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Adsorption of Alkaline Earth Cations on Mercury as Studied with the Perbromate Kinetic Probe

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Reduction of perbromate was used as a kinetic probe of double layer parameters for weak specific adsorption of double layer parameters for weak specific adsorption of alkaline earth cations at the mercury/electrolyte solutions interface. The results are interpreted as evidence for weak specific adsorption of Sr^{2+} and particularly Ba^{2+} in 10 mM solutions at negative electrode charge densities. The limitation of the use of an anionic probe for the quantitation of cation specific adsorption is discussed.

The weak specific adsorption of alkali metal cations at the interface between mercury and aqueous electrolyte solutions has given rise to controversy because of the seemingly conflicting results obtained from various experimental methods.[1–10)] Damaskin[11)] showed that such results are, in fact, quite to be expected for sub-equivalent specific adsorption of ions, for which the usual thermodynamic method is not sufficiently sensitive. A similar situation applies to alkaline earth cations, for which Frumkin and Nikolaeva-Fedorovich[12)] reported a slight increase in the rate of peroxydisulfate reduction in going from Ca^{2+} to Ba^{2+}, whereas Parsons *et al.*[13,14)] observed approximate agreement between experimental data and double layer calculations assuming the absence of specific adsorption for both Mg^{2+} and Ba^{2+}. In the present communication, we report results similar to those of Frumkin and Nikolaeva-Fedorovich, using perbromate as a kinetic double layer probe.

Experimental

The dc, ac, and pulse polarograms were obtained on an instrument described earlier[15–17)] which features phase-resolved ac polarograms, IR compensation and a simple integral pulse circuit based on the 60 Hz line frequency. Chemicals of reagent grade were used without further purification. The rate constants $k_\mathrm{c}^\ominus$'s were calculated from dc polarograms using the Koutecký formalism[18–21)] and from integral pulse polarograms using an equivalent method based on the relations of Brinkman and Los.[22)] Polarographic maxima of the first kind in the dc polarograms were avoided by using low perbromate concentrations ($\leqslant$0.1 mM), and maxima of the second kind by using low mercury flow rates ($\approx$0.15 mg s^{-1}); maxima on the integral pulse polarograms such as reported by Fonds *et al.*[23)] were initially observed, but were eliminated by proper IR compensation. Charge densities were obtained by integration of capacitance data from IR-compensated quadrature ac polarograms at 159 Hz ($\omega = 10^3$ rad s^{-1}). The potentials of zero charge required as integration constants were taken at the diffuse layer minima in the capacitance curves. Comparison with electrocapillary measurements in 10 mM LiCl and 10 mM $MgSO_4$ showed agreement within 1 and 2 μC cm^{-2}, respectively. All potentials are referred to a saturated calomel electrode (SCE), measurements being made at 25.0 °C.

Results and Discussion

The dc polarograms of perbromate in 10 mM alkali halide solutions exhibit pronounced minima, but the corresponding minima in 10 mM solutions of alkaline earth halides or sulfates are too shallow to allow accurate numerical evaluation. Thus, integral pulse polarograms were used instead to provide sufficiently accurate rate parameters. Figure 1 shows the dependence of the ratio i/i_l on the reaction rate constant $k_\mathrm{c}^\ominus$ for the dc and integral pulse polarograms. Heterogeneous rate constants up to *ca.* 0.05 cm s^{-1} could be obtained with reasonable accuracy from pulse-polarographic i/i_l ratios. Where the pulse-polarographic limiting current was not directly observable, and its value was calculated from the dc limiting current and the known ratio of dc and pulse-polarographic limiting currents in our instrument as determined with Cd^{2+} and Zn^{2+} ions. The results for 10 mM alkaline earth chlorides and for 10 mM $MgSO_4$ are shown in Fig. 2, and compared with rate constants calculated for a 2,2-electrolyte such as $MgSO_4$ on the basis of measured rate constants for 10 mM LiCl assuming the absence of specific adsorption

