Bull. Chem. Soc. Jpn., ***60***, *3109—3115 (1987)*

The Effect of the Electrical Potential Difference on the Adsorption of the Hexadecyltrimethylammonium Ion at the Polarized Nitrobenzene–Water Interface

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(Received March 4, 1987)

The adsorption of the hexadecyltrimethylammonium ion($HTMA^+$) at the polarized nitrobenzene–water interface has been studied using electrocapillary measurements. The adsorption of $HTMA^+$ was found to be markedly dependent on the potential drop across the interface. $HTMA^+$ exhibited no specific adsorption in the potential range where the aqueous phase is positive, whereas a strong adsorption occurred in the potential range where the electric potential in the aqueous phase is negative with respect to that in the nitrobenzene. The adsorption free energy depends linearly on the potential difference across the interface. The specific adsorption of $HTMA^+$ significantly alters the double-layer structure. The outer Helmholtz potential in the nitrobenzene phase was inverted from negative to positive due to the adsorption of $HTMA^+$ ions.

The electrical aspects of the adsorption of molecules and ions at metal–solution interfaces have been studied extensively, and now the double-layer structure and the adsorption mechanism have been elucidated in detail.[1] In contrast, much fewer studies have appeared for oil–water interfaces, and even fewer for air–water interfaces, mainly because of the difficulty of controlling the electrical potential difference between the phases.

Guastalla[1] first reported the change in the interfacial tension with an externally applied potential for the interface between nitrobenzene and water in the presence of the $HTMA^+$ ion. He suggested the "electroadsorption" model for the interpretation of the phenomena. Since then, the adsorption phenomena of ionic surfactants at oil–water interfaces under the influence of an externally applied electric field have been studied by Blank et al.,[3,4] Watanabe et al.,[5,6] Dupeyrat et al.,[7,8] Gavach et al.,[9–11] and Joos et al.[12,13] In the study of the adsorption of various ionic surfactants at the methyl isobutyl ketone–water interface, Watanabe et al. adopted the concept of electrocapillarity,[5] thereby introducing a thermodynamic point of view for the interpretation of electrosorption phenomena at oil–water interfaces. However, in most of the preceding studies of the adsorption phenomena at oil–water interfaces, the electrical state of the interface has not been well-defined, making an unambiguous interpretation of the results difficult. This is partly because of the uncertainty concerning the polarizability of the interfaces employed and partly because of the lack of suitable reference electrodes to define the electrical potential.

It has been shown recently that the polarizability of oil–water interfaces can be characterized in terms of the transfer free energy of ions dissolved in the two neighboring phases,[14] and experimentally[15] we can make the interface virtually ideally polarized by suitably choosing the ions dissolved in the phases. The rigorous thermodynamics of the electrocapillarity of oil–water interfaces[16] and the experimental study of the double layer structure of polarized nitrobenzene–water interfaces[17] have also been presented recently. By using such polarized interfaces, we are now able to study the adsorption of surfactants and ions at the oil–water interfaces in depth as cases of the electrosorption studies at metal–solution interfaces.[1] Only through this polarized type of interface can the electrical aspects of surfactants adsorption in equilibrium be fully explored. The electrocapillarity of nonpolarized oil–water interfaces has also been studied.[18–22] The advantage of an ideal polarized interface over a nonpolarized one in studying the adsorption behavior of surfactants is that it has an additional degree of freedom for the electrical parameter: Electrostatic potential difference or excess surface-charge density. This enables us to estimate the charge due to specifically adsorbed ions separately from the total excess-charge density.[16] The aim of this study is to establish such a new experimental approach for studying the electrochemical aspects of surface phenomena at oil–water interfaces. This paper will report the adsorption properties of the hexadecyltrimethylammonium ion, $HTMA^+$, at the polarized nitrobenzene–water interface, across which the potential difference is regulated externally.

Experimental

The interfacial tension of the nitrobenzene–water interface was measured by means of the drop-time method using a drop-by-drop ascending electrolyte solution electrode.[15] The potential drop across the interface was controlled using a four-electrode potentiostat with a positive feed back circuit for *iR* compensation. The details of the measurements and the conversion of the drop time to interfacial tension have been reported elsewhere.[23] All the measurements were made at 25.00±0.05 °C.

