ELECTROREDUCTION OF Cr(VI) FROM SOLUTIONS OF BIFUNCTIONAL ALCOHOLS

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The effect of bifunctional alcohols ethylene glycol (EG) and 1,2-propylene glycol (1, 2 PG) on the kinetic parameters for the irreversible chromate ion reduction were investigated by polarographic and coulometric methods of analysis. The electroreduction of chromate ion in neutral bifunctional alcohol solutions proceeds according to the scheme: $Cr(VI) - Cr(III) - Cr(II)$ and the values of the standard rate constant k_0^* decrease in the order $H_2O > EG > 1, 2\,PG$.

The values of real activation energy, Q, activation energy of diffusion, Q_D, and frequency factor $\log A^0$ have been calculated. The obtained values of Q_D as well as Q proved the diffusion nature of limiting current. The values of the frequency factor $\log A^0$ decrease in the order $H_2O > EG > 1, 2\,PG$, which points to a less favourable orientation of the electroactive ions at the electrode surface in glycols.

The electroreduction of chromate ions in aqueous solutions has been investigated widely[1-4]. However, its mechanism has not been elucidated up to now. It seems that estimation of kinetic parameters based on the study of the mentioned process in non-aqueous solvents similar to water can lead to a deeper insight into the mechanism of the whole reaction. A systematic investigation of the polarographic behaviour of CrO_4^{2-} anions in ethylene glycol (EG) and 1,2-propylene glycol (1, 2 PG) is the subject of the present work.

EXPERIMENTAL

The apparatus, experimental procedure and methods of reagent and solvent purification have been described elsewhere[5].

Kinetic data were obtained at the dropping mercury electrode ($m = 2$ mg/s, $\tau = 2.7$ s) by recording current–potential curves in the temperature range $20-100°C$. $0.1M$-KCl solution was used as supporting electrolyte in EG and 1, 2 PG. The potential of the working electrode was measured with respect to an aqueous saturated calomel electrode.

Coulometry has been used to determine the number of electrons involved in the electrochemical reaction. Polarograms of chromate ions recorded at $20°C$ in a fresh solution and after 2 hours practically coincide.

RESULTS AND DISCUSSION

Current–potential data for electroreduction of CrO_4^{2-} anions in EG and 1, 2 PG are presented in Figs 1 and 2.

In ethylene glycol as well as in 1,2-propylene glycol the polarograms have two clearly expressed waves with the half-wave potentials $E'_{1/2} = -0.5$ V, $E''_{1/2} = -1.01$ V for EG and $E'_{1/2} = -0.41$ V, $E''_{1/2} = -1.15$ V for 1,2 PG. According to coulometric data the first wave corresponds to the transfer of three electrons and the second to the transfer of one electron.

On the other hand, there are three steps of reduction of chromate ions in neutral aqueous solutions. Thus, electroreduction of CrO_4^{2-} anions in neutral bifunctional alcohol solutions proceeds according to the scheme $Cr(VI) - Cr(III) - Cr(II)$. The electroreduction of chromate ions to the metallic state in glycols is probably hindered by adsorption layers formed on the electrode surface from associates containing Cr(III) and Cr(II). The formation of such associates in glycols is facilitated by the low dielectric constant.

The plots of I_d vs $\sqrt{h}$ are linear and pass through the origin for all the solvents, which indicates that the current has a diffusion nature. Diffusion coefficients (D) for chromate ions in both solvents have been calculated from the Ilkovič equation[6]. The values of D in EG are equal to $6.6 \cdot 10^{-6}$ and in 1,2 PG $- 3.2 \cdot 10^{-6}$ cm^2/s. The plots of $\log [I/(I_d - I)]$ vs E are also linear for the two solvents, but the value of the slope suggests that the reductions are irreversible.

As the reduction was irreversible, the kinetic parameters were calculated by the Koutecký method[7]. The standard rate constant k_s^0 cannot be obtained, because the
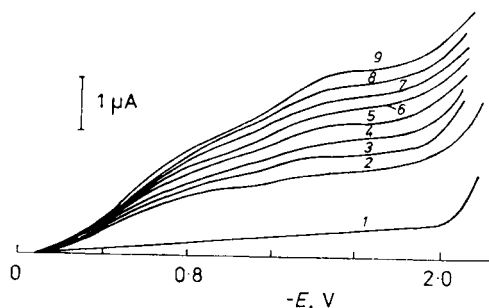

