PHYSICAL CHEMISTRY

S. G. MAIRANOVSKII

1963

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

S. G. MAIRANOVSKII

VOLUME KINETIC WAVES IN THE POLAROGRAPHY OF SALTS OF WEAK ACIDS IN UNBUFFERED SOLUTIONS

(Presented by Academician A. N. Frumkin, January 21, 1963)

The study of kinetic waves of the reduction of weak acids in unbuffered solutions makes it possible to obtain information that investigations in buffered solutions do not provide with sufficient accuracy. Thus, from experiments in unbuffered solutions it is possible to determine directly the rate constants of protonation under the action of water (^1). Kinetic waves in unbuffered media can be used to study protolytic reactions under conditions in which it is difficult or impossible to use buffer solutions, for example, when working with acids that are difficult to reduce against a background of tetraalkylammonium salts, or in nonaqueous solvents.

In the present work we consider the case of kinetic currents when the solution contains an exactly neutralized salt of a weak acid and a strong base. If the electrochemically active form is the undissociated acid AH, then the reduction process is preceded by protonation of the acid anions A^- (salt hydrolysis) at the electrode surface:

$$\mathrm{A^- + H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} AH + OH^-}. \tag{I}$$

We shall restrict ourselves to consideration of the case in which hydrolysis of the salt in solution does not exceed 1%, i.e., we shall consider salts of acids that are not very weak ($pK_A < 8$), when equilibrium (I) is shifted strongly to the left and the concentration of AH in solution is negligibly small in comparison with $[A^-]$.

The only proton donor in the case considered is water. The concentration of hydrogen ions is very low (the pH of solutions of salts of weak acids is above 8-9), and the buffer capacity is negligible; therefore, even if all hydrogen ions delivered to the electrode from the solution by diffusion react at the electrode with A^-, the component of the kinetic current that they provide, equal to the diffusion current of hydrogen in the given solution, is so small that its magnitude may be quite neglected in comparison with the current determined by the rate of reaction (I).

Let n electrons and x water ions be consumed in the reduction of AH,

$$\mathrm{AH} + \mathrm{ne}^- + \mathrm{xH_2O} \xrightarrow{\mathrm{el}} \mathrm{RH} + \mathrm{xOH}^- + \mathrm{P}^{\mathrm{x-n}}, \tag{II}$$

where P denotes possible by-products of the electrode process (for example, halide ions in the reduction of halogen-substituted organic acids).

If the pK_A of the acid RH formed during electroreduction is less than or equal to the pK_A of the initial acid, then RH dissociates at the electrode surface:

$$\mathrm{RH} + \mathrm{OH}^- \rightleftarrows \mathrm{R}^- + \mathrm{H_2O}. \tag{III}$$

Denoting the total number of hydrogen ions consumed by ν, the overall process may be expressed by the equation:

$$\mathrm{A}^- + \mathrm{ne}^- + \ \mathrm{H_2O} \rightarrow \mathrm{R}^- \ (\text{or RH}) + \ \mathrm{OH}^- + \mathrm{P}^{\ -\mathrm{n}}. \tag{IV}$$

Let A^- and AH not be adsorbed on mercury at the reduction potential of AH, i.e., let reactions (I) proceed only in the bulk of the solution (ˆ2). Then ···

for the mean (over the lifetime of the drop) limiting kinetic current i_{pr}, one may use the Koutecký-Weber equation (^{3})

$$\frac{i_{\mathrm{pr}}}{i_{\mathrm{d}}} = \frac{0.886\sqrt{\rho t/\sigma}}{1 + 0.886\sqrt{\rho t/\sigma}} \tag{1}$$

or the equation derived on the basis of the reaction-layer concept of Brdička—Wiesner—Hanus (^{4,5}), which differs from (1) only in the value of the coefficient before the root (0.81 instead of 0.886). The first-order rate constant ρ in unbuffered solutions is equal to

$$\rho = k_1[\mathrm{H_2O}], \tag{2}$$

and the quantity σ:

$$\sigma = \frac{[\mathrm{A}^-]_s}{[\mathrm{HA}]_s} = \frac{K_A}{[\mathrm{H}^+]_s} = \frac{K_A[\mathrm{OH}^-]_s}{K_w}, \tag{3}$$

where K_A is the dissociation constant of HA, K_w is the ionic product of water, the subscript "s" means that the concentrations of the substances are taken at the electrode surface, t is the drop time of the electrode; the quantity i_{d} in (1) corresponds to the diffusion current ($i_\mathrm{d} = \varkappa c$), which would occur at $\rho \to \infty$ for the same analytical concentration $c = [\mathrm{AH}] + [\mathrm{A}^-]$ in solution, $\varkappa$ is the Ilković-equation constant $\varkappa = 607 m^{2/3} t^{1/6} n D^{1/2}$ [μa/mmole].

