

Polarizability and Electrocapillary Measurements of the Nitrobenzene-Water Interface

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Electrocapillary curves have been measured of the interface between nitrobenzene solution of tetrabutylammonium tetraphenylborate and aqueous solution of lithium chloride using a dropping electrolyte solution electrode under the precise control of the electrical potential difference and of the ion transfer current across the interface. The nitrobenzene–water interface could be electrically polarized over the voltage span of 300 mV. The residual current was explained as due to both the transfer of tetrabutylammonium ion and tetraphenylborate ion through the interface and the charging current at the interface. The electrocapillary curve was parabolic in shape. The surface charge *vs.* potential curve derived from the electrocapillary curve agreed with that obtained from the differential capacity *vs.* potential curve of the interface. The results indicate that the interface can virtually be treated as an ideal polarized interface over a certain potential range.

This paper describes the measurements of electrocapillary curves at the polarizable interface between aqueous solution of lithium chloride and nitrobenzene solution of tetrabutylammonium tetraphenylborate by the drop time method using a dropping electrolyte solution electrode. Guastalla¹⁾ was the first to show that an electric field across the interface between two immiscible solutions containing ions and ionic surfactants produces changes in the interfacial tension and he called his finding "electroadsorption." Since then, such phenomena have been studied mainly by Blank and Feig,²⁾ Blank,³⁾ Watanabe *et al.*,^{4,5)} Dupeyrat and Michel,⁶⁾ Gavach *et al.*,^{7–10)} Joos,^{11,12)} and Dupeyrat and Nakache.¹³⁾ Watanabe considered it to be electrocapillarity, while Blank and Feig and also Dupeyrat and Nakache made a distinction between electroadsorption and electrocapillarity. In most of these works, except the recent ones by Gavach *et al.*,^{9,10)} however, the electrical potential and the current across the interface were neither controlled nor measured precisely enough to define the electrical state of the interface.

Recently, polarizability of the interface between two immiscible electrolyte solutions has been discussed on the basis of the transfer free energies of ions from one solvent to the other by Koryta *et al.*,¹⁴⁾ who have showed that one can endow the liquid–liquid interface with electrical polarization in a certain range of the potential difference across the interface by choosing suitable ions to be dissolved in the two phases, *e.g.*, lithium chloride in water and tetrabutylammonium tetraphenylborate (TBATPB) in nitrobenzene. Such polarizable interfaces have been extensively used in electrochemical studies^{15,16)} of ion transfer and electron transfer at the interface.

An interface of two immiscible electrolyte solutions, which behaves practically as an ideal polarized interface, if realized, can be a subject of rigorous thermodynamic theory of an ideal polarized interface and, hence, the electric double layer structure of the interface can be elucidated on the basis of electrocapillary measurements. The purpose of this study is to demonstrate experimentally the existence of such polarized interfaces where there is only negligible ion transfer current through the interface and to establish an experimental method for electrocapillary measurements

under the precise control of the potential difference across the interface.

Experimental

A dropping electrolyte solution electrode¹⁴⁾ (DESE) was used to record current–potential curves and to determine electrocapillary curves at a polarized nitrobenzene–water interface. Figure 1 shows the cell configuration used in this study. An aqueous solution, 1, was dropped upward into a nitrobenzene solution, 2, from the tip of a poly(tetrafluoro-

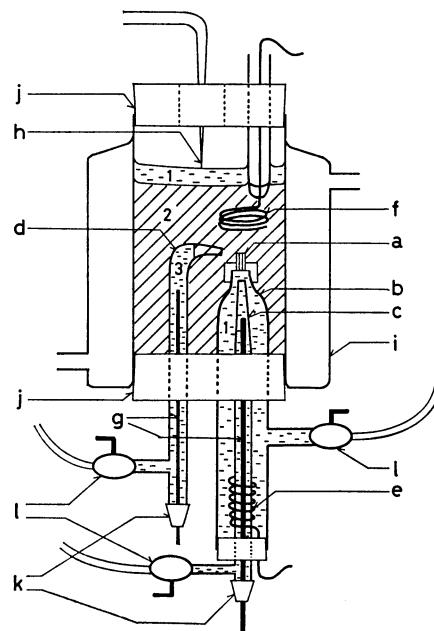


Fig. 1. Electrochemical cell with dropping electrolyte solution electrode for measuring current–potential curves and electrocapillary curves at nitrobenzene–water interface.