FIG. 1

Polarograms of CrO_4^{2-} ions in ethylene glycol solutions. *1* 0·1M-KCl. K_2CrO_4 concentration (mol l^{-1}): *2* 7·5 . 10^{-4}; *3* 1 . . 10^{-3}; *4* 1·25 . 10^{-3}; *5* 1·5 . 10^{-3}; *6* 1·75 . . 10^{-3}; *7* 2 . 10^{-3}; *8* 2·25 . 10^{-3}; *9* 2·5 . 10^{-3}
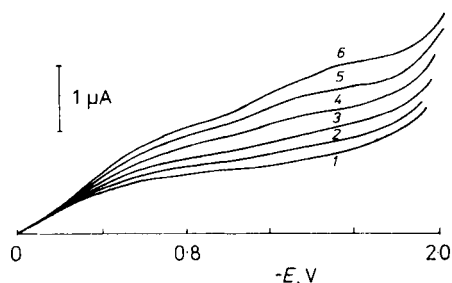
FIG. 2

Polarograms of CrO_4^{2-} ions in 1,2-propylene glycol solutions. *1* 0·01M-KCl. K_2CrO_4 concentration (mol l^{-1}): *2* 1 . 10^{-4}; *3* 2 . 10^{-4}; *4* 3 . 10^{-4}; *5* 4 . 10^{-4}; *6* 5 . 10^{-4}

value of the standard electrode potential is not known. However, the approximate value of k_0^* can be obtained by extrapolating the plot of $\log k_e$ vs E to the standard potentials of the electrode reactions Cr(VI)–Cr(III) and Cr(III)–Cr(II) in aqueous solutions[8]. The use of these potentials is based upon the assumption that the solvation energies of aqueous and glycol solutions are almost the same.

The apparent values of k_0^* confirm the irreversible nature of the electrode reactions. On the basis of the obtained values of k_e according to the equation of irreversible polarographic waves[9] the theoretical curves $(I/I_d$ vs $E)$ were plotted and a good agreement with our experimental data was obtained (Fig. 3).

By comparing the values of k_0^* in aqueous solutions with the same constants in glycols a decrease of the standard rate constants in the order $H_2O > EG > 1,2$ PG has been established. This effect can be explained by increasing distance between the electrode surface and the reactant ion in the double layer together with increasing size of solvent molecules.

A more detailed discussion of the mechanism of the irreversible reduction of chromate ions is possible on the basis of the temperature dependence of the polarographic wave. The polarograms of chromate ions in neutral EG and 1,2 PG solutions (Figs 4 and 5) seem to suggest that in glycols chromate ions are not reduced to the metal with increasing temperature. In EG solutions splitting of the first wave into two waves $(E'_{1/2} = -0.3$ V, $E''_{1/2} = -0.68$ V) with increasing temperature above 50°C was observed. According to coulometric data the formation of Cr(V) as an intermediate takes place. Such effect was not found in 1,2 PG solutions.

A similar phenomenon was observed in aqueous solution of sodium hydroxide by some authors investigating phase-selective ac polarograms[10] and potential–time curves[11] for the chromate ion reduction at room temperature. However, they suppose that Cr(IV) as an intermediate is formed.

The change of the diffusion coefficient with temperature can be expressed by

$$D = D_0 \exp\left[-\frac{Q_D}{RT} \right], \tag{1}$$

where Q_D is the activation energy of diffusion. The value of Q_D was calculated as[12]

$$Q = (Q_D + 1.85)/2, \tag{2}$$

where the value of Q (real activation energy) must be known independently. This value can be determined from the dependence of the diffusion current on temperature.

The obtained values of Q_D (see Table I) exceed the known limits $(12.6 - 21.0$ kJ/mol) for a diffusion-controlled process. This can be attributed to the high viscosity of glycols.

The value of Q_D obtained from Eq. (2) is identical with the value of Q_D obtained by plotting $1/\eta_{EG}$ vs $1/T$, showing that the Stokes radius of chromate ion is constant in the investigated temperature range.

The linear dependence of $\log I_d$ on $1/T$ which was used for the determination of Q, confirms the Arrhenius equation.
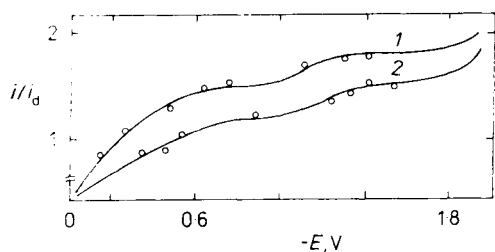

FIG. 3

Comparison of the theoretical curves for reduction of CrO_4^{2-} ions in *1* EG and *2* 1, 2 PG calculated according to the equation of irreversible polarographic waves (points) with our experimental data (line)
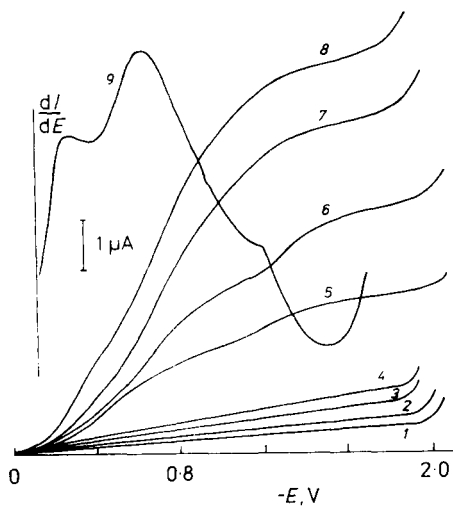
FIG. 4

