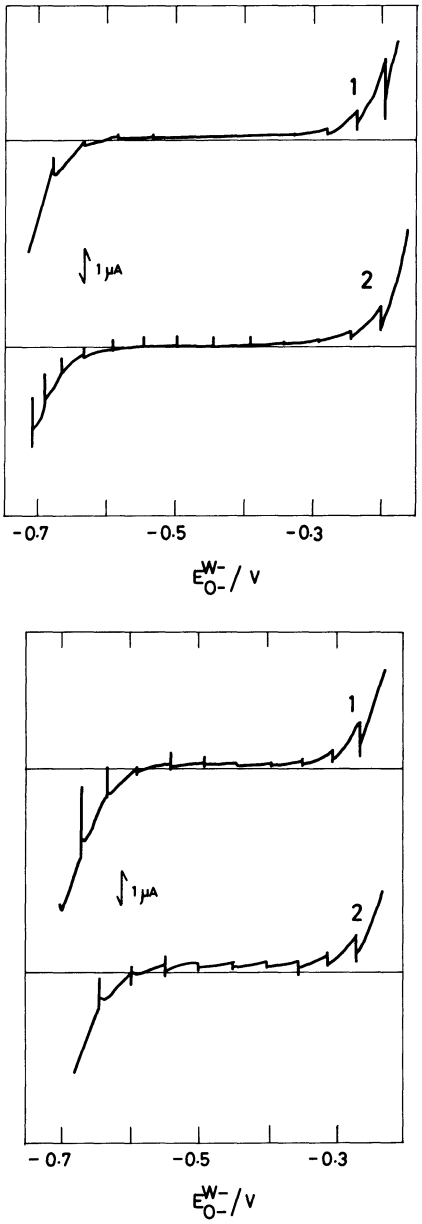

Fig. 1. a) Current vs. potential curves for the interface between aqueous solution of 0.05 mol dm^{-3} LiF and 0.1 mol dm^{-3} TPnATPB(1) or 0.1 mol dm^{-3} HTMATPB(2). b) Current vs. potential curves for the interface between aqueous solution of 0.05 mol dm^{-3} LiBr and nitrobenzene solution of 0.1 mol dm^{-3} TPnATPB(1) or 0.1 mol dm^{-3} HTMATPB(2).

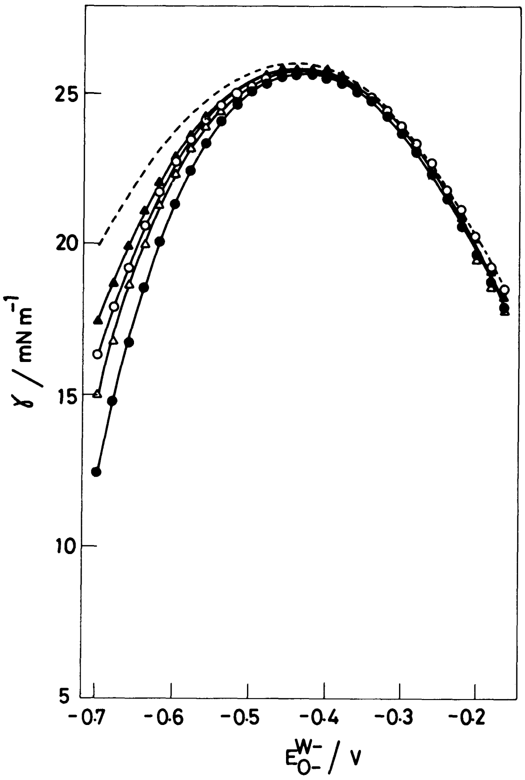

Fig. 2. Electrocapillary curves for the interface between aqueous solution of 0.05 mol dm^{-3} LiF and nitrobenzene solution of (0.1−a) mol dm^{-3} TPnATPB and a mol dm^{-3} HTMATPB, where a=0(-----), 0.01(—▲—), 0.02(—○—), 0.04(—△—), and 0.10(—●—).

in the nitrobenzene phase were the same (Fig. 1a). On the other hand, the polarized potential range for Cell (II) was narrower in comparison with those for Cell (I) irrespective of the presence of HTMATPB (Fig. 1b). This is probably due to the transfer of Br^- ions from the aqueous phase to the nitrobenzene phase in the negative extreme range of the polarized potential. The standard ion transfer potential of Br^- ion is −0.295 V and is at least 30 mV more positive than that of Cl^- ion.[11] Figure 1b shows that there still remains a polarized potential range of about 300 mV. The electrocapillary measurements for Cells (I) and (II) were made within these polarizable potential ranges.

