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Abstract

Full Text

PHYSICAL CHEMISTRY

S. G. MAIRANOVSKII, L. D. KLYUKINA, and Academician A. N. FRUMKIN

THE INFLUENCE OF THE STRUCTURE OF THE DOUBLE LAYER ON POLAROGRAPHIC SURFACE CATALYTIC WAVES OF HYDROGEN

In buffer solutions the charge of proton donors (acidic components) is always one unit higher than the charge of the bases conjugate with them; therefore, near a negatively charged electrode surface the ratio of the concentration of acids to the concentration of conjugate bases must exceed its value in the bulk of the solution (^{1}). Acids and bases in solution are in protolytic equilibrium with one another, and the ratio between the concentrations of the acid and of its conjugate base, apart from dependence on the presence of other acids and bases in the solution, is determined by the value of the dissociation constant of the given acid and by the concentration of hydrogen ions. The increase in the ratio of the concentrations acid : base near the cathode, corresponding to a shift of the protolytic equilibrium, may therefore be expressed as a decrease in pH in the near-cathode region in comparison with the bulk of the solution.

The magnitude of the pH shift under the action of the electrode field reaches its maximum value at the electrode surface and, with increasing distance from it into the solution, rapidly decreases. Therefore, if electrode processes with preceding chemical protonation of the depolarizer are considered, it is not difficult to see that the thinner the reaction layer within which the preceding protonation reaction occurs, the stronger the influence exerted on it by the electrode field (^{2}). The maximum action of the field must evidently appear for protonation processes occurring at the very surface of the electrode with participation of adsorbed substances, i.e. in the case of "surface" preceding reactions (^{3}). The increase in the concentration of hydrogen ions at the electrode surface as compared with the bulk of the solution depends on the magnitude of the potential drop in the diffuse part of the electrical double layer, usually denoted as the ψ_1-potential, and is determined by (^{4}):

$$[\mathrm{H}^+]_s = [\mathrm{H}^+]_0 e^{-\psi_1 F/RT}, \tag{1}$$

where $[\mathrm{H}^+]_s$ and $[\mathrm{H}^+]_0$ are the concentrations of hydrogen ions at the electrode surface and in the bulk of the solution, respectively.

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Fig. 1. Catalytic waves of quinine in borate buffer solution (pH 9.5) with $3 \cdot 10^{-6}\,M$ quinine at various concentrations of Na^{+}: 1—0.040; 2—0.045; 3—0.05; 4—0.055; 5—0.060; 6—0.070; 7—0.080 M

Figure 1: Fig. 1. Catalytic waves of quinine in borate buffer solution (pH 9.5) with $3 \cdot 10^{-6}\,M$ quinine at various concentrations of Na^{+}: 1—0.040; 2—0.045; 3—0.05; 4—0.055; 5—0.060; 6—0.070; 7—0.080 M

In the present work we investigated the influence of the concentration and nature of indifferent electrolytes, which change the magnitude of the ψ_1-potential, on the "surface" catalytic waves of hydrogen. The object of study was the second wave, caused by quinine (more precisely, by its hydrated derivative (^{5})) in borate solutions with a constant analytical concentration of boric acid ($0.04\,M$) at constant pH 9.5 (addition of LiOH, NaOH, or KOH, respectively) in the presence of various amounts of alkali-metal chlorides: Li, Na, K, Rb, Cs. Polarograms were recorded on a PE-312 recording polarograph in a thermostated cell with an external anode at 25°. The dropping electrode with forced detachment of drops had the characteristics: $m = 1.98$ mg/sec, $t = 0.28$ sec. To introduce corrections for the residual current, a background curve was recorded for each of the solutions studied. Oxygen from the solutions was removed by purging with nitrogen. In comparison with (^{3}), the experimental conditions in the present work were chosen so as to increase the fraction of the surface component in the total value of the catalytic current (higher pH, lower concentrations of catalyst and electrolytes). The low value of the volume current under the conditions of the experiments of the present work is evidenced by the almost complete disappearance of the catalytic wave upon a sufficient increase in salt concentration.

The shape of the surface catalytic waves can be approximately expressed by the set of equations (^{6}):

$$E = E^0_{1/2} - \frac{RT}{\alpha F} \ln \frac{i^0}{i^0_{\text{pr}} - i^0}; \tag{2}$$

$$i/i^0 = e^{-a\varphi^2}, \tag{3}$$

where (2) shows the dependence on potential of the current i^0 that would occur in the absence of desorption of the catalyst, while (3) takes into account the change in current occurring as a result of the decrease in the amount of adsorbed catalyst with increasing potential (^{7}). According to A. N. Frumkin (^{7}), $a = (c - c') : 2RT\Gamma^\infty$, where c and c' are, respectively, the integral capacitances of the double layer in the absence of a surface-active substance and at complete coverage of the electrode surface by it; φ is the potential measured relative to the potential of maximum adsorption.