The hexadecyltrimethylammonium tetraphenylborate

(HTMATPB) was prepared from hexadecyltrimethylammonium chloride and sodium tetraphenylborate and was recrystallized twice from acetone. The tetrapentylammonium tetraphenylborate(TPnATPB) and lithium tetraphenylborate were prepared as has been described previously.[24] The nitrobenzene was distilled under reduced pressure, and the middle portion of the distillate was used for preparing the solution. The water was triply distilled.

Results

We used the mixed electrolyte method,[25,26] in which the sum of the concentrations of TPnATPB and HTMATPB in nitrobenzene is held constant at 0.1 mol dm^{-3}, while the concentration of HTMA$^+$ is varied. The TPnA$^+$ ion shows no specific adsorption at the nitrobenzene–water interface.[27] The TPB$^-$ ion is also known to show no specific adsorption.[17] Accordingly, this mixed-electrolyte-solution method allows us to obtain the specifically adsorbed amount of HTMA$^+$ directly from the electrocapillary data.[25,26] An additional advantage of this method here is that it enables us to avoid the undesirable decrease in the conductivity in the nitrobenzene phase in the lower concentration range of HTMATPB.

The electrochemical cell employed in this study may be represented thus;

I	II	III	IV	V	VI	VII	VIII	
Ag	AgCl	1 mM LiCl (W)	1 mM LiTPB (W)	(0.1−x) M TPnATPB + x M HTMATPB (NB)	0.05M LiCl (W)	AgCl	Ag	(I)

where M designates mol dm^{-3} and where x was varied between 0 and 0.1. The nitrobenzene phase V contains TPnATPB and HTMATPB, such that the sum of the concentrations of these salts is 0.1 mol dm^{-3}. The HTMA$^+$ ion was thus dissolved in the nitrobenzene phase as a TPB salt. This is a key point for the study of the adsorption of the HTMA$^+$ ion when the interface is polarized. If we add the HTMA$^+$ ion to the aqueous phase, then the HTMA$^+$ ion will immediately commence transferring across the interface to dissolve into the nitrobenzene phase anywhere in the potential range studied; hence, it will be impossible to achieve the polarization condition of the interface. This is because the standard ion-transfer potential of the HTMA$^+$ ion is greatly negative; i.e., HTMA$^+$ as a whole is a very hydrophobic ion, as will be described below. The aqueous phase VI contains 0.05 mol dm^{-3} LiCl, while Phases III and IV contain 1 mmol dm^{-3} LiCl, and 1 mmol dm^{-3} LiTPB respectively. The interface between Phases V and VI is a polarized interface. The other nitrobenzene–water interface between Phases IV and V is a nonpolarized one, across which the potential drop is determined by the activities of the TPB$^-$ ions in the two adjacent phases,[24] i.e., the interface reversible to the TPB$^-$ ion. The reference electrode reversible to TPB$^-$ ion is essential in detecting the specific adsorption of cations in the nitrobenzene phase.[25,26] Since the concentrations of the TPB$^-$ ion in Phase IV and in Phase V are constant, the potential across the interface between Phases IV and V may be taken as constant, even when the concentration of HTMA$^+$ ion is varied. The liquid junction potential at the interface between Phases III and IV is also unaltered. Consequently, the change in the potential difference between the terminals of Cell (I) is directly related to the change in the potential difference across the polarized nitrobenzene–water interface. We denote the potential of the right-hand side of Cell (I), referred to that of the left, as $E^{\mathrm{W}-}_{0-}$, where the super- and subscripts indicate that the reference electrodes in the aqueous and nitrobenzene phases are both reversible to the anions.

