DETECTION OF ELECTRODE REACTIONS INTERMEDIATE PRODUCTS BY ELECTROCHEMICAL METHODS AND STUDY OF THEIR PROPERTIES

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It is shown that the rotating disc-ring electrode (R.R.D.E) method may be used for the study of complexing reactions. Monovalent indium complex of the composition $InCl_3^{2-}$ has been determined as an example of the successful applicability of the R.R.D.E. techniques.

The rotating disc-ring electrode (R.R.D.E) method is used for studying the kinetics and mechanism of electrode reactions with participation of intermediate-valency ions[1-5]. Lower-valency ions may form complexes with electrolyte components affecting electrochemical properties and often increasing the stability of these ions. It is difficult in many cases to determine the composition of complexes and thermodynamic characteristics of the complex formation reaction due to instability of lower-valency ions and their ability to disproportionation and oxidation by air oxygen. Widely used is the potentiometric method[1-12] of studying complex formation which determines the dependence of the indicator electrode potential on the complexing ion and ligand concentration.

Using the disc-ring electrode, it is possible to generate complexing ions electrochemically on a disc electrode, *e.g.* according to the anodic

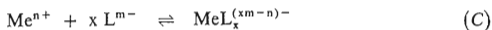$$Me^0 \ \rightarrow \ M^{n+} \ + \ ne \qquad (A)$$

and to record the equilibrium potential change of the indicator electrode for which serves a ring electrode made of the same metal.

The ring electrode equilibrium potential, φ^R, is determined by the equilibrium

$$Me^{n+} \ + \ ne \ \rightleftharpoons \ Me^0 . \qquad (B)$$
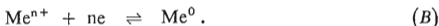
If Me^{n+} ions form a complex with a solution component, the reaction

$$Me^{n+} \ + \ x \ L^{m-} \ \rightleftharpoons \ MeL_x^{(xm-n)-} \qquad (C)$$

will affect φ^R values.

The ring electrode equilibrium potential φ^R depends on Me^{n+} ions concentration generated on the disc electrode

$$\varphi^R = \varphi_0^R + (RT/nF) \ln (Me^{n+})_s \,, \qquad (1)$$

where $(Me^{n+})_s$ is the concentration near the electrode surface. The limiting diffusion current of reduction of further oxidation of Me^{n+} ions on the polarized ring electrode is described by the equation[3]

$$i_d^R = n_R \cdot F \cdot N \cdot (D_{Me^{n+}}/\delta) \cdot (Me^{n+})_s \,. \qquad (2)$$

(n_R number of electrons participating in the electrode reaction on the ring, N collection efficiency, $D_{Me^{n+}}$ diffusion coefficient of Me^{n+}, δ diffusion layer thickness). There is a relationship[3] between currents of the disc (i^D) and of the ring (i_d^R) electrodes:

$$N = (n/n_R)(i_d^R/i^D) \,. \qquad (3)$$

Concentration of Me^{n+} ions near the electrode surface may be determined from equations (2) and (3):

$$(Me^{n+})_s = (\delta/nFD_{Me^{n+}}) \, i^D \,. \qquad (4)$$

Introducing $(Me^{n+})_s$ from equation (7) into (4), we obtain

$$\varphi^R = \varphi_0^R + \frac{RT}{nF} \ln \frac{\delta}{nFD_{Me^{n+}}} \cdot i^D = \text{const}_1 + \frac{2 \cdot 3RT}{nF} \log i^D \,, \qquad (5)$$

where $\text{const}_1 = \varphi_0^R + RT/nF \cdot \ln \delta/nFD_{Me^{n+}}$.

According to equation (5), the relation $\varphi^R - \log i^D$ is a straight line with the angle coefficient of $59/n$ mV.

If a complexing reaction (C) takes place, then φ^R is related with the ligand concentration by equation (6) (ref.[11]):

$$\varphi^R = \text{const}_2 - x \frac{2 \cdot 3RT}{nF} \log [L^{m-}] \,. \qquad (6)$$

From the angle coefficient value of the $\varphi^R - \log [L^{m-}]$ relation at a constant concentration of Me^{n+} ions at the electrode surface (constant $\log i^D$ value) it is possible to determine the number of ligands x of the $MeL_x^{(xm-n)-}$ complex.

Eq. (5) is correct if Me^{n+} ions are formed on the disc with a 100% current yield $(K_s = 1)$, and their concentration is proportional to i^D. In most cases of the electrochemical formation of lower valence ions, $K_s < 1$; therefore the ring electrode limit-

ing current, i_d^R, or the first stage current, i_1, may serve as a value which is proportional to the concentration of lower-valence ions at the ring electrode surface; i_1, the first stage current of the anode process, describes in electrochemical units the flow of Me^{n+} ions diffusing to the ring[3,5].

