Physical Chemistry

1960

SovietRxiv

Abstract

Full Text

Physical Chemistry

Kh. Z. Brainina

Reduction of Indium at a Dropping Mercury Electrode in the Presence of Certain Inorganic and Organic Cations*

(Presented by Academician A. N. Frumkin on 30 IX 1959)

The study of the mechanism of reduction of indium at a dropping mercury electrode is of interest in view of the fact that the reversibility of the process depends on the nature of the supporting medium. It is known that from sulfate and perchlorate solutions indium is reduced with a large overvoltage, whereas in the presence of Cl^-, Br^-, etc., the process proceeds reversibly at a more positive electrode potential. However, in the potential region where a diffusion current should be observed, a sharply expressed minimum appears on the polarization curve ([1],[2]).

In the present work, the influence of a series of inorganic and organic cations on the kinetics of reduction of indium ions at a dropping mercury electrode was studied. Polarization curves of indium, obtained under different conditions, are shown in Figs. 1-3. Let us consider the following cases:

1. Reduction of indium from solutions with a constant concentration of chloride ions in the presence of various cations. The first rise of the current on all polarization curves, beginning at a potential of −0.55 V, is due to the reduction of indium. At an electrode potential of −0.65-0.75 V, depending on the composition of the supporting medium, a decrease in current is observed, which is the more pronounced the higher the valence of the cation included in the supporting medium (Fig. 1, *1, 2, 5* and Fig. 2, *1, 2*). It is interesting to note that the depth of the minimum in the potential region −0.67-1.35 V increases as the concentration of La^{3+} ions increases while the concentration of chloride ions in the solution is kept constant (Fig. 1, *4, 3, 1*). Conversely, the rate of the reaction increases in the potential interval 0.65-1.28 V in the series $Na^+ < Rb^+ < Cs^+$. The further rise of the current in sufficiently concentrated supporting solutions (0.9 N) is due to the reduction of hydrogen ions or to a mixed electrode process.

On polarograms obtained in 0.5 N chloride solutions (Fig. 2) (pH 3.0), the rise of the current after the minimum is observed somewhat earlier than in more concentrated solutions with the same cation; moreover, on the polarization curve obtained for the reduction of indium in 0.5 N NaCl, there is a distinct inflection

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

at a potential of −1.4 V (Fig. 2, *2*). In the case of RbCl and $LaCl_3$ (Fig. 2, *3, 1*) an inflection is also observed at potentials of 1.48 and 1.5 V, respectively, but it is less sharp. From a comparison of curves *4* and *5*, obtained in 0.5 N NaCl at pH 3.0 and in 0.5 N $LaCl_3$ (pH 3.0) without indium, with curves *2, 3* and *1*, it is seen that the rise of the current after the minimum is due to the reduction of indium; however, instead of a diffusion-current plateau, the polarogram has a more or less sharply expressed inflection, which is connected with the reduction of hydrogen ions beginning in this potential region.

In addition, from Figs. 2, 7, and 8 it is seen that the surface tension of mercury at the potentials of the negative branch of the electrocapillary curve in an RbCl solution is somewhat lower than in an NaCl solution, which agrees with measurements of the differential capacitance of the electrical double layer on mercury in the corresponding solutions (^{3}).

2. Reduction of indium in the presence of various cations from solutions with the same activity of chloride ions. Comparing curves 5 and 6 in Fig. 1, one can note that in the presence of the trivalent cation (La^{3+}) the retardation of the electrode process in the potential interval 0.65–1.23 V is expressed more weakly. Curve 6 is located above curve 5, obtained in the reduction of indium from a potassium chloride solution.