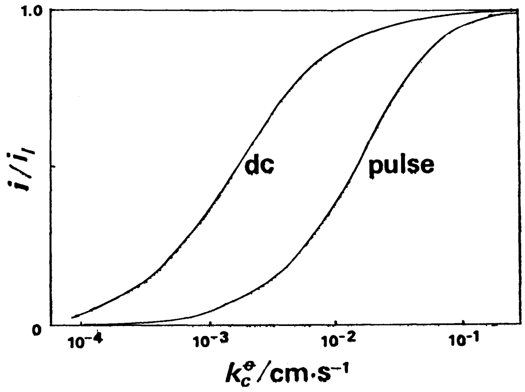

Fig. 1. The ratio of current i to limiting current i_l as a function of rate constant $k_\mathrm{c}^\ominus$ for an irreversible reduction or oxidation in dc and integral pulse polarography respectively. The curves were calculated with the following specific parameter: $D = 2.5 \times 10^{-5}$ cm^2 s^{-1}, sampling time (for dc and pulse) 4.2 s after drop birth, sampling interval from 16.7 to 33.3 ms after application of the pulse.

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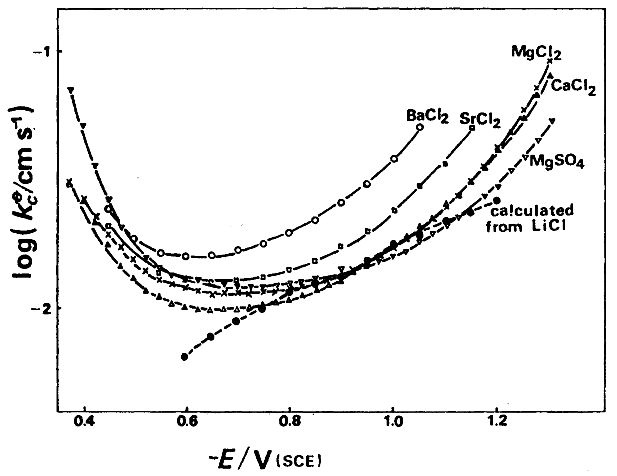

Fig. 2. Rate constants calculated from the integral pulse polarograms of 0.06 mM KBrO$_4$ in 10 mM aqueous alkaline earth electrolytes.

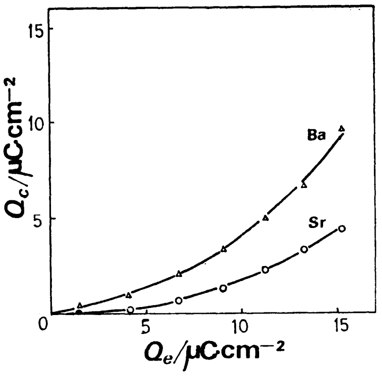

Fig. 3. Specifically adsorbed charge density Q_c as a function of electronic charge density Q_e, calculated from the data of Fig. 2 for 10 mM SrCl$_2$ and BaCl$_2$ on the assumptions that the Gouy-Chapman-Stern theory and simple Frumkin correction apply and that Mg^{2+} is not at all specifically adsorbed from 10 mM aqueous MgCl$_2$.

of both Li$^+$ and Mg^{2+}.† At potentials more negative than −0.8 V *vs.* SCE, the data for MgSO$_4$ coincide with those calculated from LiCl within experimental error. Comparison of the results for MgSO$_4$ and MgCl$_2$ indicates that the nature of the anion is not very important at sufficiently negative potentials, where the double layer predominantly contains cations. Coincidence of the curves for MgCl$_2$ and CaCl$_2$ suggests that Ca^{2+} is not specifically adsorbed to any appreciable extent from 10 mM aqueous halide solutions either. However, Sr^{2+} and particularly Ba^{2+} appear to be specifically adsorbed. Estimation of such specific adsorption can be made on the assumption that MgCl$_2$ is not specifically adsorbed at all. The results are shown in Fig. 3. Calculation of the specifically adsorbed charge densities Q_c of Sr^{2+} and Ba^{2+} from the difference of their measured rate constants was made by assuming complete absence of specific adsorption of Mg^{2+} as follows.