(1) 0.1 mol dm⁻³ LiCl aqueous solution; (2) 0.1 mol dm⁻³ TBATPB nitrobenzene solution; (3) 0.1 mol dm⁻³ TBACl aqueous solution; (a) dropping electrolyte solution electrode tip; (b) glass tube; (c and d) reference electrodes with Luggin capillaries; (e and f) auxiliary electrodes; (g) Ag/AgCl electrodes; (h) fine glass capillary; (i) water-jacketed cell; (j) silicon rubber stopper; (k) silicone rubber cap; (l) stop cock.

ethylene) (PTFE) capillary, a, whose inner diameter and length were 0.5 and 4 mm, respectively. The PTFE capillary was fitted on the top opening of a glass tube, b. By using a PTFE capillary, which neither water nor nitrobenzene wets the surface of, very reproducible drop time was achieved. The cell had four electrodes, *i.e.*, two reference electrodes (c and d) and two auxiliary electrodes (e and f) to meet with a four-electrode potentiostat^{17,18)} for precise control of the potential drop across the interface. The reference electrodes were Ag/AgCl electrodes, g, immersed in 0.1 mol dm⁻³ LiCl aqueous solution, 1, and in 0.1 mol dm⁻³ tetrabutylammonium chloride (TBACl) aqueous solution, 3. Luggin capillaries sensed the potential of the aqueous and nitrobenzene phases, respectively, in close proximity to the DESE. The auxiliary electrodes were coiled platinum wires. A fine glass capillary, h, was connected to an aspirator to suck off excess aqueous solution flowing out of the DESE, so that the hydrostatic pressure above the tip of the DESE was kept constant during each measurement. The cell assembly was mounted on a heavy molding board which was placed on four cushions made of rubber damper plates and soft rubber balls. This table effectively eliminated most of ambient vibration and resulted in good reproducibility of the drop time of the DESE. The cell was water-jacketed (i in Fig. 1) to maintain the temperature of the cell at 25.00±0.05 °C.

The DESE was connected to an electrolyte solution reservoir of a 200 ml separatory funnel through a PTFE tubing of 2 mm inner diameter. In the middle of this PTFE tubing a PTFE capillary of 0.25 mm inner diameter and 6 m length was inserted to regulate the flow rate of aqueous electrolyte solution. The flow rate, v , was typically 3×10^{-4} cm³ s⁻¹ when the height of the solution reservoir, H , was 75 cm. The PTFE capillary regulator was immersed in a water bath controlled at 25.00±0.05 °C to regulate precisely the flow resistance, $\alpha=v/H$, of the PTFE capillary regulator. The flow rate was determined to the precision of 0.01×10^{-4} cm³ s⁻¹ using a 1 ml serological pipet and the α -value of the DESE was determined to be 4.63×10^{-6} cm² s⁻¹ for 0.1 mol dm⁻³ LiCl at 25.00±0.05 °C.

For converting the drop time, t_d , to the interfacial tension, γ , we used the following two equations,^{19,20)} which have been derived by assuming a spherical drop:

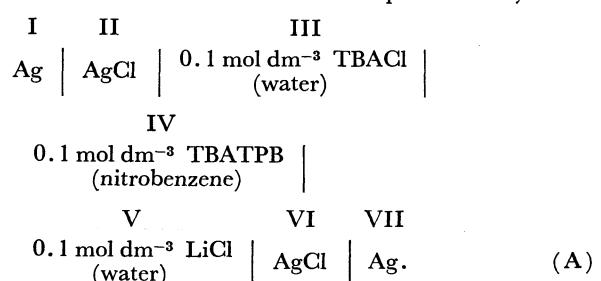
$$\frac{\alpha t_d}{3} = \sigma^3 \ln \left(\frac{x_0(1-x)}{x(1-x_0)} \right) + \sigma^2 \left(\frac{1}{x} - \frac{1}{x_0} \right) + \frac{\sigma}{2} \left(\frac{1}{x^2} - \frac{1}{x_0^2} \right) + \frac{1}{3} \left(\frac{1}{x^3} - \frac{1}{x_0^3} \right) \quad (1)$$

