DETERMINATION OF THE CHARGE OF REACTING PARTICLES IN THE PRESENCE OF CHEMICAL EQUILIBRIA IN THE VOLUME OF THE SOLUTION

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UDC 541.13

The method proposed by Frumkin and his co-workers for the determination of the charge of a reacting particle in the presence of ψ_1 effects was extended to electrode processes controlled by an electron transfer stage and complicated by the formation of ion pairs or by complex-forming reactions in the volume of the solution.

In papers by Frumkin and his co-workers [1, 2] a method was proposed for determination of the charge of a reacting particle from the dependence of the electrochemical reduction rate on the electrode potential and the concentration of the supporting electrolyte in the presence of ψ_1 effects. In the light of certain new experimental data [3-6] it seemed of interest to discuss the possibilities of this method under conditions where ion pairs are formed between the reacting anion and the cations of the supporting electrolyte or where complex-forming reactions occur with the anions of the supporting electrolyte. From the qualitative standpoint the complications arising in the latter case were examined briefly in [1, 2].

As in [1, 2], we will compare the rates of addition of electrons to the particles being reduced in two systems (I and II) satisfying the following conditions.

1. The adsorption of the anions of the supporting electrolyte Γ_A and the adsorption of the reacting particles are small compared with the adsorption of the cations: $|\Gamma_A| \ll |\Gamma_C|$, and the cations are surface-inactive.

2. On passing from system I to system II the equation $\varphi - (RT/nF)\ln c = \text{const}$ is satisfied, where φ is the difference in the metal/electrolyte potentials, n is the charge, and c is the concentration of the supporting electrolyte cations.

In addition, we will assume that there is no retardation of the chemical stages in the transformation of one form of the reacting substance to another in the investigated processes. This condition is satisfied when the rate of the discharge stage is small compared with the rate of the corresponding chemical stage. Finally, we will assume that the field of the double layer does not have an effect on the equilibrium constant.

Let us first consider the case of the formation of ion pairs in the volume of the solution. Let us suppose that the anion A^z with charge z forms ion pairs with the supporting electrolyte cations C^+ in the volume of the solution according to the equation

$$A^z + C^+ \rightleftarrows CA^{z+1}, \tag{1}$$

and that the A^z anions and the CA^{z+1} particles then both take part in the electrochemical reduction reaction. The sum $[A^z] + [CA^{z+1}]$ remains constant with variation in the concentration of the salt CA in the solution. Therefore, denoting $[A^z] + [CA^{z+1}]$ by c_0 and the concentrations $[CA^{z+1}]$ and $[A^z]$ by c_1 and c_2, respectively, we obtain

$$c_1 = \frac{cc_0}{c+K}, \tag{2}$$

M. V. Lomonosov Moscow State University. Translated from Élektrokhimiya, Vol. 10, No. 5, pp. 756-764, May, 1974. Original article submitted December 3, 1973.

$$c_2 = \frac{Kc_0}{c+K}, \tag{3}$$

where $K = cc_2/c_1$ is the equilibrium constant.

If the condition $\varphi - (RT/F)\ln c = \text{const}$, which approximately corresponds to $\varphi - \psi_x = \text{const}$, is satisfied, the current i passing in the circuit is equal to:

$$\begin{aligned} i &= k_1'c_1 \exp\left[-\frac{(z+1)\psi_x F}{RT}\right] + k_2'c_2 \exp\left[-\frac{z\psi_x F}{RT}\right] = \\ &= k_1' \frac{c_0 c}{c+K} \exp\left[-\frac{(z+1)\psi_x F}{RT}\right] + k_2' \frac{Kc_0}{c+K} \exp\left[-\frac{z\psi_x F}{RT}\right], \end{aligned} \tag{4}$$

where ψ_x is the potential at distance x from the interface (read from a point in the depth of the solution); k_1', k_1, k_2', and k_2 are constants (formal reaction rate constants). As was shown in [1, 2],

