16. A.M.Sukhotin, "Voprosy Teorii Elektrolitov v Sredakh s Nizkoi Dielektricheskoi Pronitsaemost'yu" (Problems of the Theory of Electrolytes in Media of Low Dielectric Constant), Goskhimizdat, Leningrad, 1959.

Mendeleev Moscow Institute of Chemical Technology

Received 4th July 1963

U.D.C. 541.13

ELECTROCHEMICAL REDUCTION OF THE HEXAFLUOROPLATINATE ION AT A DROPPING MERCURY ELECTRODE

N.V.Nikolaeva-Fedorovich, S.M.Ikonopisov, and B.N.Rybakov

The electrochemical reduction of the PtF_6^{2-} anion has not yet been investigated. Among the other hexahalogenoplatinates, the electrochemical reduction of $PtCl_6^{2-}$ and $PtBr_6^{2-}$ at a dropping mercury electrode was studied in detail[1].

We investigated the reduction of PtF_6^{2-} at a dropping mercury electrode by a method based on the determination of the polarisation $I-\varphi$ curves and the $I-\tau$ curves showing the variation of the current flowing through the drop with the growth time of the drop. The capillary employed had the following characteristics: flow rate of the mercury $m = 1.58$ mg s^{-1} and drop time $\tau = 5.2$ s in 0.01 N KF solution at a potential $\varphi = -1.0$ V. All the potentials quoted are given in volts relative to the normal calomel electrode. The Figures show only the parts of the $I-\varphi$ curves which are undistorted by first-order maxima and which have been corrected for the charging currents.

The electrochemical reduction of PtF_6^{2-} begins at potentials corresponding to positive charges on the mercury; in the region of the zero-charge point in dilute supporting electrolyte solutions the rate of reaction diminishes, the current reaches a minimum value at $\varphi = -0.8$ V, and then begins to increase until the limiting diffusion current is attained (Fig. 1, curve *1*). The polarisation curves for the reduction of 10^{-3} N K_2PtF_6, recorded at various time intervals (up to 24 h) after preparation of the solution, showed that the limiting current for the reduction of PtF_6^{2-} and the current at the minimum of the $I-\varphi$ curves are independent of time, which indicates the absence of appreciable hydrolysis of K_2PtF_6. The polarisation curves also do not change with time in 10^{-3} N K_2PtF_6 solutions with added KCl and KBr (to give a concentration 0.01 N) but introduction of KNO_2 or KCSN into the solution changes the shape of the $I-\varphi$ curves, indicating the occurrence of double-decomposition reactions in the bulk of the solution[2].

The $I-\tau$ curves show that the current at the minimum of the curve is determined by the reaction kinetics since it is proportional to the growth time of the drop raised to the power 2/3. The fall of the current in the region of the zero-charge potential and the "kinetic" origin of the current at the minimum indicate that the rate-determining stage in the reduction of PtF_6^{2-} is the electrochemical discharge stage and the rate of reduction should depend, as in the case of $S_2O_8^{2-}$ and $PtCl_6^{2-}$, on the structure of the electrical double layer[1]. An increase in the concentration of the indifferent electrolyte does indeed increase the rate of reaction and at high values of this concentration the fall of the current vanishes (Fig. 1). The increase of the limiting current with the concentration of the supporting electrolyte can be explained by the removal of restrictions on migration. This effect is more pronounced than in the case of $PtCl_6^{2-}$ and $PtBr_6^{2-}$ and may be due to the higher mobility of the PtF_6^{2-} anion. The rate of reduction of PtF_6^{2-} increases with the radius of the cation of the supporting electrolyte (Fig. 2) and when organic cations are added to the solution (Fig. 3).

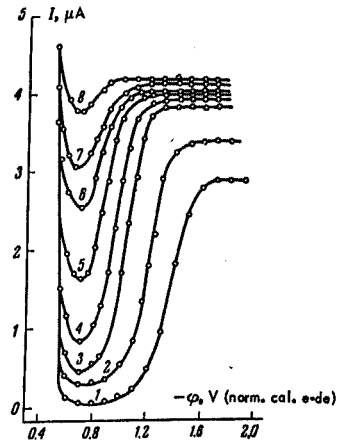

Fig.1. Polarisation curves for the reduction of 10^{-3} N K_2PtF_6 at a dropping mercury electrode in the presence of KF of various concentrations (N):
1) 0; 2) 1×10^{-3}; 3) 5×10^{-3}; 4) 1×10^{-2}; 5) 2×10^{-2}; 6) 4×10^{-2}; 7) 6×10^{-2}; 8) 0.5.

