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Abstract

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ON THE ADSORPTION OF HYDROGEN IONS AT A NEGATIVELY CHARGED MERCURY-ELECTROLYTE INTERFACE

It is known that in a number of cases a definite sequence is observed in the change of the properties of aqueous solutions containing monovalent cations in the series
H^+—Li^+—Na^+—K^+—Rb^+—Cs^+, and the behavior of the lithium and hydrogen cations proves to be similar. Such a conclusion follows directly, for example, from a comparison of the dependence of activity coefficients on concentration in aqueous solutions of acids and salts of alkali metals ([1]). In this connection it was of interest to compare the influence of hydrogen ions and alkali metals on the differential capacitance C of the double layer and on the kinetics of electrode processes.

As follows from Grahame' s measurements ([2]), in the case of a mercury dropping electrode the values of C in $0.1\,N$ solutions of HCl and LiCl at potentials more positive than -0.7 V (N.C.E.) practically coincide, whereas at more negative potentials C in HCl is 1-2% lower than in $0.1\,N$ LiCl. However, Grahame' s measurements were carried out only up to a hydrogen overvoltage $\eta \sim 0.66$ V. We measured the values of C on a dropping mercury electrode in $0.1\,N$ solutions of HCl and LiCl at a frequency of 1000 Hz and 25° by means of an impedance bridge. The measurements in HCl solutions were extended to $\eta \sim 1.15$ V. The potentials φ are given in volts relative to the N.C.E. (Fig. 1a). The bridge-balancing time was determined with an accuracy of 0.01-0.02 sec. In contrast to Grahame' s work, in which the second electrode in the cell was a platinum sphere symmetrically surrounding the electrode under study, in our work a mercury anode in the form of a cup was used, above the center of which the dropping mercury electrode was placed. The use of a mercury anode was dictated by the need to avoid possible contamination of the solution by traces of platinum, which sharply lower the overvoltage of hydrogen evolution. Since in our experiments the measuring arm of the bridge consisted of series-connected capacitance and resistance boxes, while during the occurrence of an irreversible process at the electrode its impedance becomes equivalent to a capacitor with leakage, in order correctly to separate the ohmic and capacitive components of the total impedance at potentials more negative than -1.3 V in HCl solutions it was necessary to recalculate the experimental results for the electrical circuit

Figure 1

Figure 1: Figure 1

shown in Fig. 1b.

The results obtained are compared in Fig. 1a with Grahame’ s data. As is seen from the figure, the values of C in 0.1 N HCl at negative surface charges are somewhat lower than the values of C in 0.1 N LiCl*. Hence, and from (^{2}) and (^{3}), it follows that the capacitance of the double layer at negative surface charges increases in the series $H^+ < Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. The decrease the capacity of the double layer upon replacing Li^+ by H^+ is in agreement with the results of measurements of potential jumps at the free surface of soap solutions (^{4}).

According to Horiuti’s theory of hydrogen overvoltage (^{5}), the rate of the process of hydrogen evolution on mercury is determined by the irreversible discharge of molecular hydrogen ions H_2^+, adsorbed on the electrode surface and in equilibrium with H^+ ions in solution. A. N. Frumkin (^{6}) pointed out that the differential capacitance of the Helmholtz layer with an ionic lining formed by H_2^+ ions should be twice as large as the value C in neutral solutions. Matsuda (^{7}), who considered the effect of the gradual transition of H^+ ions attracted by the surface into H_2^+ ions with increasing η, which according to Horiuti’ s theory should occur, came to the conclusion that on the C—φ curve in acid solutions, at potentials more negative than the electrocapillary zero, there should be observed a maximum exceeding $2C$, after which, with a further increase in $-\varphi$, the capacitance would again reach normal values. The experimental results obtained by Grahame and in the present work show the complete absence of such effects and, consequently, the erroneousness of the notion of the presence of H_2^+ ions adsorbed on the mercury surface. It should be noted that normal values of

Fig. 1. *a*—curves of differential capacitance in 0.1 N HCl (1) and LiCl (2), 1*a* and 2*a*—Grahame’ s data for 0.1 N HCl and LiCl, respectively; *b*—equivalent electrical scheme of a cell with an electrode on which an irreversible reaction proceeds: C—capacitance of the double layer, R_1—solution resistance, R_2—polarization resistance

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* The difference between C in the acid and in the salt decreases with increasing negative value of φ. This phenomenon may be explained if one assumes that the hydrated H_3O^+ cation is deformed more strongly than Li^+ at negative φ. It must be borne in mind, however, that the accuracy of measurements in HCl solutions at the potentials of hydrogen evolution is somewhat reduced; elucidation of the indicated effect requires additional investigation.

Fig. 2. Polarization curves of reduction of $10^{-3}\,N$ $K_2S_2O_8$ in the presence of HCl (a) and LiCl (b) at concentrations: 1 $-10^{-2}N$, 2 $-5 \cdot 10^{-2}N$, 3 $-10^{-1}N$.

Figure 2: Fig. 2. Polarization curves of reduction of $10^{-3}\,N$ $K_2S_2O_8$ in the presence of HCl (a) and LiCl (b) at concentrations: 1 $-10^{-2}N$, 2 $-5 \cdot 10^{-2}N$, 3 $-10^{-1}N$.

capacitance on the mercury electrode in $1\,N$ acid solutions were also obtained by Watanabe, Tsuji, and Ueda by the resonance method (^{8}).