Composition of complexes may be determined from $\varphi^R - \log i_d^R$ or $\varphi^R - \log i_1$ relations when changing the L^{n-} concentration. Thus, to study the unstable complexing ions additional experiments are needed for determining the i_d^R dependence on i^D.

EXPERIMENTAL

By the R.R.D.E. method Cu^+ ions complexing in lithium chloride solutions ($0 \cdot 1 - 10 \cdot 8$ mol/l) and In^+ ions in $ZnCl_2$ solutions ($8 - 12 \cdot$ mol/l) have been studied. Using the disc-ring electrode, complexing ions are generated electrochemically on a disc electrode according to the anode oxidation reaction, and the equilibrium potential change of the indicator ring electrode is registered. The experiments were conducted at a temperature of $25°C$ and electrode rotation rate of 480 rev./min. Collection efficiency is 0·45. Potential values are related to the saturated calomel electrode.

The disc electrode has functioned at galvanostatic conditions, its potential was recorded by means of the potentiometer P-307. The potentials of the unpolarized ring electrode were recorded with a recorder type KSP-4. When recording monovalent indium ions the potential of the platinum ring electrode used has been set from the potentiostat type P-5848.

RESULTS AND DISCUSSION

Monovalent copper in chloride solutions is stable and $Cu(I)$ chloride complexes has been well studied, therefore, the results obtained by the RRDE method may be compared with literature data.

For determining the composition of $Cu(I)$ chloride complexes in $0 \cdot 2M$-HCl + + $0 - 10 \cdot 8M$-LiCl solutions, anode currents, i^D, from 0·5 to 5·0 mA have been successively assigned to the copper disc electrode. $Cu(I)$ ions diffusing from the disc to the non-polarized copper ring electrode impose the φ^R equilibrium potential on it, which, in accordance with equations (5) and (6), is determined by the current value on the disc. Fig. 1 shows the dependencies of the ring equilibrium potential, φ^R, on the logarithm current on the disc in LiCl solutions. Angle coefficients of the dependencies are in the $56 - 60$ mV range which corresponds to a one electron process. A considerable displacement of $\varphi^R - \log i^D$ dependencies along the potential axis with the increase of LiCl concentration indicates a strong $Cu(I)$ complexing in chloride electrolytes.

On the basis of Fig. 1, the φ^R dependence on the logarithm of chloride ions concentration ($[HCl] + [LiCl]$) has been built (Fig. 3, curve 1) at $\log i^D = 0.25$. The plot consists of three linear portions with different angle coefficients of 112 mV (ab) — up to 1·2 g-ion/l Cl^-, 160 mV (bc) — from 1·2 to 5·0 g-ion/l and 225 mV (cd) — above

5·0 g-ion/l. The x values are 1·5; 2·7; and 3·8. Composition of Cu(I) complexes in chloride solutions depends on chloride ions concentration. At the Cl^--ions concentration up to 1·2 g-ion/l mainly $CuCl_2^-$ complexes are present in solution; at 1·2 to 5·0 g-ion/l-$CuCl_3^{2-}$, and above 5·0 g-ion/l-$CuCl_4^{3-}$.

To check the results obtained, the dependencies of the copper disc equilibrium potential, φ^D, were determined by the potentiometric method in 0·2m-HCl + + (0·1—10·0)m-LiCl with introduction of $2 . 10^{-3}—1 . 10^{-1}$m-CuCl into the solution (Fig. 2). From the data of Fig. 2 at $\log[CuCl] = -1·5$ the $\varphi^D - \log[Cl^-]$ dependence has been built (Fig. 3, curve 2). The dependence consists of three linear $a'b'$, $b'c'$, $c'd'$ portions in concentration ranges up to 1·2 g-ion/l Cl^-, 1·2—5·2 and above 5·2 g-ion/l. Angle coefficients are 115 mV, 167 mV and 250 mV respectively; x values are 2·0; 2·8; and 4·2. Thus, the classical potentiometric method confirms the results obtained by the R.R.D.E method.