$$\psi_x = \text{const} + \frac{RT}{F}\ln c, \tag{5}$$

and, therefore,

$$i = k_1 \frac{c_0 c^{-z}}{c+K} + k_2 \frac{Kc_0 c^{-z}}{c+K} = (k_1 + k_2 K)\frac{c_0 c^{-z}}{c+K} \tag{6}$$

and

$$n^* = \left(\frac{\partial \lg i}{\partial \lg c}\right)_{\left(\varphi - \frac{RT}{F}\ln c\right), c_0} = -z - \frac{c}{c+K}. \tag{7}$$

This equation differs from that obtained in [1, 2] by the presence of the second term on the right side. With sufficiently small c and large K values this term can be neglected, and we arrive at the previously derived equation [1, 2].

It is easy to show that n* is equal in absolute value to the average charge of the particles being reduced in the solution.

Equation (7) also holds in those cases where only the A^z particles or only the CA^{z+1} particles are subject to reduction. Thus, in the case of the formation of ion pairs between the investigated anion A^z and the supporting electrolyte cations, the magnitude of n* for fairly large negative surface charges is determined by the average charge of the particles in the volume of the solution, irrespective of the nature of the reacting particle.

For aqueous solutions of alkali-metal persulfates the second term on the right side of Eq. (7) can be evaluated approximately by using the dissociation constants for $NaSO_4^-$ and KSO_4^-, which amount to 0.19 and 0.11, respectively [7]. With supporting electrolyte concentrations in the order of 10^{-2} M this term can amount to about 0.05 in the case of Na^+ and about 0.08 in the case of K^+. These values are evidently rather high, since the dissociation constants for $NaS_2O_8^-$ and $KS_2O_8^-$ should in all probability be greater than those for $NaSO_4^-$ and KSO_4^-. In practice [1,2] the n* values in the reduction of persulfate amount on the average to 1.78 in the LiCl + NaCl supporting electrolyte, 1.85 in NaF, 1.90 in KCl, and 1.93 in CsCl. Thus, the observed departures of n* from 2 and their dependence on the nature of the supporting electrolyte cation cannot be explained by the formation of ion pairs in the volume of the solution. As supposed in [1,2], these deviations are due to the fact that the condition $|\Gamma_C| \gg |\Gamma_A|$ is not satisfied sufficiently rigorously in the investigated range of surface charges.

In order to extend Eq. (7) to surface charges where the condition $|\Gamma_C| \gg |\Gamma_A|$ breaks down, it is necessary to use the equation of the diffuse layer theory for the potential of the outer Helmholtz plane $\psi_x = \psi_0$:

$$\psi_0 = \frac{2RT}{F} \operatorname{arcsh}\left(\frac{\varepsilon}{2A\sqrt{c}}\right), \tag{8}$$

where ε is the surface charge and A is a constant [8]. Using this equation in place of Eq. (5), for the discharge of a doubly charged anion in the presence of equilibrium (1) we obtain:

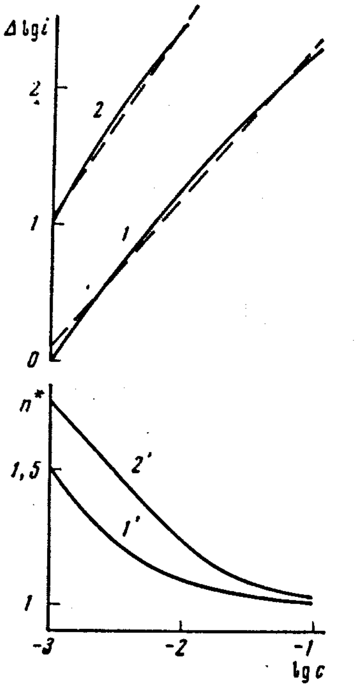

Fig. 1

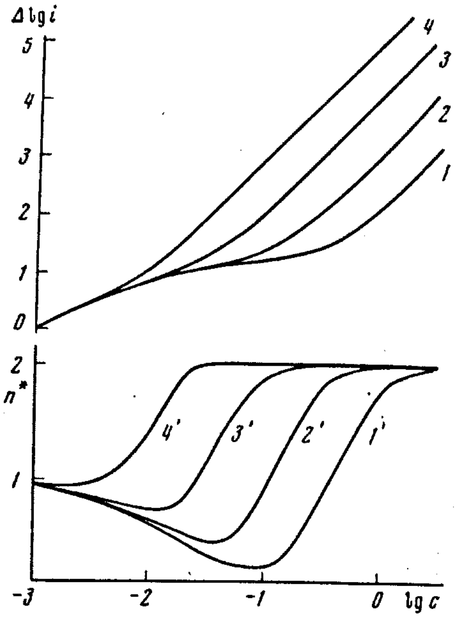

Fig. 2

Fig. 1. Dependence of the electrochemical reduction rate and n* values on the concentration of the salt with constant surface charge under conditions where ion pairs are formed. The solid curves represent calculation according to Eqs. (6) and (7) for z = −2, K = 10^{-3} (1, 1') and K = 3 · 10^{-3} (2, 2'). The dashed lines represent straight lines with gradients 1.1 and 1.45. The location of curves 1 and 2 and also the Δ log i, log c curves in all the subsequent figures on the ordinate axis was selected arbitrarily.

Fig. 2. Dependence of the electrochemical reduction rate and n* values on the concentration of the salt with constant surface charge, calculated by means of Eqs. (13) and (14) with K = 1.7 · 10^{-2} and $\varkappa$ = 10 (1, 1'), 1 (2, 2'), 0.1 (3, 3'), and 0.01 (4, 4').

$$n^* \approx \left(\frac{\partial \lg i}{\partial \lg c}\right)_\varepsilon = -\frac{2\varepsilon}{\sqrt{4A^2c+\varepsilon^2}} - \frac{c}{c+K}, \tag{9}$$

and for the discharge of a singly charged anion

$$n^* \approx \left(\frac{\partial \lg i}{\partial \lg c}\right)_\varepsilon = 1 - \frac{\varepsilon}{\sqrt{4A^2c+\varepsilon^2}} - \frac{c}{c+K}. \tag{10}$$

The first term on the right side of Eq. (9) amounts to 1.85 when ε = −5 μC/cm² and c = 0.03 and 1.96 when ε = −10 and c = 0.01. During the discharge of a singly charged anion the sum of the first two terms on the right side of Eq. (10) is equal to 1.93 when ε = −5 μC/cm² and c = 0.03 and 1.98 when ε = −10 and c = = 0.001. Thus, the breakdown of the condition $|\Gamma_C| \gg |\Gamma_A|$ is reflected significantly in the n* value when $|\varepsilon| < 10$ μC/cm² and c > 0.03 M.

In addition, it is necessary to take account of the fact that with breakdown of the condition $|\Gamma_C| \gg |\Gamma_A|$ the conditions $\varphi - (RT/F)\ln c$ = const and ε = const are not identical and, consequently, n* ≠ $\left(\frac{\partial \lg i}{\partial \lg c}\right)_\varepsilon = \left(\frac{\partial \lg i}{\partial \lg c}\right)_{\varphi-\psi}$. To determine the error due to the difference in these quantities it is possible to use the general equations

$$\left(\frac{\partial u}{\partial x}\right)_z = \left(\frac{\partial u}{\partial x}\right)_y + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \quad \text{and} \quad \left(\frac{\partial y}{\partial x}\right)_z = -\left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y,$$

where u = log i; x = log c; $y = \varphi - \psi_0$; and $z = \varphi - (RT/F)\ln c$. As a result of algebraic rearrangements with allowance for the equation of the theory of retarded discharge, in the case of the electrochemical reduction of the doubly charged anion we finally obtain:

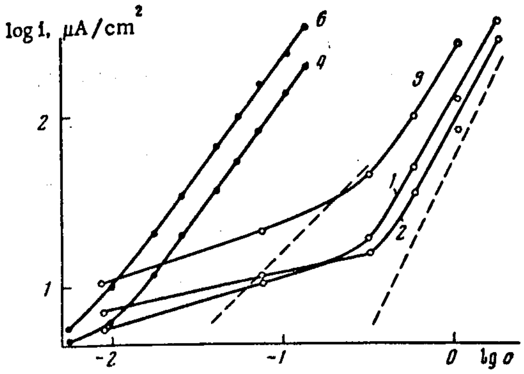

Fig. 3. Experimental dependences of the electrochemical reduction rate of 10^{-3} N K_2PtCl_4 on the concentration of KCl (1–3) and CsCl (4,5) at a dropping mercury electrode with $\varphi - (RT/F)\ln c = \text{const}$. The log i values in solutions with the lowest concentrations of potassium and cesium chlorides were recorded at $\varphi = -1.1$ (1,4), −1.2 (2,5), and −1.3 (3) V (s.c.e.). The dashed lines represent straight lines with gradients 1 and 2.

$$n^* = \left(\frac{\partial \lg i}{\partial \lg c}\right)_{\left(\varphi - \frac{RT}{F}\ln c\right),\, c_0} = -\frac{2\varepsilon}{\sqrt{4A^2C+\varepsilon^2}} - \frac{c}{c+K} - \left[\alpha - (2+\alpha)\, C \cdot \frac{2RT}{F} \cdot \frac{1}{\sqrt{4A^2c+\varepsilon^2}}\right]\left[1 + \frac{\varepsilon}{\sqrt{4A^2c+\varepsilon^2}}\right]. \quad (11)$$

where α is the transfer coefficient and C is the differential capacitance of the double layer. When $\varepsilon = -5$ $\mu C/cm^2$ and $c = 0.03$ the last term amounts to only about 0.005 and can be practically neglected.

Thus, the calculations show that the conditions $\varphi - (RT/F)\ln c = \text{const}$ and $\varepsilon = \text{const}$ or $\varphi - \psi_0 = \text{const}$ practically coincide for comparatively small negative surface charges, and consequently the difference in n* from 2 during the discharge of the persulfate anion is largely due to breakdown of the conditions $|\Gamma_C| \gg |\Gamma_A|$.

The aqueous solutions of potassium ferricyanide the dissociation constant of $KFe(CN)_6^{2-}$ is 0.064 [7]. When c = 0.003 the second term in Eq. (7) amounts to only about 0.04. Thus, in the reduction of ferricyanide in aqueous solutions the n* values should be close to 3, and this is observed in practice [1,2].

According to [4], during the reduction of persulfate anions in ethylene glycol the n* values are equal to about 1.1 in $NaClO_4$ and KCl supporting electrolyte and about 1.45 in CsCl. This result can only be explained in terms of the formation of ion pairs in the volume of the solution. Using Eq. (7) we come to the conclusion that the dissociation constant of the ion pairs $NaS_2O_8^-$ and $KS_2O_8^-$ in ethylene glycol must amount to about 10^{-3} and the dissociation constant of $CsS_2O_8^-$ to about $3 \cdot 10^{-3}$. The dependence of n* and Δ log i on log c calculated by means of Eqs. (6) and (7) for these K values is shown in Fig. 1. With increase in the concentration of the supporting electrolyte the "charge" of the reacting particle changes from −2 to −1. Thus, the dependence of log i on log c is nonlinear. However, the departures from linearity in the range of supporting electrolyte concentrations investigated in [4] are relatively small, and the experimental data can to a first approximation be represented by straight lines with gradients 1.1 and 1.45 (the dashed lines in Fig. 1). Consequently, with sufficiently well-defined formation of ion pairs their dissociation constants can evidently be evaluated from the dependence of the electrochemical reduction rate on the supporting electrolyte concentration according to Eq. (7). It would be interesting to check this conclusion by independent determinations of the dissociation constants for $NaS_2O_8^-$ and $CsS_2O_8^-$ in ethylene glycol.