The concentration $[\mathrm{OH}^-]_s$ at the electrode surface, as is seen from (IV), increases with increasing current; moreover, if the removal of OH^- from the electrode obeys (^{1}) the Ilković equation with the proportionality factor $\varkappa_{\mathrm{OH}^-}$ ($\varkappa_{\mathrm{OH}^-} = i_{\mathrm{diff\,OH}^-}/[\mathrm{OH}^-]$), then for $[\mathrm{OH}^-]_s$ one may write:

$$[\mathrm{OH}^-]_s = iv/n\varkappa_{\mathrm{OH}^-}, \tag{4}$$

where i is the current value at any point of the wave, including at i_pr. Substituting expressions (2), (3), and (4) into (1), after simple transformations we obtain:

$$i_\mathrm{pr}^{3/2} = Q(c - i_\mathrm{pr}/\varkappa), \tag{5}$$

where

$$Q = 0.886 \left(\frac{k_1 [\mathrm{H_2O}]\, t K_w n \varkappa_{\mathrm{OH}^-}}{K_A v} \right)^{1/2} \varkappa. \tag{6}$$

Calculation by the Brdička—Wiesner—Hanus method gives a similar expression for Q (^{1}), but with the numerical coefficient 0.81.

Expression (1) is valid for the case when the concentrations of proton donors and of the bases conjugate with them are constant within the thickness of the reaction layer μ, equal in the present case to (^{1}):

$$\mu = \sqrt{D/k_2[\mathrm{OH}^-]_s} = \sqrt{\frac{D \varkappa_{\mathrm{OH}^-} n}{k_2 i v}}, \tag{7}$$

where D is the diffusion coefficient of HA, k_2 is the rate constant of the reverse reaction (I). Therefore equation (5) is strictly valid only when the thickness of the reaction layer μ is much smaller than the extent of the diffusion layer of the OH^- ions, and the concentration of OH^- within the layer μ may be regarded as constant, equal to $[\mathrm{OH}^-]_s$. Such a situation occurs, as is seen from (7), at sufficiently high currents. As experiment shows (^{1,6}), it is fulfilled with sufficient accuracy at current values above a certain “transition”value, which for electrodes with forced drop detachment amounts to tenths of a μa.

To derive the equation for the wave shape we shall use the method based on the reaction-layer concept (^{4,5}). From the balance of rates of processes in the near-electrode layer it follows:

$$i = nsF\mu\,(k_1[\mathrm{A}^-]_s[\mathrm{H_2O}] - k_2[\mathrm{AH}]_s[\mathrm{OH}^-]_s) \tag{8}$$

$$i_{\mathrm{pr}} = nsF\mu_{\mathrm{pr}}k_1[\mathrm{A}^-]_s[\mathrm{H_2O}], \tag{9}$$

where μ_{pr} corresponds to the thickness of the reaction layer according to (7) under limiting-current conditions, s is the mean surface area of the electrode, and F is Faraday’ s number.

The quantities i and i_{pr} are much smaller than i_{d}, especially under the conditions for which (5) is valid; therefore $[\mathrm{A}^-]_s$ changes only very slightly along the wave. Taking this into account, from comparison of (8) and (9) we find

$$i = \frac{i_{\mathrm{pr}}\mu}{\mu_{\mathrm{pr}}} - nsF\mu k_2[\mathrm{AH}]_s[\mathrm{OH}^-]_s. \tag{10}$$

It follows from (7) that $\mu/\mu_{\mathrm{pr}} = (i_{\mathrm{pr}}/i)^{1/2}$, so that

$$i_{\mathrm{pr}}^{3/2} - i^{3/2} = nsF\mu k_2[\mathrm{AH}]_s[\mathrm{OH}^-]_s i^{1/2},$$

whence, taking (4) and (7) into account, we obtain

$$[\mathrm{AH}]_s = \frac{i_{\mathrm{pr}}^{3/2} - i^{3/2}}{insF}\left(\frac{n\chi_{\mathrm{OH}^-}}{\nu k_2 D}\right)^{1/2}, \tag{11}$$

On the basis of A. N. Frumkin’ s theory of delayed discharge [7], for the current of an irreversible electrode process (II) (without the participation of hydrogen ions in the potential-determining stage) one may write:

$$i = nsF[\mathrm{AH}]_s k_{\mathrm{el}}^0 \exp\left(-\frac{\alpha n_{aEF}}{RT}\right), \tag{12}$$

where k_{el}^0 is the rate constant of electron transfer at $E = 0$, n_a is the number of electrons participating in the potential-determining stage, and α is the transfer coefficient.