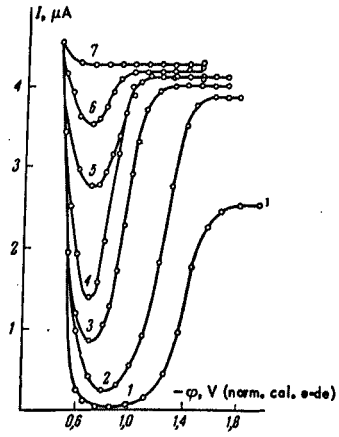

Fig.2. Polarisation curves for the reduction of 10^{-3} N K_2PtF_6 at a dropping mercury electrode in the presence of various additives:
1) no additive; 2) 10^{-2} N NaF; 3) 10^{-2} N × × KF; 4) 10^{-2} N CsF; 5) 0.1 N NaF; 6) 0.1 N KF; 7) 0.1 N CsF.

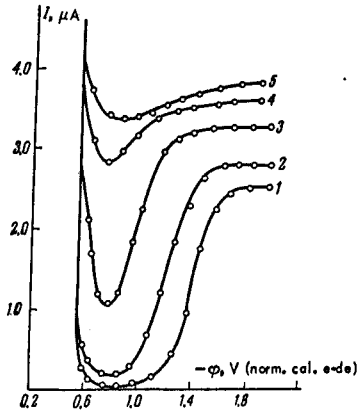

Fig.3. Polarisation curves for the reduction of 10^{-3} N K_2PtF_6 at a dropping mercury electrode in the presence of $[(C_2H_5)_4N]_2SO_4$ at various concentrations (N):
1) 0; 2) 10^{-4}; 3) 4×10^{-4}; 4) 2×10^{-3}; 5) 6×10^{-3}.

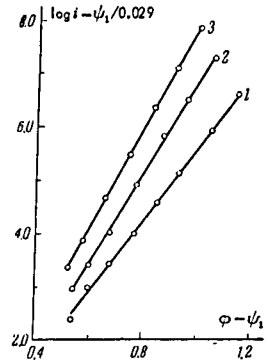

Fig.4. Corrected Tafel plots for the reduction of 10^{-3} N K_2PtF_6 in the presence of various additives: 1) 10^{-2} N NaF; 2) 10^{-2} N KF; 3) 10^{-2} N CsF.

In the reduction of $PtCl_6^{2-}$ the current at the minimum of the $I-\varphi$ curve in the presence of an indifferent electrolyte at concentrations in excess of 10^{-3} N always attains half the value of the limiting current. The explanation[3] is that the octahedral $PtCl_6^{2-}$ anion, which participates in the first stage of the reaction, is more sensitive to additives than the planar $PtCl_4^{2-}$ anion, the rate of whose reduction in fact determines the rate of the overall reaction at high concentrations of the supporting electrolyte. This is not observed in the case of the PtF_6^{2-} anion (Fig. 1). The retardation of the reaction is gradually reduced with increase in the concentration of the cation of the supporting electrolyte and vanishes completely in the presence of 0.5 N KF. This behaviour can be understood if it is supposed that the second stage of the electrochemical reduction of PtF_6^{2-} is more rapid than the first. On this hypothesis, both stages are indistinguishable in polarisation measurements. The test of the hypothesis is complicated by the fact that so far it has been proved impossible to synthesise the complex K_2PtF_4 and we are unable to study the second stage of the process in isolation.

The quantitative test of the applicability of the slow-discharge theory to the reduction of PtF_6^{2-} consisted in the determination of the transfer coefficient α and the charge of the reacting species n_1 by the method of Frumkin and Petrii[4]. The calculation of the charge of the reacting species from the variation of the kinetic current with the electrode potential and the concentration of the cations of the supporting electrolyte showed that at potentials between -1.05 and -1.2 V n_1 varies from -1.7 to -2.0, in good agreement with the theoretical value $n_1 = -2$.

To determine the transfer coefficient α, the variation of the reaction rate with the electrode potential was represented by a plot of $\log i + n_1 \psi_1 F/2.3RT$ against $\varphi - \psi_1$, where i is the experimental current corrected for the concentration polarisation, ψ_1 the potential of the diffuse part of the double layer, n_1 the charge of the species undergoing reduction ($n_1 = -2$), and φ the electrode potential. In the literature such curves are called corrected Tafel plots. The ψ_1 potentials in NaF solutions were calculated from the charges given by Grahame[5]; for KF solutions the ψ_1 potentials for KCl solutions were employed and for CsCl those calculated by Petrii[6].