$$\Delta \rho g/x^3 = 2\pi r y [1 - r(4\pi/3)^{1/3} x] \quad (2)$$

with $\sigma = 2\gamma(4\pi/3)^{1/3}/P$, $x = (3/4\pi)^{1/3}/R$ and $x_0 = (3/2\pi)^{1/3}/r$, where R is the radius of a drop, r the radius of the orifice of the DESE tip, P the effective hydrostatic pressure, $\Delta \rho$ the difference between the densities of the nitrobenzene and the aqueous solution phases, and g is the acceleration of gravity. By solving these two simultaneous equations numerically, we obtain γ as a function of t_d for given values of α , r , P , and $\Delta \rho$. The density of the aqueous solution and nitrobenzene solution was determined using a Lipkin-Davison pycnometer. The r value was calibrated as 0.240 mm by using mutually saturated nitrobenzene and water at 25.0 °C, the value of 25.1 mN m⁻¹ being used for the interfacial tension.²¹⁾ The drop time, typically 50 s at $H=75$ cm, was measured to the precision of 0.01 s with an electronic stopwatch. The relative standard deviation of the drop time of the DESE was 0.2% for several consecutive drops.

Since the potential difference across the interface was

controlled with respect to the two reference electrodes, the electrochemical cell studied can be represented by



The interface between the phases III and IV is a non-polarizable one and the potential drop across the interface is determined by the activities of TBA⁺ ion in the two phases.^{18,22,23)} Therefore, the left-hand-side half cell, Ag/AgCl/III(W)/IV(NB), virtually functions as a reference electrode reversible to TBA⁺ ion in the nitrobenzene phase IV. The interface III/IV was made just inside the Luggin capillary in nitrobenzene phase. The right-hand-side half cell V(W)/AgCl/Ag is reversible to Cl⁻ ion in the phase V. The potential applied to the cell(A), $E=E_{0+}^{W-}$, is defined by the potential of the right-hand-side reference electrode, E_{right} , with respect to that of the left, E_{left} ; $E_{0+}^{W-}=E_{right}-E_{left}$, where the superscript W- and subscript O+ indicate that the reference electrodes in aqueous and nitrobenzene phases are reversible to an anion and a cation, respectively.

When one applies a potential difference across the interface between the phases IV and V by using the four electrode potentiostat, the uncompensated solution resistance between the tips of the two Luggin capillaries mostly resides in the solution thread in the PTFE capillary tip of the DESE, whose resistance was calculated to be 21 kΩ for 0.1 mol dm⁻³ LiCl at 25 °C. Since the residual current flowing through the interface was usually less than 0.2 μA in the polarization potential range (see Fig. 2 below), the iR drop across the uncompensated solution resistance should be less than 4 mV. The error in the potential control due to this iR drop was further minimized to less than 0.1 mV by using the positive feedback circuit equipped in the four-electrode potentiostat.¹⁸⁾

Lithium chloride monohydrate (a Merk's spurapur grade product) was dissolved into twice distilled water to prepare the stock solution of LiCl. The concentration of LiCl was determined by potentiometric titration with a standard silver nitrate solution. A 0.1 mol dm⁻³ LiCl aqueous solution was prepared from this stock solution. TBATPB was prepared as described previously.²⁴⁾ TBACl was first recrystallized from aceton-ether mixture. Then, trace impurities of iodide ion were removed from aqueous TBACl solution by metathesis with silver chloride. Nitrobenzene was distilled under reduced pressure and the middle 60% of the distillate was collected and shaken with active alumina overnight. The last treatment was important to reduce the residual current to a low level. After filtration, nitrobenzene was washed and equilibrated with twice distilled water at 25 °C. Nitrobenzene solution of TBATPB was prepared in dark immediately before use.