Fig. 1. Catalytic waves of quinine in borate buffer solution (pH 9.5) with $3 \cdot 10^{-6}\,M$ quinine at various concentrations of Na^{+}: 1—0.040; 2—0.045; 3—0.05;

4—0.055; 5—0.060; 6—0.070; 7—0.080 M

In Fig. 1, as an example, the values of the catalytic currents in a $3 \cdot 10^{-6}\,M$ solution of quinine in the presence of various amounts of sodium chloride are given (as points); the curves were constructed from equations (2) and (3). The data used in constructing these curves are given in Table 1. The values of c for solutions of NaCl and KCl salts were found by graphical integration of the differential-capacitance curves (8), followed by interpolation of the obtained values for the corresponding salt concentrations. All values of c were taken for $E = -1.85$ V (sat. cal. el.); for c' in all cases 5.0 μF/cm^2 was used. Owing to the irreversibility of the "surface" catalytic wave (9), the values of $E^0_{1/2}$ became more positive with increasing salt concentration by the magnitude of the change in the ψ_1-potential (see Table 1) (4).

As is seen from Fig. 1, with increasing concentration of sodium ions the height of the catalytic wave decreases. For surface currents close to the limiting value, one may write (6):

$$i^0_{\text{pr}} = sF\rho_s\Gamma^0_{\text{i}}\left[\frac{\Gamma}{\Gamma^0} i_{\text{pr}}\right] = sF\rho_s\Gamma, \tag{4}$$

where Γ^0_{i} and Γ are the surface concentration of adsorbed catalyst in the given solution at the potential of maximum adsorption and at the given potential, respectively; $\rho_s = k_1[\text{DH}_1^+]_s + k_2[\text{DH}_2^+]_s + ...$ is the total rate constant of protonation of the catalyst under the action of the various acids [DH$^+$] in solution.

Table 1

Influence of the concentration of NaCl and KCl on the catalytic waves in quinine solution

Total conc. M^+	NaCl: $-\psi_1$, mV, calc.	NaCl: i^0_{pr}, µA	NaCl: i_M, µA	NaCl: $E^0_{1/2}$, V	NaCl: a, V^{-2}	KCl: i^0_{pr}, µA	KCl: i_M, µA	KCl: $E^0_{1/2}$, V	KCl: a, V^{-2}
0.040	157.6	106.0	1.18	1.85	8.5	154.0	1.52	1.81	9
0.045	154.4	92.8	1.10	1.845	8.5	121.5	1.38	1.80	9
0.050	151.8	76.8	0.93	1.84	8.55	107.5	1.22	1.80	9
0.055	149.3	69.7	0.83	1.84	8.6	–	–	–	–
0.060	147.2	61.3	0.73	1.835	8.6	70.0	0.88	1.79	9
0.070	142.7	42.5	0.535	1.83	8.7	50.2	0.608	1.79	9.1
0.080	139.5	35.1	0.43	1.83	8.8	–	–	–	–

Neglecting the proton-donor action of water in comparison with the action of H$^+$ and H_3BO_3, one may write:

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Fig. 2

Figure 2: Fig. 2

$$\rho_s = k_{\mathrm{H}^+}[\mathrm{H}^+]_s + k\ [\mathrm{H_3BO_3}]_s = k[\mathrm{H}^+]_s, \tag{5}$$

since the change in the effective $[\mathrm{H_3BO_3}]_s$ is proportional to $[\mathrm{H}^+]_s^{(10)}$.

In the following discussion we shall assume that $k = \mathrm{const}$, neglecting the small salt effects (changes in the dissociation constants and reaction rates when the ionic strength of the solution changes).

From (4), taking into account (1) and (5), we obtain

$$i^0_{\mathrm{pr}} \simeq sFk\Gamma^0[\mathrm{H}^+]_0 e^{-\psi_1 F/RT}. \tag{6}$$

Fig. 2. Dependence of i^0_{pr} on $e^{-F\psi_1/RT}$ for catalytic waves in solutions with different concentrations:
1—Na^+ ($C \quad = 3 \cdot 10^{-6}\ M$),
2—K^+ ($C \quad = 6 \cdot 10^{-6}\ M$);
1′, 2′—the same dependence for i_{m}.

Figure 2 gives the dependence of i^0_{pr} on $e^{-\psi_1 F/RT}$ for solutions containing Na^+ (1) and K^+ (2). The values of ψ_1 were calculated according to the theory of the diffuse double layer, assuming a constant capacitance of the Helmholtz layer $c = 18\ \mu\mathrm{F/cm}^2$ (11).

The linear character of the dependence of i^0_{pr} on $e^{-\psi_1 F/RT}$ (straight lines 1 and 2) indicates the validity of equation (6). In the same Fig. 2, curves 1′ and 2′ represent the change in the observed catalytic current at the wave maximum, i_{m}, as a function of $e^{-\psi_1 F/RT}$. As is seen from Fig. 2, proportionality between i_{m} and $e^{-\psi_1 F/RT}$ is not maintained. This was to be expected, since, as the concentration of salts increases, owing to the increase in capacitance c, the value of the coefficient a in (3) increases, which means a more rapid fall in the adsorbability of the catalyst with increasing negative potential (7).