Figure 1 shows the current-potential curves for Cell (I) when the concentration of the HTMA$^+$ ion in Phase V, c, equals 0 (Curve 1) and 0.1 (Curve 2) mol dm^{-3}. The polarized potential range where the current passing through the interface is negligible is between −0.55 and −0.2 V for c=0; i.e., the interface has a potential window of 0.35 V voltage span. The current-potential curve for c=0.1 mol dm^{-3} also has almost the same polarized potential range, demonstrating that the adsorption of HTMA$^+$ as well as the double layer structure of the interface can be studied under a polarized condition. This sugests that

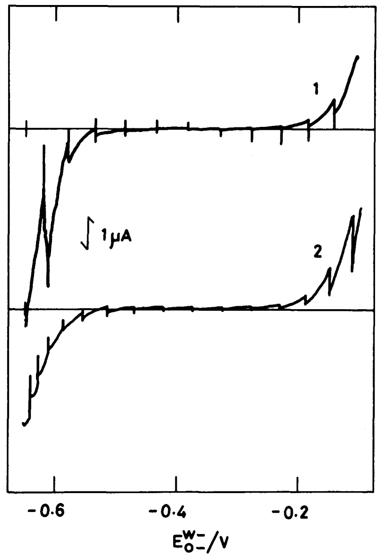

Fig. 1. Current-potential curves recorded using dropwise ascending electrolyte solution electrode for 0.05 mol dm^{-3} LiCl in water and 0.1 mol dm^{-3} TPnATPB(Curve 1) or 0.1 mol dm^{-3} HTMATPB-(Curve 2) in nitrobenzene.

the standard ion-transfer potential of the $HTMA^+$ ion is at least not more positive than those of the Cl^- and $TPnA^+$ ions.

The electrocapillary equation for Cell (I) at a constant temperature and pressure is given by:[16,26]

$$-d\gamma = q^{w}dE^{w-}_{0-} + \Gamma_{TPnA^+}RTd\ln(1-m) + \Gamma_{HTMA^+}RTd\ln m \qquad (1)$$

where γ is the interfacial tension, q^w is the excess surface-charge density in the aqueous phase, E^{w-}_{0-} is the potential of the terminal of the right hand side of Cell (I) with respect to the left, Γ_j is the relative surface excess of the j ion (j=$TPnA^+$ and $HTMA^+$), and m=x/0.1. R and the T are the gas constant and the absolute temperature respectively. In deriving Eq. 1, the activity coefficients of the ions in Phase V are assumed to be constant when the composition of this phase is changed. This assumption will not introduce any serious error, because the ionic strength in Phase V is kept constant. If we assume that Γ_{TPnA^+} and the nonspecifically adsorbed portion of Γ_{HTMA^+} follow the Gouy-Chapman diffuse layer theory, Eq. 1 may be rewritten as:[25,26]

$$-d\gamma = q^{w}dE^{w-}_{0-} + \Gamma^{1}_{HTMA^+}RTd\ln m + RTm\left[\int_{x_1}^{x_2}\left\{\exp\left(-\frac{F\varphi}{RT}\right)-1\right\}dx\right]d\ln m \qquad (2)$$

where $\Gamma^1_{HTMA^+}$ is the specifically adsorbed amount of the $HTMA^+$ ion, φ is the the electrostatic potential, F is the Faraday constant, and x_1 and x_2 are the positions of the outer Helmholtz planes in the nitrobenzene phase for the $HTMA^+$ and $TPnA^+$ ions respectively. The last term in the r.h.s. of Eq. 2 represents the contribution that arises from the difference in the size of the ions. In the following, we will neglect this last term. Therefore, the change in γ due to the change of m may be considered to be a direct measure of the specific adsorption of the $HTMA^+$ ions. (The term *specific adsorption* refers to the part of the adsorption which cannot be explained by the Gouy-Chapman theory.)