Results and Discussion

Current-potential Curve. Figure 2 shows a current-potential curve (d.c.polarogram) obtained with the DESE in the dark for the interface between 0.1 mol dm⁻³ LiCl aqueous solution and 0.1 mol dm⁻³ TBATPB

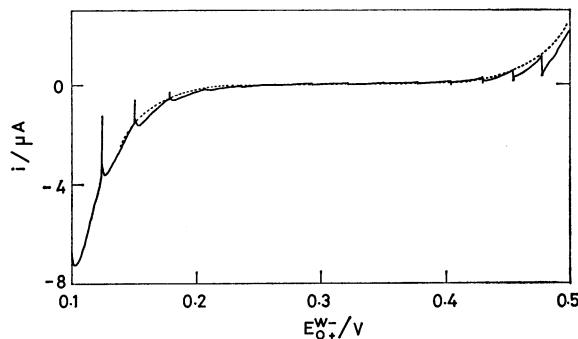


Fig. 2. Current-potential curve for the interface between 0.1 mol dm^{-3} LiCl aqueous solution and 0.1 mol dm^{-3} TBATPB nitrobenzene solution at 25°C . (—): Experimental. The potential was scanned from 0.1 to 0.5 V with the scan rate of 0.5 mV s^{-1} . (---): calculated by Eq. 3.

nitrobenzene solution. The transfer of a positive charge from the aqueous to the nitrobenzene phase was taken as the positive direction of the current. This polarogram indicates that the current across the interface is negligible except for a trace residual current (less than $0.6 \mu\text{A cm}^{-2}$) in the potential range between 0.22 and 0.42 V and that the interface can be polarized over a voltage span of almost 300 mV.

The standard ion transfer potentials of j ion across the water(W)-nitrobenzene(NB) interface, $\Delta_{\text{NB}}^{\text{W}}\phi_j^0$, are -0.248 , 0.395 , 0.372 , and $-0.324^{25,26}$ for $j=\text{TBA}^+$, Li^+ , TPB^- , and Cl^- , respectively. Since $\Delta_{\text{NB}}^{\text{W}}\phi_{\text{TBA}}^0$ is less negative than $\Delta_{\text{NB}}^{\text{W}}\phi_{\text{Cl}}^0$ and $\Delta_{\text{NB}}^{\text{W}}\phi_{\text{TPB}}^0$ is less positive than $\Delta_{\text{NB}}^{\text{W}}\phi_{\text{Li}}^0$, TBA $^+$ and TPB $^-$ ions are most easily transferable through the interface among the four ions. Accordingly, the "residual" current in the polarization potential range should be attributed to the transfer of TBA $^+$ or TPB $^-$ ion or both. Then the current increase in the positive direction at the positive extreme of the applied potential in Fig. 2 should be mainly due to the transfer of TPB $^-$ ion and the current increase in the negative direction at the negative extreme to that of TBA $^+$ ion from the nitrobenzene to the aqueous phase. The transfer of Li $^+$ and Cl $^-$ ions may be negligible compared with that of TBA $^+$ and TPB $^-$ ions in the potential range considered. It can be shown that the current-potential relationship for the transfer of TBA $^+$ and TPB $^-$ ions from the nitrobenzene to the aqueous phase, where LiCl serves as the supporting electrolyte for the mass transfer of TBA $^+$ and TPB $^-$ ions in the aqueous phase, can be expressed, in analogy to the electrolytic current at a dropping mercury electrode in the absence of supporting electrolyte,^{27,28} by

$$i = 4.168 F v^{2/3} t_d^{1/6} c_s A \quad (3)$$

with

$$A = \frac{(D_{\text{TPB}}^{\text{W}})^{1/2}/q - (D_{\text{TBA}}^{\text{W}})^{1/2}/p}{1 + \frac{(1-t_{\text{TBA}}^{\text{NB}})}{p} \left(\frac{D_{\text{TBA}}^{\text{W}}}{D_s^{\text{NB}}} \right)^{1/2} + \frac{t_{\text{TBA}}^{\text{NB}}}{q} \left(\frac{D_{\text{TPB}}^{\text{W}}}{D_s^{\text{NB}}} \right)^{1/2}} ,$$