According to the slow-discharge theory, in the absence of specific absorption of the species undergoing reduction and the reaction products, the corrected Tafel plots should be linear, which was confirmed for the cathodic reduction of hydrogen at a dropping mercury electrode[6]. However, in the reduction of the anions $S_2O_8^{2-}$, $Fe(CN)_6^{3-}$, and $PtCl_4^{2-}$ in the vicinity of the zero-charge potential of mercury the Tafel plots deviate appreciably from linearity, which was explained[6] by the adsorption of these anions. Fig. 4 shows that the corrected Tafel plots for the reduction of PtF_6^{2-} are linear, indicating the absence of specific adsorption of this anion on mercury. This conclusion is supported by the fact that the beginning of the descending part of the $I-\varphi$ curve is closer to the zero-charge point than in the case of the $S_2O_8^{2-}$, $Fe(CN)_6^{3-}$, and $PtCl_4^{2-}$ anions, and also by the fact that along the descending branch of the $I-\varphi$ curves the reaction rate varies with the concentration and nature of the cation of the supporting electrolyte much less than along the ascending branch (Fig. 2). It is interesting to note that the slope of the corrected Tafel plots increases on going from Na^+ to Cs^+. The transfer coefficients calculated from the slopes of the straight lines were found to be $\alpha = 0.42$ for NaF, $\alpha = 0.48$ for KF, and $\alpha = 0.52$ for CsCl. This can be explained by supposing that the PtF_6^{2-} anion is strongly hydrated. The interaction of the anion with the cations of the double layer would than depend on the degree of hydration of the latter and would increase on going from Na^+ to Cs^+, since this would involve a closer approach of the activated complex to the electrode surface and hence an increase in α.

Thus all the experimental findings obtained in the study of the reduction of the PtF_6^{2-} anion can be explained by postulating that the electrochemical discharge stage is rate-determining.

The authors thank A. V. Babaeva and N. I. Ushakova for providing the potassium hexafluoroplatinate. They should also like to take this opportunity to express their gratitude to A. N. Frumkin for frequent consultations in the course of this work.

SUMMARY

1. A study has been made of the electrochemical reduction of the PtF_6^{2-} anion at a dropping mercury electrode in the presence of inorganic and organic supporting electrolyte cations. The electrochemical discharge stage is rate-determining in the reduction of PtF_6^{2-}.
2. The experimental findings were compared quantitatively with the slow-discharge theory by determining the charge of the species undergoing reduction and the transfer coefficient α.

1. A.N.Frumkin and G.M.Florianovich, Dokl.Akad.Nauk SSSR, 80, 907 (1951); G.M.Florianovich and A.N.Frumkin, Zhur. Fiz.Khim., 29, 1829 (1955); N.V.Nikolaeva-Fedorovich and O.A.Petrii, *ibid.*, 35, 1270 (1961) [Russ.J.Phys.Chem., 623 (1961)].
2. N.V.Nikolaeva and V.N.Presnyakova, Dokl.Akad.Nauk SSSR, 87, 61 (1952).
3. N.V.Nikolaeva-Fedorovich and O.A.Petrii, Zhur.Fiz.Khim., 35, 1270 (1961) [Russ.J.Phys.Chem., 623 (1961)].
4. A.N.Frumkin and O.A.Petrii, Dokl.Akad.Nauk SSSR, 147, 418 (1962); O.A.Petrii and A.N.Frumkin, *ibid.*, 146, 1121 (1962).
5. D.C.Grahame, J.Amer.Chem.Soc., 76, 4819 (1954).
6. O.A.Petrii, Thesis, Moscow, 1962.

Lomonosov Moscow State University

Received 10th July 1963

U.D.C. 541.183

VARIATION OF THE PRE-EXPONENTIAL FACTOR WITH ACTIVATION ENERGY FOR DIFFUSION IN ACTIVATED CARBONS

I.E. Ampilogov

The activation energy is known to vary with temperature although the magnitude of this variation cannot always be determined because of experimental difficulties. Apart from temperature, the activation energy and the pre-exponential factor also vary with the nature of the bond between the molecules at the surface and with the nature of the surface itself[1]. The relation between the activation energy and the pre-exponential factor was observed experimentally many years ago by Constable[2]. This type of relation was found in the kinetics of both homogeneous and heterogeneous reactions[3-6]. It was particularly clearly demonstrated in the work of Todes and Margolis[7,8] and there can be no doubt about its existence[1]. On the basis of literature data, Zhorov and Panchenkov[9] obtained the relation between the activation energy and the pre-exponential factor in the following form:

$$\ln k_0 = -9.33 + 0.88\times10^{-3}E. \quad (1)$$

They were thus able to express the rate constant for the cracking of cumene as a function of temperature and activation energy.