Let us now consider processes of electrochemical reduction of anions complicated by complexing reactions. Such electrode processes have been analyzed in a fair amount of detail in the literature but in the absence of ψ_1 effects (for a review see [9]). The relations between the electrochemical reduction rate and the electrolyte concentration observed in the presence of ψ_1 effects can be conveniently discussed for the specific processes of reduction of K_2PtCl_4 and $K_3Co(C_2O_4)_3$, which were investigated experimentally in [2,3].

In aqueous solutions of K_2PtCl_4 the following equilibrium is established:

$$PtCl_4^{2-} + H_2O \rightleftharpoons PtCl_3H_2O^- + Cl^- \quad (12)$$

with $K = [PtCl_3H_2O^-][Cl^-]/[PtCl_4^{2-}] = 1.7 \cdot 10^{-2}$ [10]. If it is assumed that the $PtCl_4^{2-}$ and $PtCl_3H_2O^-$ anions are subject to discharge at the same time, for the reaction rate with alkali metal chlorides as supporting electrolyte and with $\varphi - (RT/F)\ln c = \text{const}$ we obtain the following equation:

$$i = k_1'[PtCl_3H_2O^-]\exp\left(\frac{\psi_x F}{RT}\right) + k_2'[PtCl_4^{2-}]\exp\left(\frac{2\psi_x F}{RT}\right) = k_1\frac{Kc_0c}{c+K} + k_2\frac{c_0c^2}{c+K}, \quad (13)$$

from which

$$n^* = \frac{K}{c+K} + \frac{2c^2}{K\varkappa + c^2}, \quad (14)$$

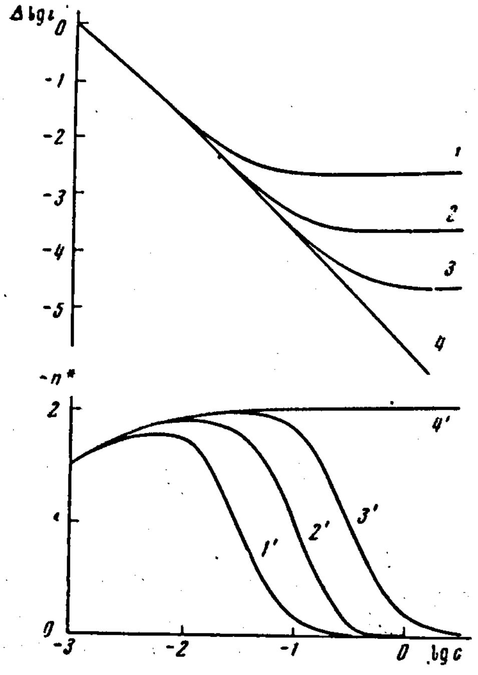

Fig. 4. Dependence of electrochemical reduction rate and n* values on the concentration of the salt with constant surface charge, calculated by means of Eqs. (18) and (19) with $K = 10^{-3}$ and $\varkappa = 1$ (1, 1'), 10 (2, 2'), 100 (3, 3'), and ∞ (4, 4').