The electrocapillary curves were recorded at intervals of 20 mV for seven different concentrations of HTMATPB, from x=0 to 0.1. Some of the results are shown in Figs. 2 and 3. For both cases the interfacial tension was lowered with the increase of the HTMATPB concentration in the negative branch, i.e., $E^{W-}_{O-}-E_{pzc}<0$, where E_{pzc} is the potential of zero charge at x=0. This lowering of the interfacial tension indicates the existence of the specific adsorption of $HTMA^+$ ion at the interface.[9]

The electrocapillary curves at x=0.1 mol dm^{-3} for LiF, LiCl, and LiBr as the electrolyte in aqueous phase are compared in Fig. 4, in which the potential scale is relativized with respect to the E_{pzc} obtained with different reference electrodes. The degree of interfacial tension depression was larger in the sequence of LiF, LiCl, and LiBr. The result in Fig. 4 indicates that the specific adsorption of $HTMA^+$ ion is enhanced in this order. Since in the negative branch the potential of the aqueous phase is negative with respect to the nitrobenzene phase and the anionic species (F^-, Cl^-, or Br^-) exceeds the cationic species in the vicinity of the aqueous side of the interface, this enhancement of the adsorption strongly suggests the existence of a specific interaction between the charged head group of the adsorbed $HTMA^+$ ions and the anions in the aqueous side of the interface. This anion effect ensures that the polar head groups of the adsorbed $HTMA^+$ molecules are exposed to the aqueous phase so that it can interact with the counterion in the aqueous phase. The trend of the counterion effect in Fig. 4 is in marked contrast with the results reported by Watanabe et al.[6] They studied the adsorption of $HTMA^+$ ion at the methyl isobutyl ketone-water interface under the less polarized conditions compared with Cells(I) and (II) and found that the interfacial tension in the negative branch was decreased in the order, I^-, Br^-, Cl^-, and F^-.

The specifically adsorbed amount of the $HTMA^+$

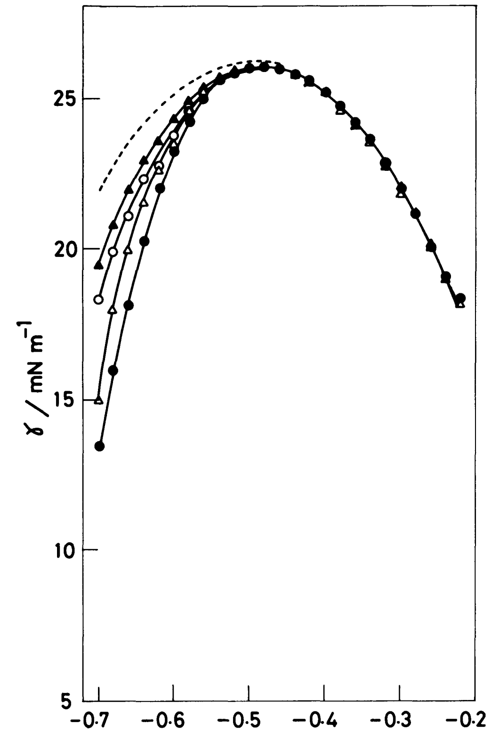

Fig. 3. Electrocapillary curves for the interface between aqueous solution of 0.05 mol dm^{-3} LiBr and nitrobenzene solution of (0.1−a) mol dm^{-3} TPnATPB+a mol dm^{-3} HTMATPB, where a= 0(-----), 0.02(−▲−), 0.03(−○−), 0.05(−△−), and 0.10(−●−).

