AUTOCATALYTIC ELECTRODE REACTION MECHANISM IN NONBUFFER LANTHANUM CHLORIDE SOLUTIONS

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It has been pointed out in the literature that there is a marked acceleration in the discharge of ions of cobalt [1], lanthanum [2], praseodymium [3], and other rare earth elements [4, 5], as well as of indium [6] and iron [7], at a mercury drop cathode when the pH of the solution is increased. A proposal [1,2,7] has been advanced to the effect that, at the pH at which hydrolysis of the metal salt begins, there is a great increase in the number of hydroxyl ions, which, since the degree of hydration is less, are discharged at a higher rate than the simple hydrated ions are discharged. Attention is called to the fact that the final rise in current in the polarization curve for 0.1 M $LaCl_3$ solution (the solution is often used as a background in studying the reduction of anions of nitrate type), coming from the initial discharge of lanthanum ions, occurs so steeply in weakly acid solutions that it is practically the same as the jump type increase in current strength observed in the autocatalytic reduction of anions. In this connection it was not without interest to verify whether or not the discharge of lanthanum ions or water molecules with liberation of hydrogen actually goes by an autocatalytic mechanism on a mercury drop electrode in nonbuffer solutions of lanthanum salts.

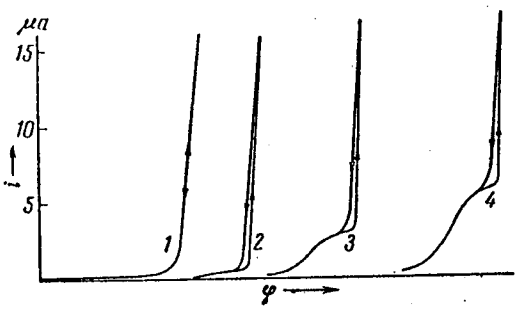

Fig. 1. Polarization curves of 0.1 M $LaCl_3$ with direct and reverse polarization. Concentration of HCl added: 1) 0 (pH ~7.5 produced by adding KOH); 2) (original solution, pH ~5); 3) $2 \cdot 10^{-4}$; 4) $4 \cdot 10^{-4}$ M. The curves are measured from −1.2 v relative to mercury in the same solution.

There is an indication in the literature [10] that there are autocatalytic processes in the electrolysis of nonbuffer $AlCl_3$ solutions.

To this end, a PÉ-312 electronic polarograph, which had been modified [8] so that the direction of the electrode polarization could be quickly changed while the polarograms were being taken, was used to take a number of polarograms of 0.1 M $LaCl_3$ solution first with cathode and then with reverse polarization. The autocatalytic mechanism of the reactions is shown by jump type increases in current strength on the polarograms, and in an even more definite way by the fact that hysteresis loops are present. As is shown by Fig. 1, the polarograms of weakly acid 0.1 M $LaCl_3$ solutions actually have clear jumps in current strength as well as hysteresis loops (curves 2–4).

This result has been confirmed by taking curves of the instantaneous current strength flowing at a single drop as a function of time, i.e., the so-called i, t curves. The measurements were made with a model TsLA oscillographic polarograph. Figure 2 gives one i, t for 0.1 M LiCl solution containing $2 \cdot 10^{-3}$ M $LaCl_3$. It may be seen that there is a jump type increase in current strength in the i, t curve, which is characteristic of autocatalysis. These jumps most likely occur from the formation and disruption of a film of insoluble electrolysis products (lanthanum hydroxide or basic salts) on the growing mercury drop.

Comparing the data obtained from the polarograms and the i, t curve shows that the i, t curve method is considerably more sensitive to autocatalysis. The autocatalytic character of the reactions may be observed by this method even when the concentration of lanthanum salt is such that the autocatalysis would not show up at all on the polarograms.