It is known that the rate of reduction of the anions $S_2O_8^{2-}$ (^{9}), $S_4O_6^{2-}$ (^{10}), $Fe(CN)_6^{3-}$ (^{11}), and $PtCl_4^{2-}$ (^{12}) increases sharply in the series $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. A. N. Frumkin, N. V. Nikolaeva-Fedorovich, and B. B. Damaskin (^{9}) explained this phenomenon on the basis of the concept of nonuniform distribu-

of the potential in the double layer, whereas Hirst $^{(13)}$ proposed that ions of the type $MeS_2O_8^-$, formed in the bulk of the solution or (at more negative potentials) activated complexes of the same composition, undergo reduction. The influence of the nature of the cation within the framework of this assumption should be explained by the facilitation of complex formation with increasing cation radius. A comparison of the dissociation pK values of $NaSO_4^-$ and KSO_4^- $^{(14)}$ leads to the conclusion that there is some increase in the stability of ion pairs formed by the larger cation, which could serve as an argument in favor of Hirst' s explanation. Since the pK for HSO_4^- at 25° is equal to 1.99 $^{(14)}$ and considerably exceeds the pK value for $NaSO_4$, equal to 0.72, then, accepting Hirst' s scheme, one would expect that the H_3O^+ cation should exert a considerably stronger accelerating influence on the electroreduction of anions than, for example, the Na^+ cation.

We studied the influence of H^+ ions on the rate of reduction of the anions $S_2O_8^-$, $Fe(CN)_6^{3-}$, and $PtCl_4^{2-}$ at negative surface charges. Solutions of the salts $K_2S_2O_8$, $K_3Fe(CN)_6$, or K_2PtCl_4, previously freed from oxygen, and solutions of HCl were mixed to form a solution of the required composition immediately before the measurements, in order to avoid distortion of the results due to changes that may occur with time in acidic solutions of the indicated anions. The polarization curves were corrected for background currents. In studying the reduction of $K_3Fe(CN)_6$, it was found that in acidic solutions reproducible results are obtained only after preliminary treatment of the glass cell and capillary with several portions of the solution under study. This is apparently connected with the extraction from the glass, by acidic solutions, of traces of multicharged cations, which sharply increase the rate of reduction of $Fe(CN)_6^{3-}$ $^{(11)}$.

Fig. 2. Polarization curves of reduction of $10^{-3}\,N$ $K_2S_2O_8$ in the presence of HCl (*a*) and LiCl (*b*) at concentrations: 1 $-10^{-2}N$, 2 $-5 \cdot 10^{-2}N$, 3 $-10^{-1}N$.

The results of measurements in solutions of $10^{-3}\,N$ $K_2S_2O_8$ and $10^{-3}\,N$ $K_3Fe(CN)_6$ with additions of acid and salts of alkali metals are presented in Figs. 2 and

Fig. 3. Polarization curves for the reduction of $10^{-3} N\,\mathrm{K_3Fe(CN)_6}$ in the presence of HCl (a) and LiCl (b) at concentrations: 1 –0, 2 –$5 \cdot 10^{-4} N$, 3 –$10^{-3} N$, 4 –$2 \cdot 10^{-3} N$, and in the presence of $10^{-3} N$ KCl ($3'$) and $10^{-3} N$ CsCl ($3''$).

Figure 3: Fig. 3. Polarization curves for the reduction of $10^{-3} N\,\mathrm{K_3Fe(CN)_6}$ in the presence of HCl (a) and LiCl (b) at concentrations: 1 –0, 2 –$5 \cdot 10^{-4} N$, 3 –$10^{-3} N$, 4 –$2 \cdot 10^{-3} N$, and in the presence of $10^{-3} N$ KCl ($3'$) and $10^{-3} N$ CsCl ($3''$).

3. As can be seen from the data obtained, the $\mathrm{H_3O^+}$ cation exerts on the reduction of anions an influence comparable with that of $\mathrm{Li^+}$, or even still weaker, which is consistent with its low adsorbability on the negatively charged surface of mercury. The polarization curves measured in $10^{-3}\,N$ $\mathrm{K_2S_2O_8}$ with additions of KCl and KOH practically coincide, as do the curves in solutions of $10^{-3}\,N$ $\mathrm{K_3Fe(CN)_6} + 10^{-3}\,N$ KCl and $10^{-3}\,N$ $\mathrm{K_3Fe(CN)_6} + 10^{-3}\,N$ KOH.

In the case of reduction of $\mathrm{PtCl_4^{2-}}$, additions of HCl at concentrations $< 10^{-2}\,N$, just like additions of inorganic salts at the same concentrations (12), are only slightly effective. With larger additions of HCl, the hydrogen-evolution wave, which shifts strongly toward positive potentials,

in the presence of traces of platinum, which are formed on the cathode, is superimposed on the reduction current of $\mathrm{PtCl_4^{2-}}$, which makes it difficult to interpret the results obtained in this case.

It should, however, be emphasized that the conclusion concerning the relatively low adsorbability of the hydrogen ion and its weak interaction with anions in the surface layer applies only to interfaces bearing a negative charge, which attracts hydrogen ions and repels anions. It cannot be extended to uncharged surfaces in the presence of specific adsorption of the anion, as follows from the increased adsorbability of acids in comparison with neutral salts on mercury at the maximum of the electrocapillary curve (15) and at the free surface of water (16). It is possible that in these cases undissociated acid molecules are formed in the adsorbed layer.

Fig. 3. Polarization curves for the reduction of $10^{-3} N$ $\mathrm{K_3Fe(CN)_6}$ in the presence of HCl (a) and LiCl (b) at concentrations: 1 –0, 2 –$5 \cdot 10^{-4} N$, 3 –$10^{-3} N$, 4 –$2 \cdot 10^{-3} N$, and in the presence of $10^{-3} N$ KCl ($3'$) and $10^{-3} N$ CsCl ($3''$).

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