Academician of the Academy of Sciences of the Ukrainian SSR Yu. K. DELIMARSKII and K. M. KALABALINA

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Abstract

Full Text

PHYSICAL CHEMISTRY

Academician of the Academy of Sciences of the Ukrainian SSR Yu. K. DELIMARSKII and K. M. KALABALINA

POLAROGRAPHIC STUDY IN MOLTEN BORAX

POLAROGRAPHY OF COPPER AND CADMIUM

Recently, the polarography of molten salts has been attracting ever increasing attention ([1,2]). Direct polarographic analysis of melts (metallurgical slags and molten industrial electrolytes) is of considerable practical interest. However, oxides have been the least studied in this respect. The present communication gives the results of a polarographic study of the oxides of copper and cadmium dissolved in molten borax.

The investigation was carried out on a polarograph with automatic recording, to which a mirror galvanometer of the M 21-2 type with a sensitivity of $1.5 \cdot 10^{-9}$ A/mm was adapted. The electrolyzer was a crucible made of unglazed porcelain. The cathode was a platinum wire 0.25 mm in diameter, and the anode was a plate with an area of 2.5 cm^2. Renewal of the electrodes was achieved by depolarization when they were short-circuited. The experiments were carried out at 820°. Figure 1 shows the polarograms of CuO and CdO (for one of the concentrations), as well as the polarogram of the background, which decomposes at a voltage of 1.34 V. For both oxides we established a direct proportionality between the limiting diffusion current and the mole fraction of the dissolved oxide

$$i_d = kN. \tag{1}$$

Fig. 1. Polarograms of copper oxides ($N_{\mathrm{CuO}} = 0.009675$), cadmium ($N_{\mathrm{CdO}} = 0.0060$) and borax (background) $t = 820°$; $\delta = 1/2500$

Black and DeVries ([3]) found that the polarogram of the melt KCl—ZiCl—$\mathrm{NiCl_2}$,

Fig. 2

Figure 2: Fig. 2

obtained on platinum electrodes at a temperature of 413°, is satisfactorily described by the Kolthoff and Lingane equation (^{4})

$$E = E_M^0 - \frac{2.3RT}{nF}\lg\frac{k_s}{f_s} + \frac{2.3RT}{nF}\lg(i_d - i). \tag{2}$$

In some earlier investigations ($^{5-7}$) it was shown that polarographic waves recorded on platinum electrodes in molten salts are described not by equation (2), but by the Heyrovský-Ilkovič equation

$$E = E_{\frac{1}{2}} - \frac{2.3RT}{nF}\lg\frac{i}{i_d - i}. \tag{3}$$

To clarify the question of what equation describes the polarographic wave recorded on solid electrodes in the melts we studied, graphs were constructed both in the coordinates $E,\ \lg(i_d - i)$ and in the coordinates $E,\ \lg\frac{i}{i_d - i}$. The corresponding points were taken from the experimental data obtained by us. Examples of such graphs are given in Fig. 2. It follows from them that the polarographic waves are described by equation (3), and not by equation (2).

Fig. 2. Dependence of $\lg\frac{i}{i_d - i}$ (curves a) and $\lg(i_d - i)$ (curves b) on the applied voltage:
I—for copper oxide ($N_{\mathrm{CuO}} = 0.00194$), II—for cadmium oxide ($N_{\mathrm{CdO}} = 0.0060$)

From the Kolthoff and Lingane equation it follows that the half-wave potential must depend on the concentration, i.e.

$$E_{\frac{1}{2}} = E_M^0 + \frac{2.3RT}{nF}\lg K' f_s + \frac{2.3RT}{nF}\lg\frac{N}{2}, \tag{4}$$

where N is the mole fraction of the dissolved substance. From graphs plotted on the basis of our experimental data, the values of the half-wave potentials were found and compared with the corresponding concentrations. The results obtained are given in Table 1. Also included here are the values of $\frac{i_d}{N}$, as well as the calculated and experimentally established values of the prelogarithmic coefficients of equation (3). As is seen from these data, for one and the same sensitivity the values of $\frac{i_d}{N}$ retain good constancy, which confirms the validity of equation (1) and indicates the accuracy of determining oxide concentrations in melts by means of diffusion currents. Since the dependence of $E_{\frac{1}{2}}$ on $\lg \dfrac{N}{2}$ does not