For calculating the stability constants β_i of complexes by the equation[11,12]

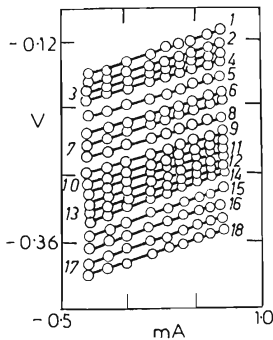$$\log \beta_i = \frac{\Delta\varphi}{RT/nF} - x \log[Cl^-], \qquad (7)$$

Fig. 1

Dependence of the copper ring equilibrium potential on the disc current ($\log i^D$). 0·2 mol/l HCl, conc. of LiCl (mol/l): *1* 0; *2* 0·1; *3* 0·2; *4* 0·3; *5* 0·5; *6* 0·8; *7* 1·0; *8* 1·5; *9* 2·0; *10* 2·5; *11* 3·0; *12* 3·5; *13* 4·0; *14* 5·0; *15* 6·0; *16* 7·0; *17* 9·0; *18* 10·8
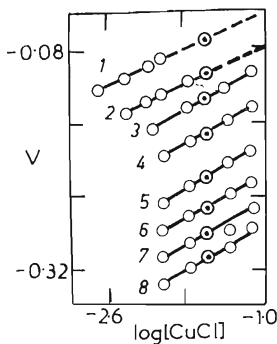
Fig. 2

Dependence of the copper disc equilibrium potential on CuCl concentration in LiCl solutions. 0·2 mol/l HCl, conc. of LiCl(mol/l): *1* 0·1; *2* 0·5; *3* 1·0; *4* 2·0; *5* 4·0; *6* 6·0; *7* 8·0; *8* 10·0

it is necessary to have the $\Delta\varphi$ value — a difference between electrode equilibrium potentials in the presence of complex Cu^+ ions and noncomplex hydrated Cu^+ ions of similar concentration. It is known that ClO_4^- ion does not form complexes with metal ions or interacts weakly with them. Therefore, perchloric acid and its salts are used as inert electrolytes in studying the complex formation.

For φ^R determination of Cu^+ ions, highly-concentrated perchloric acid is used (8·6; 9·6 and 10·9м) in which monovalent ions concentration is high enough[2]. In $HClO_4$ solutions φ^R measurements has been carried out for different currents $(0·25 - 50\ mA)$ on the disc. Using i_d^R values at similar i^D currents the $\varphi^R - \log i_1$ dependence has been built (Fig. 4). All points, irrespective of $HClO_4$ concentration, lie on the same straight line; therefore, Cu(1) complexing in $HClO_4$ does not take place. The angle coefficient of the dependence is 60 mV, corresponding to a one electron process. From the $\varphi_P^R - \log i_1$ dependence in $HClO_4$, φ^R value of a non--complex hydrated Cu^+ ion may be determined for any i_1, or i^D value; it is $+101$ mV for $\log i_1 = 0.25$.
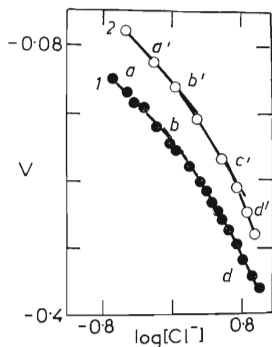

FIG. 3

Dependence of the copper ring electrode equilibrium potential for $\log i^D = 0·25\ 1$ and copper disc electrode equilibrium potential for $\log [CuCl] = -1·5\ 2$ on Cl^- concentration in LiCl solutions
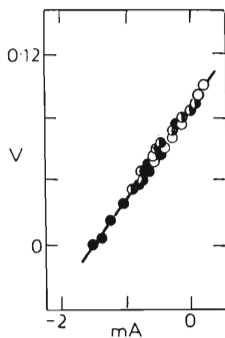
FIG. 4

Dependence of the copper ring electrode equilibrium potential on the first stage current $(\log i_1)$ for copper ionization in concentrated $HClO_4$ solutions

Table I lists calculated $\Delta\varphi$ data for: $\log i_1 = 0.25$, values of $x \log [\text{Cl}^-]$ and $\log \beta_i$ and β_i values determined by equation (7). As seen from Table I, for each x value with change of the Cl^--ions concentration, β_i values change slightly, in spite of the fact that x and β_i calculations use chlorine-ions concentrations but not their activities. Composition of Cu(1) complexes in chloride agrees with the data given in literature[13,14]. Data for a complex CuCl_4^{3-} ion are not available in literature, however, its existence has been suggested[13].