Figure 2 shows the electrocapillary cruves for a given cocentration of HTMATPB. The interfacial tension decreases with the increase in the concentration of $HTMA^+$ in the potential range negative to the electrocapillary maximum (ecm), which we will hereafter call "the negative branch," while the interfacial tension remaines unchanged in the potential range positive to the ecm, "the positive branch." Obviously, the $HTMA^+$ ion specifically adsorbs only in the potential range where the potential of the aqueous phase is negative with respect to that of the nitrobenzene phase. At the potential in the neighborhood of the ecm, the change in the interfacial tension with $HTMA^+$ concentration is very small, indicating that the adsorption at the ecm is almost negligible. The specifically adsorbed amount of $HTMA^+$ was calculated from the electrocapillary curves through Eq. 2 by using numerical differentiation with a third-order B-spline function.[28] The results are plotted in electrical units, q^*=$F\Gamma^1_{HTMA^+}$, in Fig. 3 as a function of E^{w-}_{0-}. As is to be expected from the electrocapillary curves, the specific adsorption of the $HTMA^+$ ion in the negative branch increases with the concentration and with the decrease in the potential.

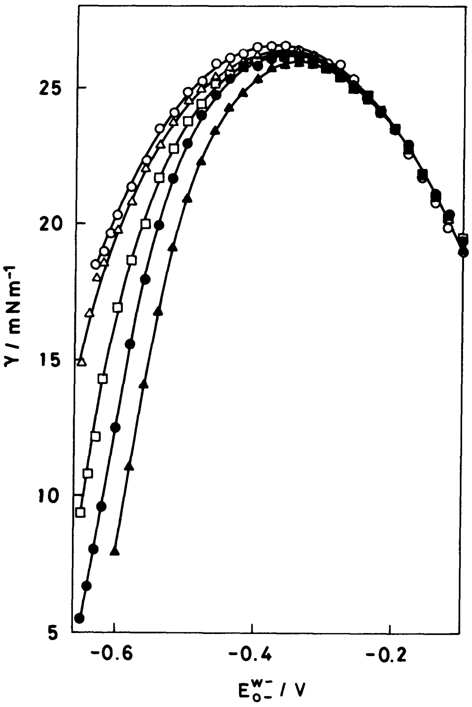

Fig. 2. Electrocapillary curves for the interface between 0.05 mol dm^{-3} LiCl aqueous solution and (0.1−x) mol dm^{-3} TPnATPB+x mol dm^{-3} HTMATPB nitrobenzene solution at 25 °C: x=0(○), 0.005(△), 0.02(□), 0.05(●), and 0.1(▲).

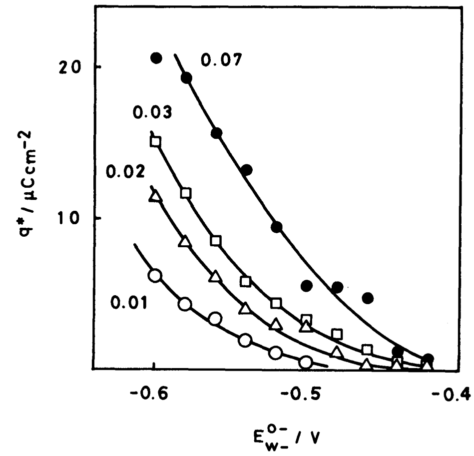

Fig. 3. Specifically absorbed change q^*=$F\Gamma^1_{HTMA^+}$ of $HTMA^+$ for c=0.01(○), 0.02(△), 0.03(□), and 0.07(●) mol dm^{-3}.

Figure 4 shows the adsorption isotherms for HTMA$^+$ for different values of E_{0-}^{w-}. These isotherms were analyzed with a virial isotherm of the form:

$$\ln\left(\frac{c}{q^*}\right)=\frac{\Delta G_a{}^0}{RT}+2vq^* \tag{3}$$

where $\Delta G_a{}^\circ$ is the adsorption free energy and where v is the second virial coefficient. This isotherm at a given electrode potential was recently proposed by Vorotyntsev;[29,30] it is suitable for describing the adsorption of ions at the metal–solution interface, especially when the discreteness-of-charge effect previals at a lower surface coverage. The $\ln(c/q^*)$ vs. q^* plots at a given value of E_{0-}^{w-} were found to be straight lines (Fig. 5), indicating that Eq. 3 well describes the present experimental isotherms. We also tested the isotherm based on the Grahame–Parsons model of the inner layer at a constant q^{w}[31,32] and obtained.a less satisfactory fitting of the experimental data. In particular, the $\Delta G_a{}^\circ$ value thus obtained increased with the decrease in E_{0-}^{w-}, which seems physically unreasonable.