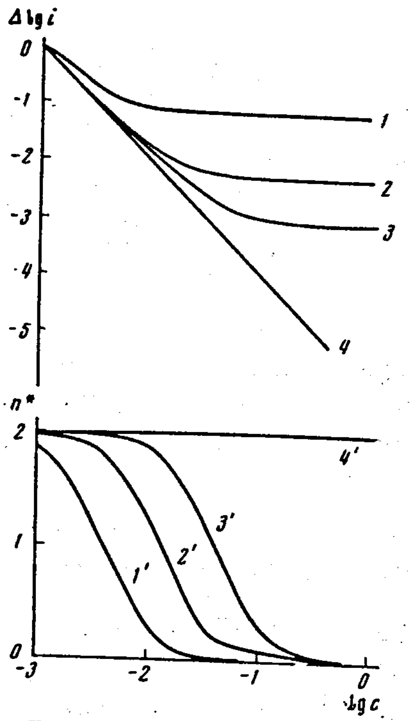

Fig. 5. Dependence of the electrochemical reduction rate and n* values on the concentration of the salt with constant surface charge, calculated by means of Eqs. (18) and (19) with $K = 1.75 \cdot 10^{-5}$ and $\varkappa = 1$ (1, 1'), 10 (2, 2'), 100 (3, 3'), and ∞ (4, 4').

where c_0 is the total concentration of $PtCl_4^{2-}$ and $PtCl_3H_2O^-$ in the solution, and $\varkappa = k_1/k_2$ is the ratio of the reduction rate constants of the singly and doubly charged anions.

The dependences of the reaction rate and n* values on the concentration of the alkali-metal chloride, calculated by means of Eqs. (13) and (14) with $K = 1.7 \cdot 10^{-2}$ and with various $\varkappa$ values, are shown in Fig. 2. As expected, with low chloride concentrations the slope of the relation between log i and log c is equal to unity, and with an excess of chloride it becomes equal to 2. With intermediate chloride concentrations the dependence of the reaction rate on c is lower than observed in the discharge of singly charged anions, although by stipulation the singly and doubly charged anions discharge at the same time. This effect is more clearly expressed the greater the k_1/k_2 ratio and is due to the transition from preferential discharge of singly charged anions to discharge of doubly charged ions with a lower rate constant.

The experimental data obtained during reduction of K_2PtCl_4 in potassium chloride and cesium chloride are given in Fig. 3. In potassium chloride the slope of the initial section of the curves is in fact less than unity. During comparison of the curves in Figs. 2 and 3 it can clearly be concluded that with potassium chloride as supporting electrolyte $k_1/k_2 \simeq 10$. Thus, in order to explain the dependence of the rate of reduction of K_2PtCl_4 in potassium chloride supporting electrolyte on the concentration of the salt there is no need to presuppose participation of uncharged $PtCl_2(H_2O)_2$ particles [2]. Moreover, according to the constant for the formation of $PtCl_2(H_2O)_2$ [10], the concentration of this complex even in the presence of 10^{-2} N potassium chloride is too small for it to be able to make a significant contribution to the observed currents. The dependence of the reduction rate on the cesium chloride concentration can be explained if it is supposed that in this case $k_1/k_2 < 1$. The rate constant for the discharge of the doubly charged anion becomes greater than the constant for the singly charged anion as a result, probably, of specific adsorption of the Cs^+ cation on the mercury and the more clearly defined formation of ion pairs between these cations and the $PtCl_4^{2-}$ ions compared with $PtCl_3H_2O^-$ (within the limits of the double layer [11]).

Study of the electrochemical reduction of $Co(C_2O_4)_3^{3-}$ [3] led to the conclusion that it is necessary to take account of the following equilibrium:

$$Co(C_2O_4)_3^{3-} \rightleftarrows Co(C_2O_4)_2^{-} + C_2O_4^{2-}. \tag{15}$$

For simultaneous reduction of $Co(C_2O_4)_3^{3-}$ and $Co(C_2O_4)_2^{-}$ in $K_2C_2O_4$ with $\varphi - (RT/F)\ln c = \text{const}$ we obtain:

$$i = k_1'[Co(C_2O_4)_2^{-}]\exp\left(\frac{\psi_x F}{RT}\right) + k_2'[Co(C_2O_4)_3^{3-}]\exp\left(\frac{3\psi_x F}{RT}\right)$$