An estimate of the influence of various factors on the change in i_{m} is only approximate, since i_{m} corresponds not to the limiting current i^0_{pr}, but to the current on the rising part of the wave (3). Thus the current i_{m} is affected not only by the rate of the direct reaction $\rho_s\Gamma$, but also, to a certain extent, by the reverse reaction $\rho_s\sigma_s\Gamma^+$, leading to deprotonation of the catalyst. With increasing ionic strength of the solution, the surface equilibrium constant

$$\sigma_s = [\mathrm{BH}]_s/[\mathrm{BH}^+]_s = K_A/[\mathrm{H}^+]_s$$

increases and, consequently, at potentials at which i^0_{pr} is not yet reached (in particular, in the region of i_{m}), the influence of the reverse reaction increases, leading to a greater decrease in i_{m} than for i^0_{pr}. Thus, with increasing ionic strength of the solution, the observed catalytic currents decrease both because of the fall in the negative ψ_1-potential, which leads to a decrease in the concentration of proton donors at the electrode, and because of the reduction in the adsorbability of the catalyst.

The nature of the cation of the indifferent electrolyte also has a large influence on surface waves. It has recently been shown (8,12,13) that alkali-metal cations with large radii exhibit over-equivalent adsorption on the electrode surface. A consequence of this is a decrease in the absolute value of the ψ_1-potential and an increase in the capacitance of the double layer in solutions of alkali-metal salts from lithium to cesium (12,13).

The influence of the nature of the cations is seen from the data of Table 2. The change in the ψ_1-potential on going from Li^+ to K^+ leads, according to (6), to a decrease in i^0_{pr}. On the other hand, the increase in c, and consequently also in a, increases the steepness of the decline on the observed waves and lowers the value of their i_{m}. Even more noticeably the decrease in catalytic currents is manifested upon introducing salts of Rb^+ and Cs^+ into the solution. Table 2 gives the results of experiments in which, at an unchanged quinine concentration ($3 \cdot 10^{-6}\,M$), salts of the alkali metals were additionally introduced into a $0.04\,M$ solution of lithium borate (pH 9.5). From the data of Table 2 it is seen that the effect of the salts on i^0_{pr} and i_{m} of the catalytic waves increases markedly from Li^+ to Cs^+. Thus, bringing the

Table 2

Comparative influence of the nature of the cation of the indifferent electrolyte on the catalytic waves of quinine in a $0.04\,N$ $\mathrm{Li_2B_4O_7}$ solution

Added salt	Salt conc.	i^0_{pr}, μA	i_{m}, μA observed	$E^0_{1/2,\mathrm{op}}$, V	$\overline{C}$, μF/cm^2	a, V^{-2}
–	–	300	2.8	1.9	18.00	8.35
LiCl	$5 \cdot 10^{-3}$	278	2.6	1.9	18.00	8.35
LiCl	$1 \cdot 10^{-2}$	242	2.5	1.89	18.10	8.40
NaCl	$5 \cdot 10^{-3}$	248	2.55	1.87	18.25	8.50
NaCl	$1 \cdot 10^{-2}$	196	2.40	1.87	18.25	8.50
KCl	$5 \cdot 10^{-3}$	222	2.2	1.87	19.00	9.00
KCl	$1 \cdot 10^{-2}$	172	1.7	1.87	19.00	9.00
RbCl	$5 \cdot 10^{-3}$	183	1.64	1.86	19.8	9.5
CsCl	$1 \cdot 10^{-3}$	182	1.86	1.85	20.02	9.6
CsCl	$5 \cdot 10^{-3}$	27.7	0.4	1.80	20.02	9.6

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Fig. 3

Figure 3: Fig. 3

solution to $1 \cdot 10^{-3}\,M$ in CsCl exceeds in effect a $1 \cdot 10^{-2}\,M$ NaCl solution, while a $5 \cdot 10^{-3}\,M$ RbCl solution has a considerably greater effect than $1 \cdot 10^{-2}\,M$ LiCl.

Fig. 3. 1 —catalytic wave constructed taking into account the change of a with potential. 2 —constructed on the assumption that $a =$ const; points are experimental current values for a $6 \cdot 10^{-6}\,M$ quinine solution in $0.04\,N$ $K_2B_4O_7$. Lower curve —dependence of a on E.

In constructing theoretical curves according to equations (2) and (3) (for example, the curves in Fig. 1), because of the laboriousness of the calculations we assumed that $a =$ const. In reality, however, owing to an increase of c, especially at potentials close to -1.9 to -2.0 V (sat. cal. el.), the value of a increases somewhat with increasing cathodic potential (as a result of the increase of c). If the change of a with potential is taken into account (curve 3 in Fig. 3), then the theoretically constructed curve agrees better with the experimental one (see Fig. 3).

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