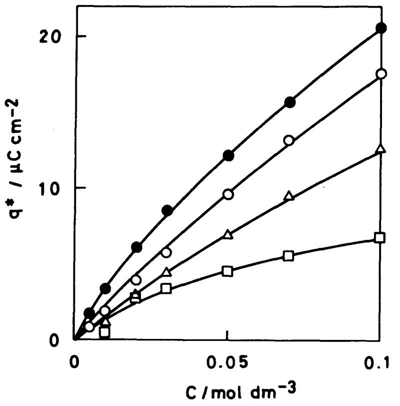

Fig. 4. Adsorption isotherms for specifically adsorbed HTMA$^+$ ions at E_{0-}^{w-}=−0.50(□), −0.52(△), −0.54(○), and −0.56(●)) V.

Discussion

The results clearly indicate that the adsorption of the HTMA$^+$ ion at the nitrobenzene–water interface has a remarkable dependence on E_{0-}^{w-} and, hence, on the potential drop across the interface. This is in marked contrast with the case of the nonionic surfactant adsorption at oil–water interfaces; e.g., Span 60 showed a positive adsorption throughout the polarized potential range at the nitrobenzene–water interface.[33] The fact that the HTMA$^+$ ion does not adsorb in the positive branch means that even a surfactant may not exhibit any surface activity, depending on the electrical potential drop across the interface. In the negative branch, the apparent surface activity of HTMA$^+$ increases with the increase in the potential difference. A similar asymmetric adsorption has previously been reported by Watanabe et al. for various ionic surfactants, but they used less polarized and, hence, electrochemically less characterized, methyl isobutyl ketone–water interfaces.[5]

The adsorption free energy for HTMA$^+$ was evaluated from the intercepts of the plots in Fig. 5. The $\Delta G_a{}^\circ$ value thus obtained refers to the reference states of infinite dilution for both nitrobenzene and adsorption layers and to the standard states of 1 mol dm^{-3} for the nitrobenzene solution and of 1 μC cm^{-2} for the adsorption layer. $\Delta G_a{}^\circ$ values are plotted in Fig. 6 against E_{0-}^{w-} (Curve 1). $\Delta G_a{}^\circ$ was linearly dependent of E_{0-}^{w-}. The slope of this plot gave 5.0×10^4 C mol^{-1}. In general, various factors contribute to the dependence of $\Delta G_a{}^\circ$ on the potential difference across the interface. The change in the applied potential causes not only the change in the inner-layer structure, but also the change in the diffuse-layer structure in the aqueous phase. The effect of the diffuse layer on the aqueous side of the

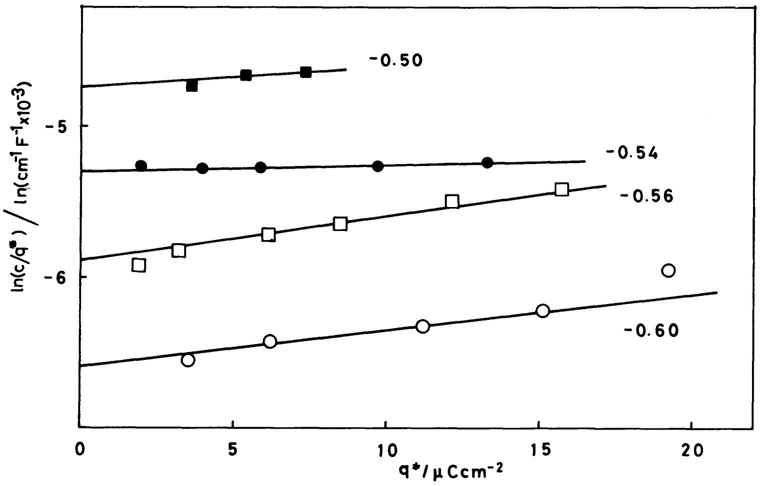

Fig. 5. Plots of $\ln(c/q^*)$ against q^* at E_{0-}^{w-}=−0.50(■), −0.54(●), −0.56(□), and −0.06(○) V.

