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KINETICS OF INTERACTION BETWEEN SOLUTION COMPONENTS AND AN INTERMETALLIC COMPOUND PRODUCED DURING CATHODIC INCORPORATION

I. A. Avrutskaya, I. G. Kiseleva,
A. V. Chekavtsev, V. S. Shinkarev,
M. Ya. Fioshin, and B. N. Kabanov

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The kinetics of interaction between benzalhydantoin or p-hydroxypropiophenone as solution components and the intermetallic compound produced during the cathodic incorporation of lithium into gallium has been studied. A method for determining the rate of chemical reaction between the intermetallic compound and the solution has been proposed. The rate constant of the reaction between the intermetallic compound LiGa and p-hydroxypropiophenone has been determined.

The electrochemical incorporation of alkali metals into the cathode metal is known to play an important part in the electrochemical reduction of organic compounds [1, 2]. It had been shown in [3] that the intermetallic compounds produced by incorporation are directly involved in the reduction of organic compounds. In particular, it appears that the reduction of p-hydroxypropiophenone, benzalhydantoin, and indolalhydantoin to a significant extent occurs by interaction with intermetallic compounds.

In the present work we have examined the kinetics of interaction of the intermetallic compound LiGa with benzalhydantoin and p-hydroxypropiophenone.

The measurements were conducted at G-000 liquid gallium in a 0.6 N lithium perchlorate solution in propylene carbonate. Twice recrystallized salt which had been dried for 36 h at 140-150°C and 10^{-3} mm Hg was used to prepared the solutions. For part of the experiments (Fig. 1), the propylene carbonate was purified by vacuum distillation at 1 mm Hg in a fractionating column with an efficiency of 15 theoretical plates and a reflux ratio of 10. For the other experiments we used propylene carbonate after distillation in a fractionating column at 1 mm Hg. The gallium electrode was placed into the solution in a glass cup. The electrode surface area was 1 cm^2. A silver–silver chloride electrode in a 0.6 N lithium perchlorate solution in propylene carbonate was used as reference electrode. The potential of this electrode relative to a lithium electrode in the same solution was 2.9 V. The measurements were conducted at 29.5°C. The cell was thermostated with a U-8 "ultra" thermostat. Cathodic polarization of the electrodes was performed under potentiostatic conditions (P-5827 potentiostat). Anodic chronopotentiograms were recorded upon application of a constant current, and using a KSP-4 potentiometer.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. D. I. Mendeleev Institute of Chemical Technology, Moscow. Translated from Élektrokhimiya, Vol. 13, No. 10, pp. 1516-1519, October, 1977. Original article submitted July 15, 1976.

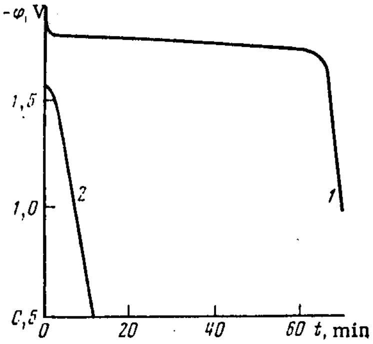

Fig. 1

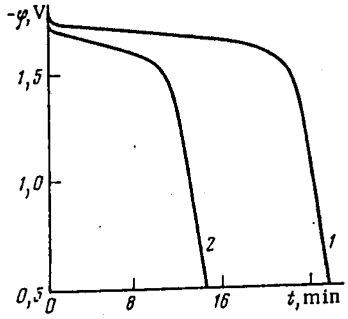

Fig. 2

Fig. 1. Anodic chronopotentiograms at liquid gallium in 0.6 N $LiClO_4$ solution in propylene carbonate (the base electrolyte) (1) and in the base-electrolyte solution + 10^{-3} M benzalhydantoin (2); $i_a = 0.09$ mA/cm². Cathodic prepolarization of the gallium: $\varphi_c = -2.0$ V, $t_c = 70$ min, $i_c = 8.9 \cdot 10^{-5}$ A/cm².

Fig. 2. Anodic chronopotentiograms at liquid gallium: 1) base electrolyte; 2) cathodic polarization in base electrolyte, anodic polarization in the presence of benzalhydantoin (0.3 g liter); $i_a = 2 \cdot 10^{-5}$ A/cm². Cathodic prepolarization of the gallium: $\varphi_c = -1.9$ V, $t_c = 7$ min, $i_c = 2.5 \cdot 10^{-4}$ A/cm².