where i is the current, v the flow rate of an aqueous solution, c_s the concentration of TBATPB in the nitrobenzene phase, t_d the drop time, $t_{\text{TBA}}^{\text{NB}}$ the transport number of TBA $^+$ ion in the nitrobenzene phase, D_s

the diffusion coefficient of j ion ($j=\text{TBA}^+$ or TPB $^-$) in the aqueous(W) and nitrobenzene(NB) phases, and p , q and D_s^{NB} are given by

$$p = \exp \left[\frac{F}{RT} (\Delta\phi - \Delta_{\text{NB}}^{\text{W}}\phi_{\text{TBA}}^0) \right]$$

$$q = \exp \left[-\frac{F}{RT} (\Delta\phi - \Delta_{\text{NB}}^{\text{W}}\phi_{\text{TPB}}^0) \right]$$

and

$$D_s^{\text{NB}} = \frac{2 D_{\text{TBA}}^{\text{NB}} D_{\text{TPB}}^{\text{NB}}}{D_{\text{TBA}}^{\text{NB}} + D_{\text{TPB}}^{\text{NB}}} ,$$

where F , R , and T are used in the usual meaning. $\Delta\phi$ is the potential difference across the interface and is related to the applied potential by

$$E = E_{0+}^{\text{W}} = \Delta\phi + E_{\text{ref}} \quad (4)$$

where E_{ref} is the constant which depends only on the reference electrode system. In deriving Eq. 3 we assumed that the surface concentrations of TBA $^+$ and TPB $^-$ ions in the two phases, $c_{\text{TBA}}^{\text{W},0}$, $c_{\text{TBA}}^{\text{NB},0}$, $c_{\text{TPB}}^{\text{W},0}$, and $c_{\text{TPB}}^{\text{NB},0}$ are related by Nernst equations:

$$\Delta\phi = \Delta_{\text{NB}}^{\text{W}}\phi_{\text{TBA}}^0 + \frac{RT}{F} \ln \frac{c_{\text{TBA}}^{\text{NB},0}}{c_{\text{TBA}}^{\text{W},0}}$$

and

$$\Delta\phi = -\Delta_{\text{NB}}^{\text{W}}\phi_{\text{TPB}}^0 - \frac{RT}{F} \ln \frac{c_{\text{TPB}}^{\text{NB},0}}{c_{\text{TPB}}^{\text{W},0}}$$

and that the transfer of Li $^+$ and Cl $^-$ ions across the interface is negligibly small compared with that of TBA $^+$ and TPB $^-$.

In Fig. 2 the dashed line is a theoretical polarogram which was calculated from Eq. 3 with $c_s=0.1 \text{ mol dm}^{-3}$, $t_d=50 \text{ s}$, $v=0.00036 \text{ cm}^3 \text{ s}^{-1}$, $D_{\text{TBA}}^{\text{W}}=D_{\text{TPB}}^{\text{W}}=5.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $D_{\text{TBA}}^{\text{NB}}=D_{\text{TPB}}^{\text{NB}}=2.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$,¹⁷ and $E_{\text{ref}}=0.25 \text{ V}$. For the sake of simplicity, the diffusion potential which may exist in the vicinity of the interface was not taken into account. Agreement between the experimental curve and the theoretical one is good, indicating that the "residual" current in the polarization potential range is largely due to the transfer across the interface of the most easily transferable ions in the two phases.