Fig. 1. Polarization curves obtained in the reduction of 0.001 M $InCl_3$ from solutions: 1 –0.9 N $LaCl_3$; 2 –0.9 N $SrCl_2$; 3 –0.2 N $LaCl_3$ + 0.7 N KCl; 4 –0.05 N $LaCl_3$ + 0.85 N KCl; 5 –0.9 N KCl ($a = 0.56$); 6 –$LaCl_3$ ($a = 0.56$, pH 3.0)

Fig. 2. Polarization curves obtained in the reduction of 0.001 M $InCl_3$ from solutions: 1 –0.5 N $LaCl_3$; 2 –0.5 N NaCl; 3 –0.5 N RbCl; 4, 5 –0.5 N NaCl and $LaCl_3$, respectively, without indium; 6 –0.5 N CsCl; 7, 8 –electrocapillary curves of mercury in 0.5 N NaCl and RbCl, pH 3.0

3. Reduction of indium in the presence of tetraalkylammonium salts. Figure 3 presents polarograms of indium reduction on a background of 0.9 N KCl with additions of tetra-salts. From comparison of curves 1–3 with polarization curve 4 it is seen that tetrabutylammonium chloride at a concentration of $5 \cdot 10^{-5}$ M noticeably decreases the limiting current of indium. When its concen-

---

* L. S. Perkina took part in the experimental part of the work.

Fig. 3

Figure 3: Fig. 3

tration is increased to $1.5 \cdot 10^{-4}$ M, the wave is almost completely suppressed. Tetramethylammonium chloride acts much more weakly.

It is known that in chloride solutions indium forms complexes ([1],[2]). On the basis of data on the value of the half-wave potentials of indium as a function of the activity of chloride ions in solution:

a_{Cl^-} :	0.08	0.23	0.33	0.53	0.69	1.14	1.74
$-\varphi_{1/2}$ V	0.560	0.574	0.580	0.590	0.595	0.610	0.622

using the DeFord and Hume method ([4]), we calculated the composition of the indium complexes.

The value of the half-wave potential of the reversible reduction of indium in the absence of chloride ions required for the calculations was found by extrapolating to the value $C_{\mathrm{Cl}} = 0$ the dependence, obtained by Kocci and Vivarelli ([1]), of the half-wave potential of indium on the concentration of chloride ions at constant

ionic strength of the solution. According to Deford and Hume, the F-function, as a function of the activity of Cl^- ions, for the last complex existing under these conditions has the form of a straight line parallel to the abscissa axis; the corresponding dependence for the preceding complex is a straight line with a positive slope. In all other cases the dependence is curvilinear. From Fig. 4 it may be concluded that in 0.1-3.0 N KCl solutions the complexes InCl^{2+}, InCl_2^+, and InCl_3^0 exist.

Reduction of indium at the dropping mercury electrode from chloride solutions begins at potentials close to the potential of zero charge of mercury. Under these conditions orientation of the indium complex with its negative end toward the electrode surface is possible, with the formation of a kind of "anion bridges," which, as A. N. Frumkin pointed out ([6]), facilitates electron transfer from the electrode surface to the species being reduced. However, such orientation is possible only in a rather narrow potential region lying near the half-wave potential of indium, since with increasing cathodic polarization, as the negative charge of the mercury surface grows, adsorption of anions becomes impossible. Apparently, in passing from more positive to more negative electrode potentials, the orientation of the complex particle in the electrical double layer changes, creating unfavorable conditions for the electrode reaction to proceed.

Fig. 3. Polarization curves obtained in the reduction of indium from solutions of $10^{-3}\,M\,\mathrm{InCl_3} + 0.9\,N\,\mathrm{KCl} + n\mathrm{R_4NCl}$ (R–organic radical), pH 2.5: 1 – $0.02\,M\,(\mathrm{CH_3})_4\mathrm{NCl}$, 2 –$5 \cdot 10^{-5}\,M\,(\mathrm{C_4H_9})_4\mathrm{NCl}$, 3 –$1.5 \cdot 10^{-4}\,M\,(\mathrm{C_4H_9})_4\mathrm{NCl}$, 4 –without additives

Fig. 4

Figure 4: Fig. 4

Fig. 4. Dependence of the functions $F(X)$ on the activity of chloride ions

It is natural to expect that all factors promoting orientation of the indium complex in the electrical double layer with its anionic end toward the electrode surface will favorably affect the course of the electrode process.