The autocatalytic mechanism of the reactions may also be demonstrated by recording the polarograms with a large initial resistance connected in series with the cell and then correcting the curves for the ohmic voltage drop. In the curves take in this way, when there is autocatalysis there is a part of the curve which has a negative slope where the current strength increases with decrease in potential* . Figure 3 shows that on some of the curves taken in this way for 0.1 M $LaCl_3$ solution there are actually parts with a negative slope. The fact that there are no parts of this sort on the curves for less acid (1, Fig. 3) and more acid solutions (4-6, Fig. 3) is easily explained. It is known that autocatalytic acceleration of the reduction of anions of NO_3^- type occurs as a result of alkalization of the solution near the electrode. It is obvious that the autocatalysis in $LaCl_3$ solutions has the same cause. This may also be seen from the fact that after the part with the negative slope Curves 2 and 3 run together with Curve 1, which corresponds with an unacidified solution. Consequently, even while the curve is being taken there is a change in pH of the solution near the electrode and as a result acceleration of the reaction occurs. Since Curve 1 in Fig. 3 refers to a weakly acid solution (pH ~5) no large amount of autocatalytic acceleration occurs from alkalization of the solution. As to Curves 4–6, they refer to exceedingly acid solutions in which alkalization of the solution near the electrode is no longer possible.

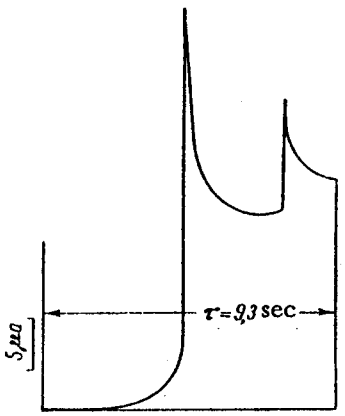

Fig. 2. i, t curve taken in 0.1 M LiCl + $2 \cdot 10^{-3}$ M $LaCl_3$ solution at a potential of −2.1 v (relative to mercury in the same solution).

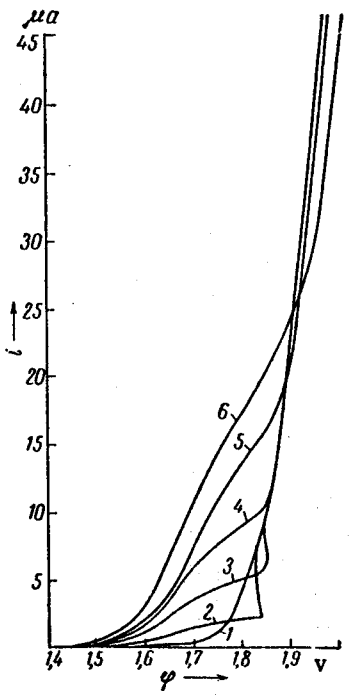

Fig. 3. Polarization curves of 0.1 M $LaCl_3$ on a mercury drop cathode, taken with an additional 15,000 ohm resistance connected in. Concentration of HCl added: 1) 0 (pH ~5); 2) 10^{-3}; 3) $2 \cdot 10^{-3}$; 4) $2.9 \cdot 10^{-3}$; 6) $4.8 \cdot 10^{-3}$ M.

Two mechanisms may be imagined for the electrolysis of nonbuffer solutions of lanthanum salt. According to the first mechanism the autocatalysis consists of discharging lanthanum ions and forming a lanthanum amalgam, which reacts with water to liberate hydrogen. The alkalization of the solution occurring with this causes a change in state of the lanthanum ions in the solution and accelerates their discharge.

According to the second mechanism, the autocatalysis may be related with the discharge of water molecules and the liberation of hydrogen, which is made easy in the presence of lanthanum salts [2]. In estimating the probability of either mechanism it must be kept in mind that the main end result of the electrolysis of nonbuffer aqueous solutions of lanthanum salts is liberation of hydrogen, since under these conditions lanthanum amalgam is only formed in insignificant amounts [9]. On the other hand, something that clearly speaks in favor of the first mechanism is the fact that reduction is facilitated by increasing the pH even in those cases (indium, cobalt) where liberation of hydrogen does not occur at all. However, the experimental material on hand is insufficient to decide which mechanism is really taking place.

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* This method was first used by Mashek in investigating autocatalysis during the reduction of the NO_3^- anion.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