Fig. 5 shows the dependence of the ring electrode equilibrium potential (φ^R) on the logarithm of the ring electrode limiting current, obtained for concentrated ZnCl_2 solutions $(8-12 \text{ mol/l})$. Angle coefficients of straight lines are 55 mV which corresponds to the degree of indium oxidation to In^+ ions. For a constant current on the ring electrode $(\log i_d^R = 0.7)$, the plot $\varphi^R - \log [\text{Cl}^-]$ has been built (Fig. 6). The angle coefficient of the straight line obtained is 0.2 V and the number of ligands is $x = 0.2/0.059 = 3.3 \approx 3$. Thus, in highly concentrated ZnCl_2 solutions $(8-12 \text{ mol/l})$ indium is present as InCl_3^{2-} particles.

TABLE I

Values of $\Delta\varphi$, $x \log [\text{Cl}^-]$, $\log \beta_i$ and β_i at various chloride-ion concentrations

$[\text{Cl}^-]$ g-ion/l	$\Delta\varphi$, B	$x \log [\text{Cl}^-]$	$\log \beta_i$	β_i	β_i average
0.2	0.027	−1.384	5.21	$1.26 \cdot 10^5$	$x = 2$
0.2	0.244	−1.040	5.17	$1.48 \cdot 10^5$	
0.4	0.256	−0.796	5.14	$1.38 \cdot 10^5$	
0.5	0.263	−0.602	5.07	$1.18 \cdot 10^5$	$1.40 \cdot 10^5$
0.7	0.283	−0.310	5.10	$1.26 \cdot 10^5$	
1.0	0.305	0	5.17	$1.48 \cdot 10^5$	
1.7	0.331	0.69	4.92	$8.32 \cdot 10^4$	$x = 3$
2.2	0.351	1.026	5.08	$12.00 \cdot 10^4$	
2.7	0.361	1.293	4.83	$6.76 \cdot 10^4$	$7.33 \cdot 10^4$
3.2	0.372	1.515	4.80	$6.31 \cdot 10^4$	
3.7	0.383	1.704	4.63	$4.27 \cdot 10^4$	
4.2	0.393	1.869	4.80	$6.31 \cdot 10^4$	
6.2	0.425	3.168	4.03	$10.70 \cdot 10^3$	$x = 4$
7.2	0.436	3.428	3.97	$9.33 \cdot 10^3$	
9.2	0.458	3.856	3.89	$7.76 \cdot 10^3$	$8.72 \cdot 10^3$
11.0	0.473	4.164	3.85	$7.08 \cdot 10^3$	

The measurements on the R.R.D.E made in $0.1-2.0$ mol/l $ZnCl_2$ solutions has shown that on indium disc electrode In^{3+} ions are generated because the angle coefficient in $\varphi - \log i^D$ coordinates has been found close 0.019 V. Processing of the obtained results in the coordinates $\varphi^R - \log [Cl^-]$ for diluted $ZnCl_2$ solutions has shown that the angle coefficient is 0.20 V (Fig. 7): therefore, the number of Cl^- ions bound with In^{3+} ion is $1 (x = 0.020/0.019 \approx 1)$ and the In^{3+} species is $InCl^{2+}$ the existence of which is indicated in[15].

The results of this work show that the R.R.D.E. method may be successfully used for the study of complexing reactions.

FIG. 5

Dependence of the indium ring electrode equilibrium potential on the limiting ring current ($\log i_d^R$) in conc. $ZnCl_2$ solutions. Conc. of $ZnCl_2$ (mol/l): *1* 8·0; *2* 9·0; *3* 10·0; *4* 11·0; *5* 12·0
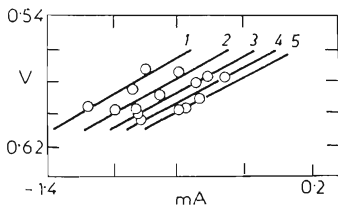
FIG. 6

Dependence of the indium ring electrode equilibrium potential on the Cl^- concentration ($\log [Cl^-]$) in concentrated $ZnCl_2$ solutions
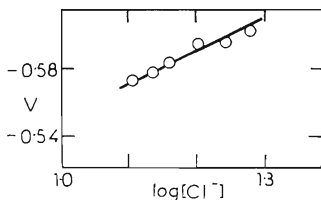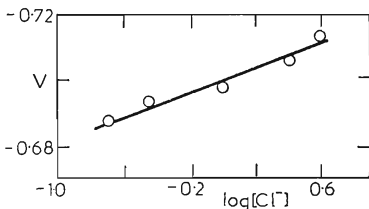
FIG. 7

Dependence of the ring equilibrium potential on Cl^- concentration for diluted $ZnCl_2$ solutions ($0.1-2.0$ mol/l)

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