From Eq. 3 we can expect that the ion transfer current becomes zero at

$$E_{i=0} = \frac{RT}{2F} \ln (D_{\text{TBA}}^{\text{W}}/D_{\text{TPB}}^{\text{W}})^{1/2} + \frac{1}{2} (\Delta_{\text{NB}}^{\text{W}}\phi_{\text{TBA}}^0 + \Delta_{\text{NB}}^{\text{W}}\phi_{\text{TPB}}^0) + E_{\text{ref}}. \quad (5)$$

In the present case $E_{i=0}$ was calculated to be 0.32 V when $E_{\text{ref}}=0.25 \text{ V}$. Thus the residual current at and in the vicinity of this potential is due to the charging current of the polarized nitrobenzene-water interface. Figure 3 shows a representative current-time curve at $E=0.31 \text{ V}$. The current increases suddenly at the moment of a drop's birth (indicated by an arrow in Fig. 3), then decays subsequently with time. This behavior is quite similar to that of the charging current usually observed at an ideal polarized dropping mercury electrode. Since $E=0.31 \text{ V}$ is 45 mV more positive than the potential of zero charge of the interface (see below), a positive-going current is observed at

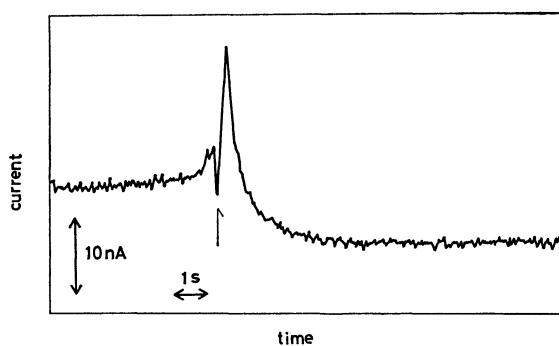


Fig. 3. Current *vs.* time curve at 0.31 V for the interface between 0.1 mol dm⁻³ LiCl aqueous solution and 0.1 mol dm⁻³ TBATPB nitrobenzene solution. The arrow indicates the instant of a drop's birth.

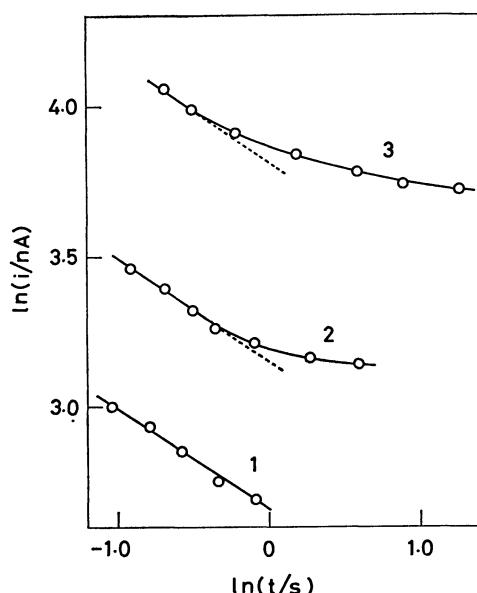


Fig. 4. $\log i$ *vs.* $\log t$ plot at 0.310(1), 0.330(2), and 0.370 V(3). Dashed lines by the curves are drawn to indicate the slope of $-1/3$.

this potential. As the drop grows and approaches to its maximum stage the residual current increases to an appreciable value, which may be attributable to residual impurities. The decaying part of the current in the current-time curves recorded at three different applied potentials are plotted in logarithmic scales in Fig. 4. At $E=0.31$ V the plot gives a straight line with the slope of $-1/3$, which is equal to the theoretical value for the charging current.²⁹ As the applied potential shifts to more positive value the slope of $\log i$ *vs.* $\log t$ curves deviates from $-1/3$ at large t , indicating that the contribution of ion transfer current (here the transfer of TPB⁻ ion) becomes appreciable with the increase of the applied potential.

Electrocapillary Curve. Figure 5 shows an electrocapillary curve for the interface between 0.1 mol dm⁻³ TBATPB nitrobenzene solution and 0.1 mol dm⁻³ LiCl aqueous solution. The vertical bars on the curve indicate the standard deviation for the thrice-repeated measurements. The pooled standard deviation was 0.16 mN m⁻¹ in the potential range between 0.2 and