The relation between k_0 and E and the dependence of k_0 on various factors in catalytic processes have been examined in Roginskii's monograph[1]. Roginskii showed that one of the conditions for the improvement of the statistical theory of catalytic processes is that this puzzling functional relation between the activation energy and pre-exponential factor be thoroughly taken into account. Vol'kenshtein believes that the relation established by Constable[2] is not necessarily significant and may often be fortuitous[10].

The aim of the present work was to establish experimentally the relation between the pre-exponential factor and the activation energy for internal diffusion of organic acid molecules from aqueous solution into the grains of coarse porous activated carbon. The activation energy was determined by the technique described previously[11] using experimental values of the effective coefficients of internal diffusion at different temperatures and the equation

$$D = D_0 e^{-E/RT}. \quad (2)$$

In most studies in which Eqn.(1) was used the kinetics of reactions in gas (vapour)–solid systems were considered. Despite the fact that the present work dealt with a different system, namely liquid–solid, the phenomenon of internal diffusion of solutes in the grains of activated carbon being investigated, the relation between the pre-exponential factor and the activation energy for internal diffusion was also found in the form of the Arrhenius equation. This is evident from the Table which lists the values of the pre-exponential factor D_0 for various concentrations of aqueous solutions of acetic and butyric acids and for two types of porous activated carbons. The Table also gives the equations for the experimental $\ln D_0$–E straight lines for each type of carbon.

All these equations have the logarithmic form of the Arrhenius equation. Those for acetic acid and the grains of the same No.4 carbon (apparatus 4, 1, and 1*a*) have coefficients A and B which do not differ markedly from one

TABLE. Activation energies for internal diffusion and the pre-exponential factors at various concentrations of aqueous solutions of acetic and butyric acids.

c, N	E, kcal × × mole^{-1}	$D_{0,\text{calc}}$	$D_{0,\text{exp}}$	$\frac{(D_{0,\text{exp}}-D_{0,\text{calc}})\times100}{D_{0,\text{calc}}}$	Acid; apparatus; type of carbon; equation of straight line
0.05	10.1	152.50	151.00	—0.99	acetic acid; apparatus 4; No. 4 carbon grain; $\ln D_0 = -12.0855 + 1.69E$
0.10	9.5	57.90	57.50	—0.69	
0.20	8.4	8.67	8.62	—0.57	
0.50	5.0	$2.75\cdot10^{-2}$	$2.78\cdot10^{-2}$	1.09	
1.00	4.2	$7.73\cdot10^{-3}$	$7.41\cdot10^{-3}$	4.00	
0.05	10.1	95.60	95.90	0.31	acetic acid; apparatus 1; No. 4 carbon grain; $\ln D_0 = -13.0155 + 1.733E$
0.10	9.5	34.40	34.70	0.86	
0.22	8.1	2.94	2.92	—0.69	
0.50	5.0	$1.29\cdot10^{-2}$	$1.28\cdot10^{-2}$	—0.80	
1.00	4.1	$3.04\cdot10^{-3}$	$3.15\cdot10^{-3}$	3.33	
0.05	10.2	173.00	176.20	1.85	acetic acid; apparatus 1*a*; No. 4 carbon grain; $\ln D_0 = -12.3300 + 1.705E$
0.10	9.5	48.20	49.20	2.08	
0.20	8.4	8.16	8.24	0.97	
0.35	6.7	$4.18\cdot10^{-1}$	$4.16\cdot10^{-1}$	—0.49	
0.50	5.0	$2.41\cdot10^{-2}$	$2.34\cdot10^{-2}$	—2.91	
1.00	4.1	$5.47\cdot10^{-3}$	$5.74\cdot10^{-3}$	4.39	
2.00	4.1	$6.18\cdot10^{-3}$	$5.76\cdot10^{-3}$	—6.77	
0.05	9.5	71.90	71.10	—1.11	acetic acid; apparatus 2; PN carbon grain; $\ln D_0 = -12.435 + 1.755E$
0.10	8.9	28.10	27.90	—0.71	
0.22	7.7	3.23	3.23	—0.31	
0.50	4.8	$1.82\cdot10^{-2}$	$1.84\cdot10^{-2}$	1.11	
1.00	4.1	$5.97\cdot10^{-3}$	$5.98\cdot10^{-3}$	0.17	
0.03	8.6	9.21	9.49	3.04	butyric acid; apparatus 1*a*; No. 4 carbon grain; $\ln D_0 = -12.0800 + 1.645E$
0.06	8.0	2.99	3.03	1.33	
0.10	7.0	$5.80\cdot10^{-1}$	$5.82\cdot10^{-1}$	0.34	
0.21	4.3	$6.76\cdot10^{-3}$	$6.57\cdot10^{-3}$	—2.80	
0.50	4.2	$6.39\cdot10^{-3}$	$7.30\cdot10^{-3}$	15.00	