$$\Delta\phi_0 = \frac{RT}{(1+2\alpha)F}\ln \Delta k_c^{\circ} \tag{1}$$

$$Q_d = \left[A\sum_i c_i\left\{\exp\left(-\frac{Z_iF}{RT}\phi_0\right)-1\right\}\right]^{1/2} \tag{2}$$

$$Q_c = -(Q_d+Q_e) \tag{3}$$

where Q_d and Q_e are the diffusion double layer and electronic charge densities, respectively. Since the charge transfer coefficient α is potential-dependent, each value was determined graphically with the use of k_{corr} *vs.* $(E-\phi_0)$ curve of perbromate reduction.†† In both cases of Sr^{2+} and Ba^{2+}, the estimates indicate weak specific adsorption, considerably less than in amount equivalent to the electronic charge density Q_e.

In an earlier work with perbromate,[9] quite good agreement with data reported was obtained for specifically adsorbed anions. However, the estimates for alkali ion adsorption were a factor of two higher than those obtained with the mixed-electrolyte approach.[6-8] Damaskin[11,24] reported a similar discrepancy with MnO$_4^-$, S$_4$O$_6^{2-}$, S$_2$O$_8^{2-}$, PtF$_6^{2-}$, and Fe(CN)$_6^{3-}$ in studying alkali ion adsorption, but good agreement when H$^+$ was used. It appears that the probe ion is attracted electostatically by the specifically adsorbed ion, and preferentially reduced close to the latter if the two have charge of opposite sign. The probe ion would undergo stronger specific adsorption than accounted for by the Frumkin correction. Because of this dynamic discreteness-of-charge effect, the data in the present communication should be qualitative.

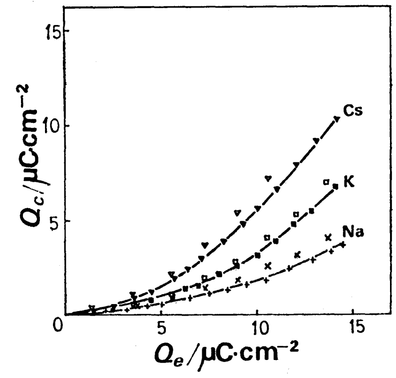

Fig. 4. Specifically adsorbed charge density Q_c as a function of electronic charge density Q_e, calculated from dc and integral pulse polarograms in 10 mM and 0.1 M aqueous alkali halide solutions respectively, based on Gouy-Chapman-Stern theory, Frumkin correction and the absence of specific adsorption of Li$^+$. Symbols used: +, ■ and ▼: 10 mM NaF, KCl, and CsCl respectively; ×, □ and ▽: 0.1 M NaCl, KCl, and CsCl respectively.

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† The rate constants calculated for a 2,2-electrolyte such as MgSO$_4$ were derived from the rate constant with the Frumkin correction k_{corr}(log k_{calcd}=log $k_{corr}+(F/2.3RT)\phi_0$, *cf.* Ref. 9) in 10 mM LiCl, and the double layer potential ϕ_0 (mean potential of OHP) was calculated by means of Gouy-Chapman-Stern theory using the electronic charge density in 10 mM LiF and 10 mM MgSO$_4$ obtained by integrating capacitance.

†† A more detailed discussion is given in Ref. 9. The value of α is sufficiently small to justify this procedure.

The same applies to the slight extension of the work of de Levie and Nemes on alkali cations (Fig. 4), where the earlier dc-polarographic results for 10 mM solutions are combined with new pulse-polarographic data for 0.1 M. The amount of specific adsorption is approximately independent of the ten-fold increase in concentration, in agreement with the observations of Damaskin and Ivanova[8] and with the buffering effect of the double layer on weak specific adsorption of cations.[11,25] The results appear to be qualitatively correct, although the specific values obtained are likely to be too high in view of the dynamic discreteness-of-charge effect. Other possible sources of systematic error, of cource, result from all other assumptions in the Gouy-Chapman-Stern theory and the Frumkin correction, specifically the assumption that the average potential at the reaction plane coincides with that of the outer Helmholtz plane.

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