$$= \frac{k_2 c_0 c}{2Kc}[2K\varkappa + c^3], \tag{16}$$

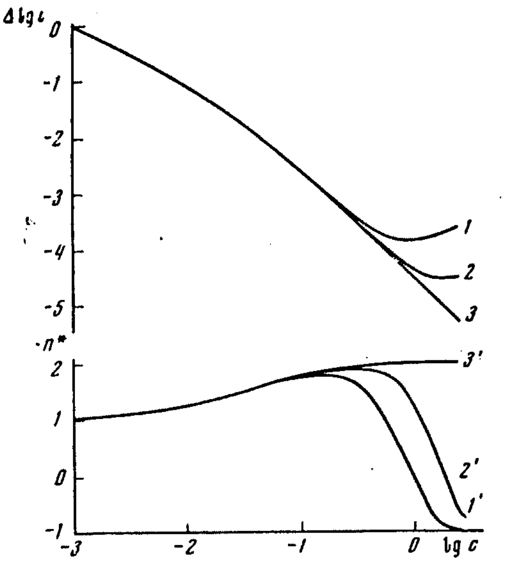

Fig. 6. Dependence of electrochemical reduction rate and n* values on the concentration of the salt with constant surface charge, calculated by means of Eqs. (20) and (21) with K = 1.2 · 10^{-2} and $\varkappa$ = 10 (1, 1'), 100 (2, 2'), and ∞ (3, 3').

from which

$$n^* = \frac{2K}{2K+c} + \frac{3c^3}{2K\varkappa+c^3}, \tag{17}$$

where K is the constant of the equilibrium (15) and c_0 is the total concentration of $Co(C_2O_4)_3^{3-}$ and $Co(C_2O_4)_2^-$ in the solution. According to Eq. (17), the n* value should change from 1 at small concentrations to 3 at large concentrations of $K_2C_2O_4$, and with average concentrations of $K_2C_2O_4$ the small n* value may be less than unity (depending on the value of $\varkappa$).

In practice the n* value in $K_2C_2O_4$ supporting electrolyte is close to 2 [3]. Such a value can be obtained from Eq. (17) for c = 0.01, if K is of the order of 10^{-6}–10^{-7}. There are no published K values for the oxalate complex of trivalent cobalt, and this makes it impossible to check the validity of the obtained conclusion. It must only be mentioned that the K value given above does not contradict the results from investigation of the dependence of the reduction rate of the cobalt oxalate complexes in potassium chloride supporting electrolytes on c, according to which n* ≃ 1.1 [3].† Nevertheless, with such a low K the dissociation rate of the $Co(C_2O_4)_3^{3-}$ complex can be comparable with the discharge rate. This fact can be reflected significantly in the interpretation of experimental data [3] on the electrochemical reduction of $Co(C_2O_4)_3^{3-}$ anions.

In conclusion, let us consider the hydrogen evolution reaction in solutions of relatively weak acids on the assumption of simultaneous slow discharge of H_3O^+ ions and undissociated molecules of the acid HA or anions HA^- (in the case of a dibasic acid) in CA or C_2A supporting electrolytes.

For simultaneous discharge of H_3O^+ and HA in CA supporting electrolytes with $\varphi - (RT/F)\ln c = \text{const}$ it is possible to write:

$$i = k_1'[H_3O^+]\exp\left(-\frac{\psi_x F}{RT}\right) + k_2'[HA] = \frac{k_2 c_0}{K+c}\left(\frac{K}{c}\varkappa + c\right), \tag{18}$$

from which

$$-n^* = \frac{c}{K+c} + \frac{K\varkappa - c^2}{K\varkappa + c^2}, \tag{19}$$

where c_0 is the total concentration of H_3O^+ and HA, $K = [H_3O^+][A^-]/[HA]$ is the constant of the equilibrium $H_3O^+ + A^- \rightleftharpoons HA + H_2O$, and $\varkappa = k_1/k_2$ is the ratio of the rate constants for the reduction of H_3O^+ and HA.