Polarograms in ethylene glycol solutions of $0\cdot1M$-KCl at different temperatures in the absence (curves *1—4*) and in the presence (curves *5—8*) of $1 . 10^{-3}M$-CrO_4^{2-}: *1, 5* 20°C; *2, 6* 50°C; *3, 7* 80°C; *4, 8* 100°C. *9* like *8*, plot dI/dE vs E

FIG. 5

Polarograms in 1,2-propylene glycol solutions of $0\cdot01M$-KCl at different temperatures in the absence (curves *1—5*) and in the presence (curves *6—10*) of $3 . 10^{-4}M$-CrO_4^{2-}: *1, 6* 20°C; *2, 7* 30°C; *3, 8* 40°C; *4, 9* 50°C; *5, 10* 60°C
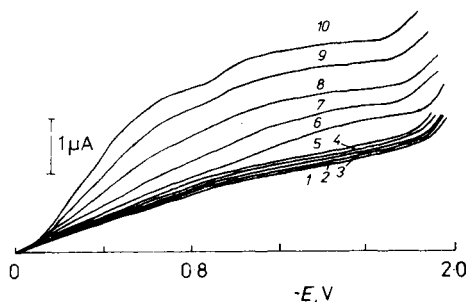
The values of Q in glycols are larger than those of Q of the diffusion processes $(7 - 11 \cdot 34 \, \text{kJ/mol})$. According to ref.[12] one of the possible explanations of this fact may be the presence of convective item in the stream of substance towards the electrode surface caused by the irregular distribution of temperature in viscous solvent.

For comparison of activation energies of several substances in different solvents with waves at different potentials the values of Q^0 were calculated from the equation[9]:

$$\frac{\alpha \eta_{1/2} nF}{2 \cdot 3RT} = \log A^0 - \frac{Q^0 - \frac{1}{2} Q_D}{2 \cdot 3RT} , \qquad (3)$$

where $\eta_{1/2} = E_{1/2} - E^0$, $\log A^0$ is the frequency factor. The standard potential for the electrode reaction $Cr(VI)-Cr(III)$ at different temperature was determined according to the equation[8]:

$$E^0(t) = E^0(25°C) + \frac{dE^0}{dT} (t - 25) , \qquad (4)$$

where $dE/dT = -1 \cdot 674 \, \text{mV/K}$. The calculated values of Q^0 lay in the usual range $(30 - 60 \, \text{kJ/mol})$.

Some information about the orientation of the ion at the electrode surface can be obtained from the value of the frequency factor. The values of $\log A^0$ were calculated from Eq. (3). It is seen from Table I that $\log A^0$ decreases in the order $H_2O >$

TABLE I

Values of kinetic parameters of Cr electroreduction

Solvent	k_0^* m/s	Q_D kJ/mol	Q kJ/mol	Q^0 kJ/mol	αn	$\log A^0$
			Cr(VI)–Cr(III)			
H_2O	$5 \cdot 01 \cdot 10^{-8}$	22·1	11·9	50·3	0·36	1·5
EG	$1 \cdot 99 \cdot 10^{-8}$	27·7	14·8	40·0	0·25	1·2
1,2-PG	$1 \cdot 12 \cdot 10^{-8}$	36·2	19·1	31·6	0·21	0·9
			Cr(III)–Cr(II)			
H_2O	$2 \cdot 01 \cdot 10^{-7}$	17·7	9·7	59·2	0·16	7·4
EG	$1 \cdot 25 \cdot 10^{-7}$	24·9	13·4	48·7	0·12	4·5
1,2-PG	$0 \cdot 51 \cdot 10^{-7}$	29·4	15·6	33·2	0·10	3·7

$>$ EG $>$ 1,2 PG for the two electrode reactions, suggesting that the depolarizer molecules have an unfavourable orientation at the electrode surface in glycols. It should be noted that the values of αn obtained for the considered temperature range indicate the same number of electrons involved in the electrode reaction.

It can be concluded that the solvent influences the electroreduction of chromate ions. Reduction of CrO_4^{2-} ions in glycols to the metal does not take place, in contrast to water. Though a similar stepwise electrode process is observed, the anion reduction rate decreases in going from water to glycols. This may be due to a change of the double layer structure and to a decrease of the frequency factor, indicating a less favourable orientation of electroactive ions at the electrode surface in glycols.

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