In a number of works by A. N. Frumkin and co-workers it has been shown that the introduction of certain cations into the solution increases the adsorption of anions even in that region of potentials where, in other cases, their adsorption is not observed (7). Hence it could be expected that introduction into the solution of Rb^+, Cs^+, Sr^{2+}, La^{3+}, and R_4N^+ ions would lead to some removal of the kinetic hindrances observed in the reduction of indium from KCl and NaCl solutions.

However, it should be taken into account that, since the indium complex as a whole is neutral or cationic, depending on the nature of the foreign cations they will have a twofold effect:
1) they will promote the drawing of the indium complex into the electrical double layer by its anionic end, and 2) they will displace the positively charged particle as a whole from the near-electrode space and decrease the reaction rate as a result of shifting the ψ_1-potential in the positive direction (7).

This effect, evidently, should increase as the charge of the cation increases.

From the experimental data it is seen that, in the case of monovalent cations, a noticeable increase in the reaction rate is indeed observed in the series
$Na^+ < K^+ < Rb^+ < Cs^+$.

The decrease in the diffusion current of indium in the presence of organic cations may be due to the slowed penetration of the reducible particles to the electrode surface. In the kinetic region, tetramethylammonium chloride does not decrease the limiting current of indium.

In the presence of polyvalent cations, the second effect predominates, which is apparently intensified by a decrease in the activity of Cl^- ions when K^+ is replaced by Sr^{2+} and La^{3+}. In solutions with sufficient electrolyte activity, an insignificant acceleration of the process is observed in the presence of La^{3+}, but it is much weaker than in the presence of Cs^+.

The increase in the rate of the cathodic process under strong cathodic polarization (Fig. 2), when the reducible particle can be oriented only with its positive end toward the electrode surface, is apparently due to the direct transfer of an electron from the electrode surface to the indium ion. If this is indeed so, then foreign cations should exert on this process the same influence as on the discharge process of hydrogen ions (5). Indeed, as is seen from Fig. 2, the overvoltage of indium increases in the series $Na^+ < Rb^+ < La^{3+}$.

Thus, the mechanism of reduction of indium ions from chloride solutions appears to be different at different potentials, which is associated with a change in the adsorption conditions of the reducible particles. In the region of potentials close to the half-wave potential, the course of the electron process is facilitated by the formation of "anion bridges" ; at more negative potentials, direct transfer of electrons from the electrode surface to the indium ion is observed.

In conclusion, I express my sincere gratitude to Academician A. N. Frumkin, N. V. Nikolaeva-Fedorovich, and V. A. Kuznetsov for valuable comments during the discussion of the results.

Ural State University
named after A. M. Gorky

Received
24 IX 1959

CITED LITERATURE

[1] J. M. Kolthoff, J. J. Linqane, *Polarography*, New-York, 1952; p. 519; L. I. Busev, *Analytical Chemistry of Indium.* Moscow, 1958; D. Cozzi, S. Vivarelli, *Z. f. Electrochem.*, **57**, 408 (1953); M. Bulovova, *Coll. Czech. Chem. Com.*, **19**, 1123 (1954).

[2] Kh. Z. Brainin, S. K. Chirkov. Abstracts of reports of the Meeting of Workers of Higher Educational Institutions and Heads of Laboratories of the South-East of the USSR, Rostov-on-Don, October 1958.

[3] D. Grahame, *J. Electrochem. Soc.*, **98**, 9, 343 (1951).

[4] D. D. De Ford, D. N. Hume, *J. Am. Chem. Soc.*, **73**, 11, 5321 (1951).

[5] A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, B. N. Kabanov, *Kinetics of Electrode Processes*, Moscow, 1952.

[6] A. N. Frumkin, *Izv. AN SSSR, OKhN*, 1957, No. 12, 1429; A. N. Frumkin, Proceedings of the 4th Conference on Electrochemistry, 1–6 October 1956, Publishing House of the Academy of Sciences of the USSR, 1959, 7; A. N. Frumkin, N. V. Nikolaeva-Fedorovich, *Vestn. MGU*, series mathematics, mechanics, astronomy, physics, chemistry, No. 4 (1957); A. N. Frumkin, B. B. Damaskin, N. V. Nikolaeva-Fedorovich, *DAN*, **115**, 4, 751 (1957).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.