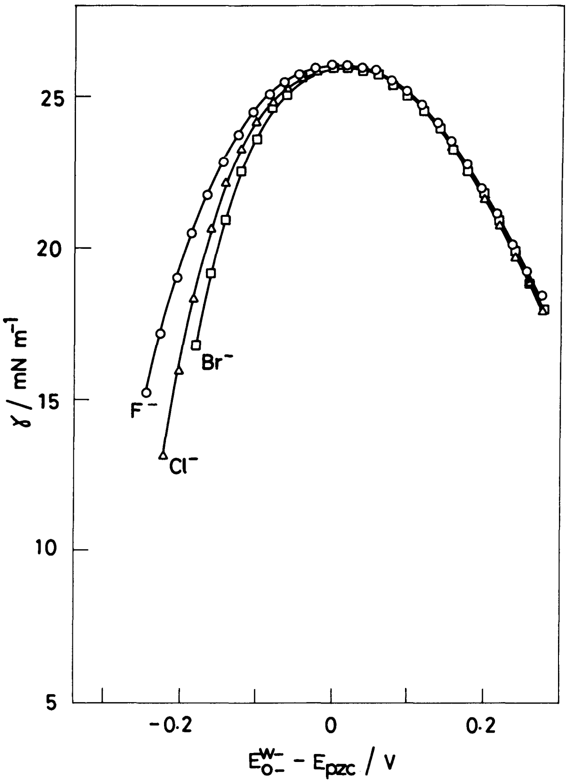

Fig. 4. Comparison of the electrocapillary curves for the interface between nitrobenzene solution of 0.1 mol dm^{-3} HTMATPB and aqueous solution of 0.05 mol dm^{-3} LiF(−○−), LiCl(−△−), or LiBr(−□−).

ions at a given potential was obtained from the electrocapillary curves by applying the electrocapillary equation modified for mixed electrolyte method.[9] The adsorption isotherms for both cases were well described by the Vorotyntsev's isotherm[14] which is a virial type isotherm of the form:

$$\ln(c/q^*) = \frac{\Delta G_a^0}{RT} + 2vq^*, \qquad (1)$$

In Eq. 1, c is the bulk concentration of the surface active compound, v is the interaction parameter, and q^* is the adsorbed amount expressed in μC cm^{-2} and is defined by $F\Gamma$, where F is Faraday and Γ the surface concentration. The adsorption free energy of HTMA$^+$ ion, ΔG_a^0, referrs to the standard states of 1 mol dm^{-3} and 1 μC cm^{-2} for the nitrobenzene solution and the adsorption layer, both based on infinite dilution. From the intercepts of $\ln(c/q^*)$ vs. q^* plots at the different potentials, ΔG_a^0's were obtained (Fig. 5). The results for LiCl reported previously are also included in Fig. 5. ΔG_a^0's were linearly dependent on the potential difference, which was also the case for LiCl. The slopes of the straight lines were 5.0×10^4, 5.0×10^4, and 3.8×10^4 C mol^{-1} for F$^-$, Cl$^-$, and Br$^-$, respectively. Thus, the curves for F$^-$ and Cl$^-$ are in parallel with each other, suggesting that the effect of the applied voltage on the ΔG_a^0 value is essentially in electrostatic nature.[9] The slope for Br$^-$ is smaller than these, but the difference is not very significant because of the experimental uncertainty. The vertical distance between these straight lines in Fig. 5 at a given potential can be seen as a direct and quantitative measure of the relative affinity of the polar head group of the HTMA$^+$ ion with the counterion in the aqueous phase. The difference in ΔG_a^0, $\Delta\Delta G_a^0$, is a quantitative measure of the affinity of the trimethylammonium head group of HTMA$^+$ ion with a counterion at the interface, provided that the maximum adsorptions of HTMA$^+$ for various counterions are the same. The maximum adsorption of the HTMA$^+$ ion is not likely to depend on the counterionic species. $\Delta\Delta G_a^0$'s at $E_{\text{O}-}^{\text{W}-} - E_{\text{pzc}} = -0.2$ V are shown in Table 1. $\Delta\Delta G_a^0$ for F$^-$–Br$^-$ pair is four times greater than $\Delta\Delta G_a^0$ for F$^-$–Cl$^-$ pair, suggesting the strong affinity of the trimethylammonio group and Br$^-$ ion at the interface. Larsen and Magid have found that the enthalpy change of Br$^-$ with respect to F$^-$ for the transfer of ion from water to 0.1 mol dm^{-3} HTMA$^+$ aqueous solution is also four times larger than the corresponding value of Cl$^-$ ion transfer.[15] This correspondence suggests the enthalpic nature of the factor that determines the counterion specificity.