Table 1

Oxide	Mole fraction N	$E_{\frac{1}{2}}$	$\dfrac{i_d}{N} \cdot 10^{-3}$	$\dfrac{\Delta E}{\Delta \lg \dfrac{i}{i_d - i}}$	Sensitivity
CuO	0.000485	0.300	15.4	0.103	1/1000
CuO	0.000970	0.432	15.5	0.210	1/1000
CuO	0.001455	0.378	15.5	0.155	1/1000
CuO	0.001940	0.400	15.7	0.209	1/1000
CuO	0.003870	0.420	12.6	0.209	1/2500
CuO	0.005805	0.378	12.6	0.168	1/2500
CuO	0.007740	0.418	12.6	0.185	1/2500
CuO	0.009675	0.456	12.7	0.232	1/2500
CdO	0.0005	0.884	13.5	0.070	1/1000
CdO	0.0010	0.898	13.5	0.070	1/1000
CdO	0.0015	0.894	13.0	0.138	1/1000
CdO	0.0020	0.870	12.8	0.081	1/1000
CdO	0.0020	0.896	9.4	0.118	1/2500
CdO	0.0040	0.896	9.4	0.094	1/2500
CdO	0.0060	0.874	9.4	0.103	1/2500
CdO	0.0080	0.904	9.4	0.063	1/2500
CdO	0.0100	0.885	9.4	0.093	1/2500
CdO	0.0120	0.854	9.4	0.098	

has a linear character, the validity of equations (4) is not confirmed for the melts investigated by us. With greater justification one may here speak of the constancy of the half-wave potential, which is in good agreement with equation (3).

At a temperature of 820°, the values of the prelogarithmic coefficients

$$\frac{2.3RT}{nF}$$

should have the following theoretical values: for $n = 1$, 0.226; for $n = 2$, 0.113; for $n = 3$, 0.075. For cuprous oxide, the experimentally established prelogarithmic coefficients correspond most closely either to $n = 2$ or to $n = 1$, which is possibly explained by the fact that at high temperatures thermal dissociation takes place:

$$2\mathrm{CuO} \rightleftarrows \mathrm{Cu_2O} + \frac{1}{2}\mathrm{O_2}.$$

Already at a temperature of 1008°, the pressure of oxygen over cuprous oxide reaches the value of its partial pressure in the atmosphere (^{8}).

For cadmium oxide the prelogarithmic coefficients

$$\frac{2.3RT}{nF}$$

correspond either to $n = 2$ or to $n = 3$. The latter is possible if the existence of complex ions in the melt is assumed.

For melts containing CdO, the temperature dependence of the diffusion currents was determined (in the temperature interval 760–875°). The results of these experiments are given in Table 2.

Table 2

$N_{\mathrm{CdO}} =$ 0.008			$N_{\mathrm{CdO}} =$ 0.006		
T, °K	i_d, μa	$\lg i_d$	T, °K	i_d, μa	$\lg i_d$
1040	21.6	1.334	1048	15.0	1.176
1061	33.6	1.526	1078	26.2	1.418
1083	41.3	1.616	1093	31.7	1.501
1109	65.3	1.815	1113	41.2	1.615
1133	75.0	1.875	1133	47.2	1.674
			1148	60.0	1.778

Fig. 3. Temperature dependence of diffusion currents for melts containing cadmium oxide.
a–$N_{\mathrm{CdO}} = 0.006$, b–$N_{\mathrm{CdO}} = 0.008$.

As is seen from Fig. 3, the graphs plotted in the coordinates $\lg i_d$, $\frac{1}{T}$ are almost straight lines, which indicates the validity of the equations

$$\ln i_d = A - \frac{B}{T} \tag{5}$$

$$i_d = ke^{-\frac{U}{RT}}, \tag{6}$$

where $A = \ln k$; $B = \dfrac{U}{R}$.

From the value of the slope coefficient of the straight line expressed by equation (5), one can calculate the value of the activation energy, which for our case proved to be equal to 31.27 kcal/mole.

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