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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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Autocatalytic Mechanism of Electrode Processes in Unbuffered Solutions of Lanthanum Chloride

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The literature has noted a marked acceleration of the discharge of cobalt ions (^{1}), lanthanum (^{2}), praseodymium (^{3}) and other rare-earth elements (^{4,5}), indium (^{6}), and iron (^{7}) at a dropping mercury cathode when the pH of the solution is increased. It has been suggested (^{1,2,7}) that this phenomenon is connected with an increase, at the pH corresponding to the onset of hydrolysis of the metal salt, in the content of hydroxy ions, the discharge of which, owing to a decrease in the degree of hydration, proceeds at a higher rate than the discharge of simple hydrated ions. Attention is drawn to the fact that the final rise of the current on the polarization curve of a 0.1 M $LaCl_3$ solution (a solution often used as a supporting electrolyte in studies of the reduction of nitrate-type anions), associated with the onset of discharge of lanthanum ions, in weakly acidic solutions proceeds so steeply that it practically does not differ from the stepwise increase in current observed in the autocatalytic reduction of anions. In this connection, it was of interest to verify whether, in fact, the discharge of lanthanum ions or of water molecules with evolution of hydrogen at a dropping mercury cathode in unbuffered solutions of lanthanum salts proceeds by an autocatalytic mechanism.

Fig. 1. Polarization curves of 0.1 M $LaCl_3$ under direct and reverse polarization. Concentration of added HCl: 1—0 (pH $\sim$ 7.5, obtained by addition of KOH); 2—0 (initial solution, pH $\sim$ 5); 3—$2 \cdot 10^{-4}$; 4—$4 \cdot 10^{-4}$ M. The curves were measured from -1.2 V relative to mercury in the same solution.

In the literature there is an indication (^{10}) of the autocatalytic course of processes during the electrolysis of unbuffered $AlCl_3$ solutions.

For this purpose, using a PE-312 electronic polarograph, into the design of which a modification (^{8}) had been introduced making it possible rapidly to change the direction of electrode polarization during the recording of a polarogram, a series of polarograms was obtained for a 0.1 M $LaCl_3$ solution with cathodic and then reverse polarization. The presence on the polarograms of a stepwise increase in current and, still more definitely, the presence of hysteresis loops indicates an autocatalytic mechanism of the processes. As Fig. 1 shows, the polarograms of weakly acidic 0.1 M $LaCl_3$ solutions indeed exhibit quite distinct current steps and hysteresis loops (curves 2-4).

This result was confirmed by measurement of curves showing the dependence of the instantaneous current flowing to an individual drop on time, i.e., so-called i, t curves. The measurements were carried out with a TsLA-model oscillographic polarograph. Figure 2 presents one i, t curve for a 0.1 M LiCl solution containing $2 \cdot 10^{-3}$ M $LaCl_3$. It is evident that the i, t curve contains a stepwise increase in current characteristic of autocatalysis. Subsequent current jumps, one of which is also visible in Fig. 2, are observed less regularly. Their appearance is most likely connected with the formation and rupture of a film of insoluble electrolysis products (hyd-

lanthanum peroxide or basic salts) on the growing mercury drop.

Comparison of the data obtained by methods of measuring polarograms and i, t-curves shows that the method of measuring i, t-curves is considerably more sensitive to autocatalysis. With this method, the autocatalytic character of the processes is detected even at such a concentration of lanthanum salt at which autocatalysis still does not appear in any way on the polarograms.

The autocatalytic mechanism of the processes is also confirmed by the method of recording polarograms with a large additional resistance connected in series with the cell and with correction of the curves for the ohmic voltage drop. On curves obtained in this way, in the case of autocatalysis, there are sections with a negative slope, on which the current increases as the potential decreases*. As Fig. 3 shows, on some curves obtained by this method for a 0.1 M solution of $LaCl_3$, sections with a negative slope are indeed present. The absence of such sections on the curves of less (Fig. 3, 1) and more acidic solutions (Fig. 3, 4–6) can be easily explained. As is known, autocatalytic acceleration of the reduction of anions of the NO_3^- type occurs as a result of alkalization of the solution near the electrode. Evidently, autocatalysis in $LaCl_3$ solutions has the same cause. This is already evident from the fact that curves 2 and 3, after the section with negative slope, merge with curve 1, corresponding to the unacidified solution. Consequently, already in the course of measuring the curve, the pH of the solution near the electrode changes and, as a result, the process is accelerated. Since curve 1 in Fig. 3 corresponds to a weakly acidic solution (pH ~ 5), no appreciable autocatalytic acceleration of the process as a result of alkalization of the solution occurs in it. As for curves 4–6, they correspond to excessively acidic solutions, in which alkalization of the solution near the electrode is no longer possible.

One may imagine two mechanisms of autocatalysis during electrolysis of unbuffered solutions of lanthanum salts. According to the first, autocatalysis is associated with the discharge of lanthanum ions and the formation of a lan-

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

thanum amalgam, which reacts with water with evolution of hydrogen. The alkalization of the solution that occurs in this case leads to a change in the state of the lanthanum ions in solution and to acceleration of their discharge.

Fig. 2. i, t-curve measured in a solution of 0.1 M $\text{LiCl} + 2 \cdot 10^{-3}$ M LaCl_3 at a potential of −2.1 V (relative to mercury in the same solution)

Fig. 3. Polarization curves of 0.1 M LaCl_3 at a dropping mercury cathode, measured with an additional resistance connected in series (15 000 Ω). Concentration of added HCl: 1—0 (pH $\sim$ 5); 2—10^{-3}; 3—$2 \cdot 10^{-3}$; 4—$2.9 \cdot 10^{-3}$; 5—$3.8 \cdot 10^{-3}$; 6—$4.8 \cdot 10^{-3}$ M

* This method was first applied to the study of autocatalysis in the reduction of the NO_3^- anion by Mashek.

According to the second mechanism, autocatalysis can be associated with the discharge of water molecules and the evolution of hydrogen, which is facilitated in the presence of lanthanum salts (^{2}). In assessing the probability of one mechanism or the other, it should be borne in mind that the principal final result of the electrolysis of unbuffered aqueous solutions of lanthanum salts is the evolution of hydrogen, since under these conditions lanthanum amalgam is formed only in insignificant amounts (^{9}). On the other hand, the circumstance that reduction is facilitated when the pH is raised even in such cases (indium, cobalt) in which hydrogen evolution does not occur at all apparently speaks in favor of the first mechanism. However, the available experimental material is insufficient for choosing the mechanism of the processes actually taking place.

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