Anodic chronopotentiograms obtained after 70 min of cathodic polarization at a potential of −2.0 V in solution of the base electrolyte alone (1) and in the presence of organic oxidizing agent (2) are shown in Fig. 1. A shorter plateau is found on the chronopotentiogram in the presence of benzalhydantoin, which is evidence for a lower concentration of intermetallic compound in the electrode. A decrease in the amount of intermetallic compound in the electrode which occurs in the presence of organic material can be due both to a decrease in the rate of cathodic formation of the intermetallic compound (which was not observed in the present case) and to reaction between the intermetallic compound and the organic material. Figure 2 shows anodic chronopotentiograms recorded under different conditions: in the absence (curve 1) and in the presence (curve 2) of the organic compound, while cathodic prepolarization in these experiments was conducted under identical conditions, viz., in the absence of the organic compound. The contraction of the plateau on curve 2 signifies that LiGa reacts with the benzalhydantoin. The difference between curves 1 and 2 is larger in Fig. 1 than in Fig. 2, since in the first case interaction between solution and intermetallic compound occurred during cathodic and anodic polarization, while in the second case it occurred only during anodic polarization.

In Fig. 3 the amount of alkali metal found at the electrode is shown as a function of the duration of cathodic polarization in base-electrolyte solution (0.6 N $LiClO_4$ in propylene carbonate) and in the same solution also containing benzalhydantoin. In the solutions containing the additive, a smaller amount of alkali metal than in the base-electrolyte solution was found at all cathodic polarization times. This difference increases with the duration of cathodic polarization.

It follows from Fig. 1 that in the absence of the organic compound, the amount of charge, Q_a, used for anodic decomposition of the intermetallic compound is equal to the amount of charge, Q_c, passed during cathodic prepolarization. Equality of quantities Q_c and Q_a shows that during cathodic polarization under the conditions described, practically only one process is taking place, i.e., the formation of intermetallic compound.

In the presence of the organic compound, Q_a is smaller than Q_c. On the assumption that the entire loss of intermetallic compound is due only to chemical reaction with the organic compound, the following equation for the mass balance of intermetallic compound is obtained:

$$i_{im} t_c = i_a t_a + i_{chem}(t_c + t_a), \tag{1}$$

where i_{im} is the rate of cathodic formation of the intermetallic compound, t_c is the time of cathodic polarization, t_a is the time of anodic decomposition of the intermetallic compound. Quantities t_c, i_a, and $i_{im} = i_c$ are predetermined, while t_a is determined from the length of the plateau on the anodic chronopotentiogram. Chemical reaction between the intermetallic compound and the organic compound occurs so long as the intermetallic

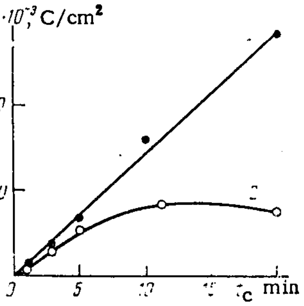

Fig. 3

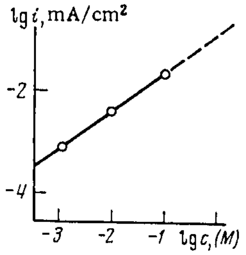

Fig. 4

Fig. 3. The amount of alkali metal found during anodic polarization of the liquid gallium, as a function of the duration of cathodic prepolarization: 1) base electrolyte, 2) base electrolyte + 10^{-3} M benzalhydantoin; $\varphi_c = -2.0$ V, $i_a = 1 \cdot 10^{-5}$ A/cm², $i_c = 4 \cdot 10^{-5}$ A/cm².