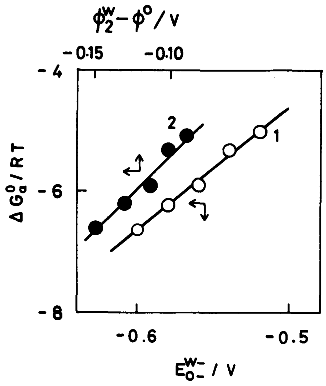

Fig. 6. Absorption free energy of HTMA$^+$, $\Delta G_a°$, as a function of E_{0-}^{W-} (Curve 1) and of φ_2^W-φ^0 (Curve 2).

interface on $\Delta G_a°$ is appreciable, especially when the head group of the HTMA$^+$ ion in its adsorption state is exposed to the aqueous phase. If the head group protrudes into the aqueous phase while leaving the hydrocarbon chain in the aqueous phase,[6)] we may expect that the electrical work required to bring the charged head group of a HTMA$^+$ ion from a bulk nitrobenzene phase to a certain point in the aqueous phase, e.g., the outer Helmholtz plane (OHP), constitutes a significant part of $\Delta G_a°$. Then, the change in the potential difference between the bulk of the nitrobenzene phase and the adsorption site caused by the change in E_{0-}^{W-} must contribute greatly to the dependence of $\Delta G_a°$ on E_{0-}^{W-} shown in Fig. 6. If we assume that the head group of an adsorbed HTMA$^+$ ion is located at the OHP in the aqueous phase, then the effective potential difference for the electrical work in the adsorption process will be $\varphi_2^W-\varphi^0$, where φ_2^W and φ^0 are the potentials at the OHP in the aqueous phase and in the bulk of the nitrobenzene phase. $\Delta G_a°$ is replotted in Fig. 6 as a function of $\varphi_2^W-\varphi^0$ on the rational potential scale (Curve 2).[34)] The slope was 6.8×10^4 C mol^{-1}. On the other hand, the electrical work for the transfer of 1 mol of monovalent ions across the potential difference of 1 V is 9.6×10^4 J mol^{-1}, and the change in this work with the potential difference is 9.6×10^4 C mol^{-1}. This is of the same order of magnitude as the experimental result, suggesting a large contribution of this electrical work to $\Delta G_a°$. The difference between the two values can be interpreted by assuming that the location of the adsorption site of the head group is on the nitrobenzene side of the OHP in the aqueous phase. In this case, the head group would not be fully exposed to the aqueous phase, and the effective potential difference should be smaller than $\varphi_2^W-\varphi^0$. However, our preliminary findings about the effect of the counterion in the aqueous phase on the adsorption of HTMA$^+$[35)] strongly suggest that the head group resides within the aqueous phase. Hence, the numerical difference between these two values seems to indicate the presence of other contributions including those opposing the electrostatic work. One such possible contribution is the work to replace the solvent molecules in the interfacial region with the head group and the hydrocarbon tail of the HTMA$^+$ ion. Since the dielectric constant of the interfacial region is probably higher than that of the hydrocarbon part of the HTMA$^+$ ion, this replacement gives rise to a positive contribution to the adsorption free energy.[36)] According to Frumkin's two-parallel-plate condenser model for the adsorption of organic compounds on electrodes, this part of the adsorption free energy depends quadratically on the electrode potential. The range of E_{0-}^{W-} studied is perhaps not enough to detect such a quadratic dependence. It is also probable that there exists another factor which counteracts this quadratic term, leading to an apparent linear dependence. For example, the increase in the concentration of Cl$^-$ at the OHP in the aqueous phase with the negative increase in E_{0-}^{W-} can increase the adsorption of HTMA$^+$ not only by screening the repulsion between the adsorbed HTMA$^+$ ions, but also by enhancing the salting-in effect for the head group of HTMA$^+$.