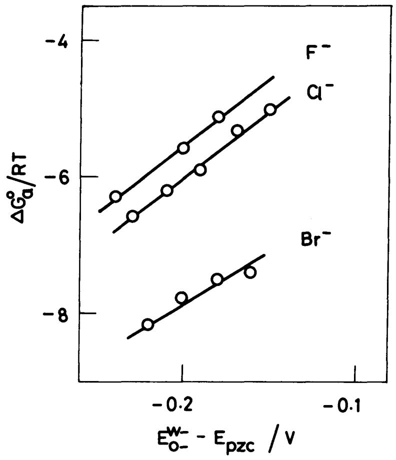

Fig. 5. Dependence of ΔG_a^0 of HTMA$^+$ ion on the potential drop across the interface between nitrobenzene and aqueous solution containing 0.05 mol dm^{-3} LiF, LiCl, or LiBr.

Table 1. Difference in Specific Interaction Energy of Halide Ions with Alkyltrimethylammonium Ions at Oil-Water Interfaces

Ion	$\Delta\Delta G_a^0$/kJ mol^{-1}			
	I[a]	II[b]	III[c]	IV[d]
F$^-$–Cl$^-$	2.2	—	2.5	1.2
F$^-$–Br$^-$	—	2.9	8.7	4.6

a) Davies.[5] b) Watanabe et al.[6] c) Goddard et al.[7] d) Present results.

Table 1 also includes the energies of the interaction between the counterion and the trimethylammonio head group of alkyltrimethylammonium ion surfactant in the monolayer estimated from various methods by Davies,[5] Watanabe et al,[6] and Goddard et al.[7] As shown in Table 1 all values obtained from three independent methods have the same order of magnitude. However, quantitatively there are discrepancies between them. Davies calculated the value from surface viscosity of the octadecyltrimethylammonium ion monolayer at the air-water interface. The value, therefore, involves the simplified assumptions which became necessary in order to estimate the interaction energies from kinetic data. Goddard et al. used the change in the surface pressure vs. area curves of docosyltrimethylammonium ion at the air-water interface at various subphase compositions. Their data also show the strong affinity of the trimethylammonio head group with Br$^-$. However, the values of $\Delta\Delta G_a^0$ are twice larger than ours. They assumed that the decrease of the surface pressure due to the specific interaction of HTMA$^+$ with the counterion was realized equivalently by increasing the ion concentration exhibiting no specific interaction with the head group. Since the specific adsorption, if any, cannot be solely attributed to the surface concentration term, their assumption is not likely to be valid in general.

Watanabe et al. calculated the ΔG_a^0 value employing the electrocapillary equation. It is interesting that they obtained a trend for ΔG_a^0 similar to ours, in spite of the fact that the effect of counterion on the surface tension depression in the electrocapillary curves they found was reverse to the present result as described above. They interpreted the lesser degree of interfacial tension depression in the negative branch as a decrease in the surface charge density caused by the counterion binding with the head group of the adsorbed surfactant. However, their interpretation contradicts the following thermodynamic reasoning of the surface charge density obtained from an electrocapillary curve. At constant temperature, pressure, and the potential, the electrocapillary equation may be written in the integral form:

$$\gamma^0 - \gamma = RT \int_0^c \Gamma \mathrm{d}\ln c, \tag{2}$$

where Γ is the surface excess, γ is the interfacial tension, and c is the concentration of a surface active substance. Thus, the magnitude of the interfacial tension depression is directly related to the adsorbed amount of the surfactant, rather than to the amount of ion-pairs formed at the interface. Secondly, the change in the surface charge density accompanied by the adsorption of a surface active substance can generally be expressed in terms of the adsorbed amount of the substance at the interface without resorting to the concept of counterion binding. It is known that the adsorption of most of the surface active substances at an electrified interface follows an adsorption isotherm of the form:[16]

$$\Gamma = \Gamma(\beta c) \tag{3}$$

where β is the adsorption coefficient and is related to ΔG_a^0 through $\Delta G_a^0 = -RT\ln\beta$. Then the change in the surface charge density, q, due to the adsorption of a surface active substance can be expressed through[17]

$$q - q^0 = RT\,\frac{\mathrm{d}\ln\beta}{\mathrm{d}E}\,\Gamma \tag{4}$$

where E is the electrical potential difference. Since $\mathrm{d}\ln\beta/\mathrm{d}E$ is not much different for F^-, Cl^-, and Br^- in the present results, the change in the slope of the electrocapillary curves can be attributed to the difference in the adsorbed amount of $HTMA^+$ ion and is not directly related to the counterion binding.