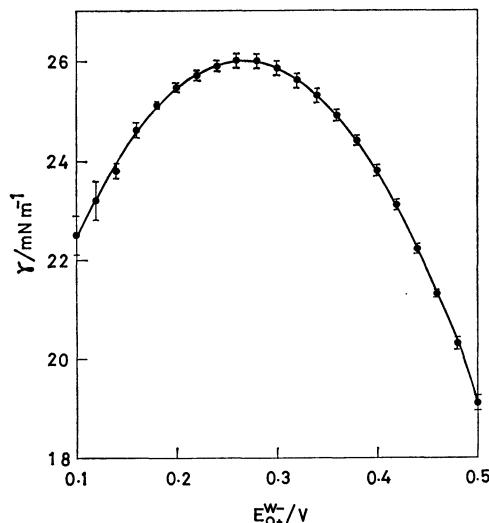


Fig. 5. Electrocapillary curve for the interface between 0.1 mol dm⁻³ LiCl aqueous solution and 0.1 mol dm⁻³ TBATPB nitrobenzene solution at 25 °C. Vertical bars indicate the standard deviation for triplicate measurements.

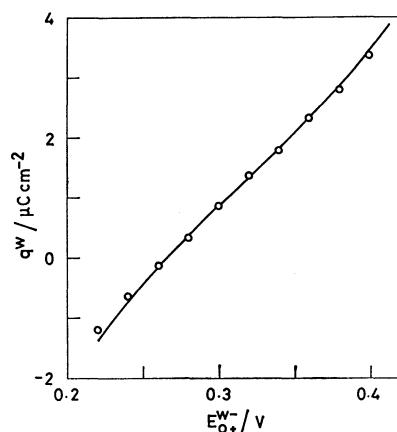


Fig. 6. Comparison of surface charge densities in aqueous solution side obtained from the differentiation of the electrocapillary curve (○) and from the integration of differential capacity curve (—) for the interface between 0.1 mol dm⁻³ LiCl aqueous solution and 0.1 mol dm⁻³ TBATPB nitrobenzene solution.

0.4 V.

Thermodynamic theory of ideal polarized interface between two immiscible³⁰ or partially miscible³¹ electrolyte solutions gives

$$-\left(\frac{\partial \gamma}{\partial E_{0+}^{w-}}\right)_{T, P, \mu} = q^w = -q^{NB} = F(\Gamma_{Li}^w - \Gamma_{Cl}^w) = F(\Gamma_{TPB}^{NB} - \Gamma_{TB}^{NB})$$

and

$$-\left(\frac{\partial^2 \gamma}{\partial E_{0+}^{w-2}}\right)_{T, P, \mu} = \left(\frac{\partial q^w}{\partial E_{0+}^w}\right)_{T, P, \mu} = C_d,$$

where q^w and q^{NB} are the surface charge densities in the aqueous and the nitrobenzene solution side, respectively, Γ_j^w the surface concentration of j ion in the aqueous ($\alpha=W$) or the nitrobenzene ($\alpha=NB$) solution side, C_d the differential capacity of the interface.

The electrocapillary curve was numerically differentiated using the moving quadratic fitting method.³²⁾ The resultant q^W vs. E_{Ox}^W curve is shown in Fig. 6, giving the potential of the electrocapillary maximum or the potential of zero charge, $E_{\text{pzc}} = 0.265$ V. Also plotted in Fig. 6 are the surface charge density data calculated from the differential capacity vs. potential curve obtained for the same interface using an a.c. polarographic method.³³⁾ Agreement between the two results is excellent. These results indicate that the interface virtually behaves as an ideal polarized interface.

The present study experimentally demonstrates that the interface between two immiscible electrolyte solutions can be electrically polarized in a certain potential range by choosing suitable electrolytes in the two phases. The residual current can be explained as due to the minute ion transfer across the interface of the most easily transferable ion or ions present in the two phases as well as the charging current of the interface. The present study also shows that the thermodynamic theory of ideal polarized interface can be applied to the interface for elucidating its equilibrium properties in a certain potential range, that is, the potential range where disturbance in the double layer structure caused by the transfer of ion or ions across the interface appears to be not appreciable. Subsequent papers will describe some detailed structure of the electrical double layer at the nitrobenzene-water interface that has been elucidated on the basis of electrocapillarity measurements.

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