For simultaneous discharge of H_3O^+ and HA^- in C_2A supporting electrolytes with $\varphi - (RT/F)\ln c = \text{const}$ we obtain:

$$i = k_1'[H_3O^+]\exp\left(-\frac{\psi_x F}{RT}\right) + k_2'[HA^-]\exp\left(\frac{\psi_x F}{RT}\right) = \frac{k_2 c_0}{2K+c}\left(\frac{2K}{c}\varkappa + c^2\right) \tag{20}$$

and

$$-n^* = \frac{c}{2K+c} + \frac{2(K\varkappa - c^3)}{2K\varkappa + c^3}, \tag{21}$$

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† In fact, when K = 10^{-7} the equilibrium concentrations of $Co(C_2O_4)_3^{3-}$ and $Co(C_2O_4)_2^-$ in 10^{-3} $K_3Co(C_2O_4)_3$ solution are about 0.99 · 10^{-3} and about 10^{-5}, respectively. If it is assumed that these concentrations remain constant with the addition of potassium chloride, when $\varphi - (RT/F)\ln c = \text{const}$, $i = k_1' \cdot 10^{-5} \cdot c + k_2' \cdot 10^{-3} \cdot c^3$, and $n^* = 1 + 2c^2/(0.01\varkappa + c^2)$. Since, evidently, $\varkappa > 1$, then n* ≃ 1 when c is of the order of 10^{-2}.

where c_0 is the total concentration of H_3O^+ and HA^-, $K = [H_3O^+][A^{2-}]/[HA^-]$ is the constant of the equilibrium $H_3O^+ + A^{2-} \rightleftharpoons HA^- + H_2O$, and $\varkappa$ is the ratio of the rate constant for the reduction of H_3O^+ and HA^-.

The results from calculation by means of Eqs. (18) and (19) for $K = 10^{-3}$ and $K = 1.75 \cdot 10^{-5}$ are given in Figs. 4 and 5. The n* values vary from −1 for infinitely small c values to zero for large c values, reaching values less than −1 in between. The latter corresponds to decrease in the concentration of H_3O^+ ions with increase in the supporting electrolyte concentration. Since the k_1 values can be obtained by studying the discharge of hydrogen ions in solutions of a strong acid (e.g., HCl), with a knowledge of K and the experimental dependence of log i on log c it is possible then to obtain k_2, i.e., to evaluate the contribution from undissociated molecules of the acid to the overall process. The K values used in the calculation examined above correspond to the equilibria $H_3O^+ + F^- \rightleftharpoons HF + H_2O$ and $H_3O^+ + CH_3COO^- \rightleftharpoons CH_3COOH + H_2O$. Equations (18) and (19) may prove useful in the experimental investigation of these systems.

The results from calculation by means of Eqs. (20) and (21) for $K = 1.2 \cdot 10^{-2}$, which corresponds to the equilibrium $H_3O^+ + SO_4^{2-} \rightleftharpoons HSO_4^- + H_2O$, are shown in Fig. 6. In this case the n* value varies from −1 to 1, reaching values close to −2 in between. Since k_1 is amenable to experimental determination, it is possible in principle to determine k_2 from the dependence of log i on log c with $\varphi - (RT/F)\ln c = \text{const}$.

Summarizing, we arrive at the conclusion that the method proposed in [1,2] for determination of the charge of the reacting particle can give valuable supplementary information during investigation of electrode processes complicated by the formation of ion pairs or by complexing reactions in the volume of the solution. The use of the relationship derived above is, however, limited to cases where it is possible to disregard the slowness of the establishment of the chemical equilibria. Analysis of the effect of the concentration of the supporting electrolyte on processes controlled by slow chemical stages [12] in the presence of ψ_1 effects is a separate problem.

We express our gratitude to Academician A. N. Frumkin for valuable comments during the discussion of the conclusions of this work.

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