Further insight concerning counterion binding may be obtained from the electrocapillary equation in the presence of ion-pair formation at the interface. Suppose that a cation $\bar{i}$ in the oil phase and an anion $\bar{q}$ in the aqueous phase form a neutral species $\bar{i}_{\nu^+_{iq}}\bar{q}_{\nu^-_{iq}}$ due to ion-pair formation,

$$\nu^+_{iq}(\bar{i}) + \nu^-_{iq}(\bar{q}) = (\bar{i})_{\nu^+_{iq}}(\bar{q})_{\nu^-_{iq}}, \tag{5}$$

where ν^+_{iq} and ν^-_{iq} are the stoichiometric numbers. If we assume for simplicity that the ion-pair exists only at the interface and is present neither in the oil phase nor in the aqueous phase, the following additional terms appear in the right-hand side of the basic electrocapillary equation for oil–water interface (Eq. 16 in Ref. 18):

$$\Gamma_{\bar{i}\bar{q}}\left[\frac{\nu^+_{\bar{i}\bar{q}}}{\nu^+_{\bar{i}j'}}\mathrm{d}\mu_{\bar{i}j'} + \frac{\nu^-_{\bar{i}\bar{q}}}{\nu^-_{p'\bar{q}}}\mathrm{d}\mu_{p'\bar{q}} - \frac{\nu^+_{\bar{i}\bar{q}}z_{\bar{j}}}{\nu^-_{i'j'}|z_{j'}|}\mathrm{d}\mu_{i'j'} - \frac{\nu^-_{\bar{i}\bar{q}}|z_{\bar{q}}|}{\nu^+_{p'q'}z_{p'}}\mathrm{d}\mu_{p'q'}\right]$$
$$+ z_{\bar{i}}\nu^+_{\bar{i}\bar{q}}\,\Gamma_{\bar{i}\bar{q}}\left(\frac{1}{z_{i'}}\mathrm{d}\tilde{\mu}_{i'} + \frac{1}{|z_{q'}|}\mathrm{d}\tilde{\mu}_{q'}\right), \tag{6}$$

where $\tilde{\mu}$ is the chemical potential and z is the ionic charge. Equation 16 in Ref. 18 as well as these additional terms are derived for the case in which the reference electrodes in the oil phase and aqueous phase are reversible to the ions i' and q', respectively. The last term in the above expression shows that the term $z_{\bar{i}}\nu^+_{\bar{i}\bar{q}}\Gamma_{\bar{i}\bar{q}}$ contributes to the derivative of γ with respect to the potential, i.e.,

$$-\frac{1}{F}\left(\frac{\partial\gamma}{\partial E^{\mathrm{W}-}_{0-}}\right)_{T.P\mu} = \sum_p z_p\Gamma_p - \sum_q z_q\Gamma_q - z_{\bar{i}}\nu^+_{\bar{i}\bar{q}}\Gamma_{\bar{i}\bar{q}} \tag{7}$$

where p and q represent cations and anions in the aqueous phase. The first two terms on the r.h.s. of this equation represent the excess surface charge density in the aqueous phase. The surface charge density in the aqueous phase is negative in the potential range where the adsorption of the $HTMA^+$ ion takes place. Therefore, the additional term $z_{\bar{i}}\nu^+_{\bar{i}\bar{q}}\Gamma_{\bar{i}\bar{q}}$ contributes in this case to the derivative such that the decrease of the surface charge density due to ion-pair formation at the interface is compensated for. Thus, the ion-pair formation does not necessarily lead to the decreae of the apparent surface charge density given by the slope of the electrocapillary curve. Equation 7 shows that the slope of the electrocapillary curve at a given potential cannot be an unequivocal measure of the ion-pair formation at the interface, as was claimed by Watanabe et al.[6] The importance of the possible ion-pair formation at the oil–water interface was first pointed out by Girault and Schiffrin.[19]

Equation 7 also shows that when the ion-pair formation occurs at the interface, the second derivative of an electrocapillary curve with respect to the potential, $-\partial^2\gamma/\partial(E^{\mathrm{W}-}_{0-})^2$, does not generally accord with the double layer capacitance defined by $\partial q/\partial E$, where q is the excess free surface charge density.[20] The decrease of the excess free surface charge density caused by the ion-pair formation thus leads to a decrease in the double layer capacitance in comparison with that in the absence of the charge neutralization. In other words, the differential capacitance can be a useful means for detecting the ion-pair formation at the interface, if one combines the capacitance data with the electrocapillary curve data.

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