From (11) and (12) follows the equation for the shape of the kinetic wave of reduction of weak acids from unbuffered solutions of their salts:

$$E = \varepsilon_0 - \frac{RT}{\alpha n_{aF}} \ln \frac{i^2}{i_{\mathrm{pr}}^{3/2} - i^{3/2}}, \tag{13}$$

where

Fig. 1. Values of $i_{\text{pr}}^{3/2}$ for waves of the dipotassium salt of maleic acid at different concentrations in a background of 1.0 N KCl

Figure 1: Fig. 1. Values of $i_{\text{pr}}^{3/2}$ for waves of the dipotassium salt of maleic acid at different concentrations in a background of 1.0 N KCl

Fig. 2

Figure 2: Fig. 2

$$\varepsilon_0 = \frac{RT}{\alpha n_{aF}} \ln k_{\text{el}}^0 \left(\frac{n\chi_{\text{OH}^-}}{\nu k_2 D}\right)^{-1/2} 10^3, \qquad (14)$$

if the currents in (13) are expressed in μa.

To verify the derived relations, polarograms were recorded for solutions of the dipotassium salt of maleic acid in a background of 1.0 N KCl, since it is known [8] that recombination of the dianions of maleic acid to electrochemically active monoanions occurs in the bulk reaction layer. The polarograms were recorded on a PE-312 polarograph with potentiometric control of potentials. The dropping electrode with a paddle for forced detachment of drops had the following characteristics: $m = 0.828$ mg/sec, $t = 0.28$ sec. The work was carried out at $25 \pm 0.2°$ in a nitrogen atmosphere, with solutions freed from O_2 and CO_2.

Fig. 1. Values of $i_{\text{pr}}^{3/2}$ for waves of the dipotassium salt of maleic acid at different concentrations in a background of 1.0 N KCl

In Fig. 1 is shown the dependence of $i_{\text{pr}}^{3/2}$ on $c - i_{\text{pr}}/\chi$, from which it follows that equation (5) is in good agreement with the experimental data. To determine the value of χ ($\chi = 2.22\,\mu$a/mmole), diffusion waves of maleic acid were recorded in a buffer with pH ≈ 3 (ionic strength 1.0), and a correction for the difference between the diffusion coefficients of the acid and its anions [9] was introduced into the value thus found. The quantity i_{pr}/χ is considerably smaller than c (especially at high c), so that expression (5) practically coincides in form with the analogous expression for bulk catalytic waves

hydrogen in unbuffered media (1). From the slope of the graph in Fig. 1 according to (6), the rate constant for protonation by water of the maleic-acid dianions (the rate constant for hydrolysis of potassium dimaleinate) was found to be
$k_1 = 2.0$ liter/mole • sec. For the calculation it was assumed that n and ν in (IV) are equal to two; the value $\chi_{\text{OH}^-} = 2.05$ μa/mmole was found from the Il' kovich equation, using the diffusion coefficient of OH^- ions in 1 N KNO_3 $-2.26 \cdot 10^{-5}$ cm^2/sec (10). For K_A of the second stage of dissociation of maleic acid in 1.0 N KCl, the value $3.2 \cdot 10^{-6}$ (8) was taken.

Fig. 2. Dependence of the current function on the potential according to equation (13) for two concentrations of the dipotassium salt of maleic acid:
1 $-c = 4.84$ mole/liter; 2 $-c = 32.7$ mmole/liter

The value $k_1 = 2.0$ liter/mole • sec is close to the analogous value–5.5–for pyridine (^{6}) (which has approximately the same pK_A as the second stage of dissociation of maleic acid), but it is considerably higher than the value that was approximately estimated by extrapolating (^{8}) the straight line of the logarithmic plot expressing the Brønsted relation for recombination of maleic-acid dianions under the action of various acids, up to the pK_A of water. The value $k_2 = k_1 K_A[\mathrm{H_2O}]/K_W$ according to the data of the present work is equal to $3.6 \cdot 10^{10}$ liter/mole • sec.

Figure 2 shows plots of the dependence of the current function on the potential according to equation (13) for waves at two concentrations of the dipotassium salt. As can be seen from the figure, at sufficiently high currents the experimental points lie on the straight line described by equation (13), with $\varepsilon_0 = -1.45$ V and an inverse slope of ~ 75 mV.

Approximately the same slope is observed for plots of the waves of reduction of monoanions of maleic acid obtained in borate buffer solutions with pH 9-9.5. It should be noted that at low current values the function $\lg i^2/(i_{\mathrm{pr}}^{3/2} - i^{3/2}) - E$, constructed from experimental values, lies below the calculated values (Fig. 2), whereas for catalytic hydrogen waves the experimental values for the currents are always higher than the calculated ones (^{1,6}).

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
21 I 1963

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