Fig. 4. Graphical determination of the reaction rate constant of LiGa with p-hydroxypropiophenone.

compound exists, i.e., throughout the cathodic and anodic polarization. Therefore* $t_{chem} = t_c + t_a$. Thus, from Eq. (1) one can find the rate of chemical reaction between intermetallic compound and solution:

$$i_{chem} = \frac{i_{im} t_c - i_a t_a}{t_c + t_a}. \tag{2}$$

According to the data of Fig. 1, the rate of interaction of LiGa with 10^{-3} N benzalhydantoin solution at liquid gallium is $8 \cdot 10^{-5}$ A/cm².† This method of determining the rate of chemical reaction of the intermetallic compound with organic compounds is based on the difference in the amounts of alkali metal which have been incorporated from solutions which do and do not contain these organic compounds. It can only be applied when formation of the intermetallic compound is occurring as the only electrochemical process during cathodic polarization, i.e., $i_c = i_{im}$. In addition, the presence of the organic compound in the solution should not have any strong effect on the rate of cathodic formation of the intermetallic compound. Usually during cathodic polarlarization more than one electrochemical process can occur at the electrode: formation of intermetallic compound, formation of solid solution, and the reduction of impurities or special additives.‡

For these more complicated conditions, another method of determining the rate of interaction between intermetallic compound and solution was developed which does not require parallel measurements in a solution not containing reducible impurities. According to this method, all measurements are conducted in the presence of the test material undergoing reduction. At least two anodic chronopotentiograms must be recorded in order to obtain the necessary information for the calculations. One of them is recorded as usual: a constant anodic current is applied to the electrode right after cathodic polarization. Another anodic chronopotentiogram is recorded, not immediately after the end of cathodic polarization but after waiting some accurately measured time t_p during which the electrode remains in the solution at open circuit. The time of chemical reaction of the intermetallic compound with the solution is increased by the length of the pause, t_p, and the mass-balance equation for the intermetallic compound assumes the form

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* It is assumed that the rate of chemical reaction between LiGa and solution is the same during cathodic and anodic polarization.

†An approximate calculation shows that this rate is close to the rate of diffusion of the reactant from the bulk of the solution to the electrode.

‡During the subsequent recording of the anodic chronopotentiograms, the predetermined anodic current may represent the sum of the rates of various processes: ionization of the intermetallic compound, ionization of the solid solution, and oxidation of the impurities and additives. But by examining only that part of the anodic chronopotentiogram where the plateau is located one can assume that decomposition of the intermetallic compound, LiGa, is occurring as the only anodic process in this region of potentials. Diffusional limitations are absent when the anodic current is not too high, and the intermetallic compound existing at the surface is practically completely decomposed within the time (t_a) over which the plateau extends.

$$i_{\mathrm{im}}t_{\mathrm{c}}=i_{a}t_{a}'+i_{\mathrm{chem}}(t_{\mathrm{c}}+t_{\mathrm{p}}+t_{a}'),\tag{3}$$

where t_a' is the length of the plateau on the anodic chronopotentiogram recorded after the pause.

By performing experiments with and without pause we obtain the system of equations (1) and (3). Considering that the cathodic polarization in both cases has been conducted under identical conditions and that, therefore, the left-hand side of the two equations are equal, we obtain

$$i_{\mathrm{chem}}=\frac{i_a(t_a-t_a')}{t_a'+t_{\mathrm{p}}-t_a}.\tag{4}$$

This equation contains the predetermined quantities i_a and t_p as well as the quantities t_a and t_a' which can be determined experimentally from the chronopotentiograms.

If in addition to the organic compound being added the solution contains other components which can interact with the intermetallic compound, then one must conduct measurements in the absence of the organic compound, and find i_{chem} of the base electrolyte from Eq. (4), then subtract this quantity from the i_{chem} found for the solution containing the organic compound being examined.

Investigations of cathodic incorporation often are complicated by changes in the surface state of the electrode during the measurements. Possible reasons for these changes are, e.g., disintegration of the surface, surface development, a change in the properties of the intermetallic compound, etc. In this case it will be appropriate to record in succession three rather than two anodic chronopotentiograms: without pause, with pause, and again without pause. Then the average value from the first and third chronopotentiogram is taken as the length of the anodic plateau in Eq. (4).

This last version of the measuring procedures was used in the present work in determining the reaction rate constant of the intermetallic compound produced during the incorporation of lithium into liquid gallium from a 0.6 N lithium perchlorate solution in propylene carbonate containing p-hydroxypropiophenone. The reaction rate of LiGa with a solution not containing p-hydroxypropiophenone (i_{chem} of the base electrolyte) was found to be $3\cdot10^{-6}$ A/cm^2. The results of measurements of i_{chem} in solutions containing various amounts of p-hydroxypropiophenone are shown in Fig. 4. The reaction rate constant of LiGa with p-hydroxypropiophenone found from this plot by extrapolation is $1.2\cdot10^{-9}$ sec^{-1}.

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