The change in $\Delta G_a°$ with E_{0-}^{W-} is thermodynamically related to the change in q^W accompanied by the adsorption:[37)]

$$\left(\frac{\partial q^W}{\partial \Gamma^1_{\mathrm{HTMA^+}}}\right)_{E_{0-}^{W-}} = -\frac{d\Delta G_a^0}{\mathrm{d}E_{0-}^{W-}} \tag{4}$$

Thus, the linear variation in $\Delta G_a°$ in Fig. 6 implies that q^W should also vary linearly with $\Gamma^1_{\mathrm{HTMA^+}}$. Figure 7 shows the plots of q^W as a function of q^* at different values of E_{0-}^{W-}. All q^W vs. q^* curves gave straight lines whose slopes are very close to each other. The slope at $E_{0-}^{W-}=-0.54$ V was 4.1×10^4 C mol^{-1}, which is very close to the value obtained from Fig. 6. This agreement ensures the internal consistency of the data analysis. It should be noted that the positive value of

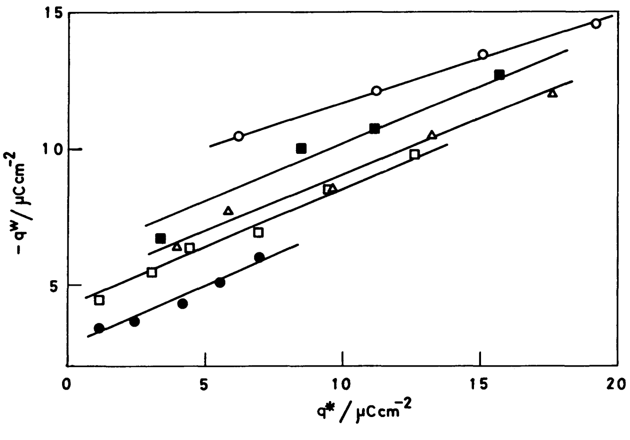

Fig. 7. Change of q^W as a function of q^* at a given value of E_{0-}^{W-}: $E_{0-}^{W-}=-0.48$(●), -0.52(□), -0.54(Δ), 0.56(●), and -0.60(○) V.

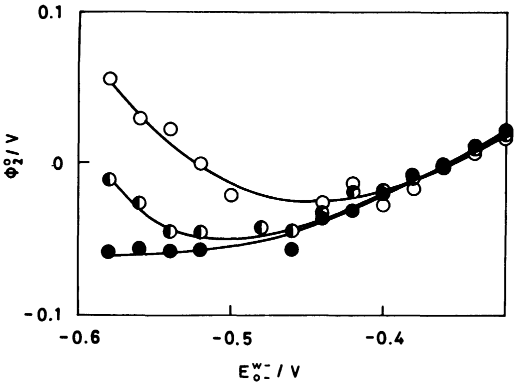

Fig. 8. Change of the potential at the outer Helmholtz plane in the nitrobenzene phase φ_2^0 with the change of E_{0-}^{W-} for the concentrations: c=0.01 (●), 0.02(○), and 0.05(○) mol dm^{-3}.

$(\partial q^W/\partial \Gamma^1_{HTMA^+})E_{0-}^{W-}$ means that the double layer capacity should increase with the adsorption of the HTMA$^+$ ion, because q^W at a constant E_{0-}^{W-} increased with the increase in $\Gamma^1_{HTMA^+}$.

The values of the interaction parameter v obtained from Fig. 5 were in the range from 0.002 to 0.015 cm^2 C^{-1}. These values are considerably lower than those estimated in the adsorption of inorganic ions at a metal–solution interface.[29] Since the intermolecular interaction between the hydrocarbon chains of adsorbed surfactants is usually small at oil–water interfaces,[38] the present results suggest that the repulsive interaction between the charged head groups is very weak.

The double-layer structure of the nitrobenzene–water interface is significantly altered by the adsorption of HTMA$^+$ ions. Figure 8 shows the φ_2^0 potential plotted against E_{0-}^{W-} for a given value of the concentration of the HTMA$^+$ ion. In the negative potential range, the sign of the φ_2^0 potential is inverted from negative to positive, that is, the specifically adsorbed charge q^* exceeds the excess charge density in the aqueous phase, q^W. The double layer structure in the presence of HTMA$^+$ adsorption in the negative branch is illustrated in Fig. 9. Thus, the adsorption of the HTMA$^+$ ion drastically affects the double layer structure especially, resulting in a change in the distribution of the potential across the interface. One important consequence of such an inversion of the φ_2^0 potential is that, by introducing ionic surfactants at the interface, one can modify the electric field sensed by ions participating in ion-transfer reaction through the interface. It may be noted that the φ_2^0 potential thus obtained is of average character and that the *micro potential*[39] could be less affected by the HTMA$^+$ adsorption, since the surface coverage of HTMA$^+$ achieved in the present study was at most 0.4, where the discreteness of the charge is certainly not negligible.

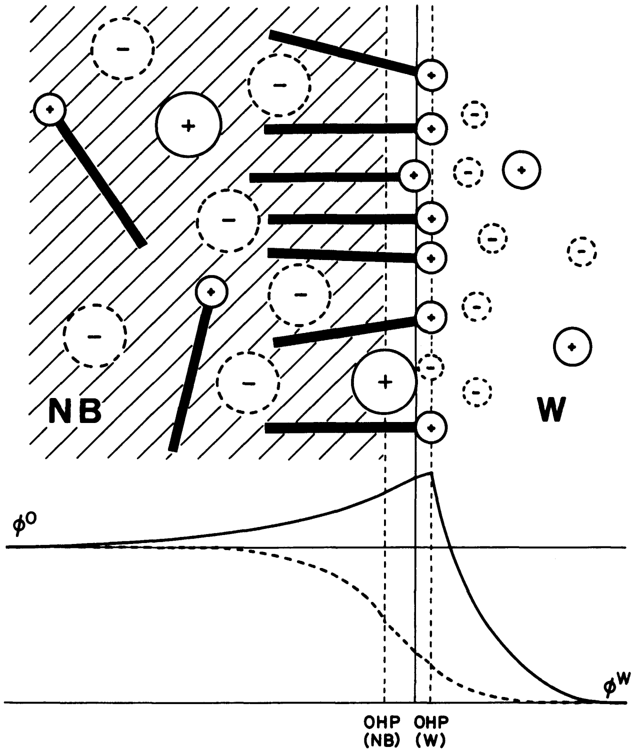

Fig. 9. Schematic representation of the double layer structure of the interface between nitrobenzene and aqueous solutions in the negative branch in the presence of the specific adsorption of HTMA$^+$ ions.

In conclusion, the adsorption of the HTMA$^+$ ion showed marked asymmetry with respect to the electrical potential applied across the interface. Such a dependence of the adsorption on the electrical potential difference is of great importance for the physical chemistry of emulsions, liposomes, micelles, and artificial and biological membranes. This potential dependence provides us with the possibility of regulating the surface activity of surfactants by applying the electrical potential difference across the interface. In the present study, the composition of the aqueous phase was held constant. If we change the composition of the aqueous phase while keeping that of the oil phase constant, then the change in the adsorption characteristics of the ions in the aquous phase due to the presence of surfactant adsorption can be investigated thermodynamically. This approach seems particularly useful in studying counterion effects in surfactant adsorption. Along this line, subsequent papers will deal with the effect of counterions in the aqueous phase on the adsorption properties of ionic surfactants.

This work was supported by Grant-in-Aids for Scientific Research No. 60211017 from the Ministry of Education, Science and Culture.

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23) See. Ref. 15. The Eq. 1 in Ref. 15 for the calculation of the interfacial tension has some typographical errors; the term on the l.h.s. and the first term on the r.h.s. of Eq. 1 should be read as:

$$\frac{vt_{\mathrm{d}}}{3} \text{ and } \sigma^{3}\ln\left[\frac{x^{0}(1-\sigma x)}{x(1-\sigma x_{0})}\right]$$

respectively.

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