Physical Chemistry

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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Determination of the Solubility and Diffusion Coefficient of Nickel in Mercury by the Method of Amalgam Polarography with Accumulation

For calculating the solubility and diffusion coefficients of metals in mercury, the currents of anodic oxidation of amalgams may be used, if they are caused by oxidation of the metal from the liquid phase of the amalgam ([1]).

The peak of anodic oxidation of nickel in amalgam polarography, according to various authors, reflects either oxidation of the metal present as a solid phase on the surface of mercury, or oxidation of nickel dissolved in mercury ([2-4]).

Fig. 1. Shape of the peaks obtained on the second drop of mercury at different nickel concentrations in the solution: 1 –background, 2 –$6 \cdot 10^{-6}$ mol/l, 3 –$8 \cdot 10^{-6}$, 4 –$1 \cdot 10^{-5}$, 5 –$2 \cdot 10^{-5}$, 6 –$4 \cdot 10^{-5}$, 7 –$6 \cdot 10^{-5}$, 8 –$1 \cdot 10^{-4}$, 9 –$2 \cdot 10^{-4}$, 10 –$4 \cdot 10^{-4}$, 11 –$6 \cdot 10^{-4}$ mol/l, 12 –peak obtained on the third drop from a solution of $8 \cdot 10^{-5}$ mol/l nickel, 13 –peak obtained on the second drop after anodic polarization of the first drop; shunt 1/3 (curve 7 –shunt 1/2).

To eliminate the component of the peak caused by anodic oxidation of nickel from the surface, we chose the following procedure: after completion of the pre-electrolysis, which was carried out at −1.4 V (vs. SCE), the potential was rapidly lowered (in approximately 5 sec) to −0.6 V; the mercury drop serving as the cathode was dropped to the bottom of the cell, and in its place a new drop was extruded, which was subjected to anodic polarization in the potential interval from −0.6 to +0.1 V (relative to SCE). The lowering of the potential to −0.6 V, carried out before the first drop was dropped, is-

includes reduction on the surface of the second drop (the reduction potential of nickel is more negative than −0.6 V).

The investigations were carried out on a PA-1 "Geologorazvedka" polarograph with a mirror galvanometer of maximum sensitivity $2.83 \cdot 10^{-3}$ μA/mm and a photographic recording scale length of 120 mm in the cell described earlier ([5]).

Experimental conditions: pre-electrolysis was carried out against a background of 0.1 N sodium chloride; electrolysis time—1 min; stirring rate 234 rev/min; temperature $25 \pm 0.2^{\circ}$C. Anodic dissolution was carried out at a linearly varying potential (260 mV/min), shunt 1/3.

Fig. 2. Dependence of the height of the nickel oxidation peak on the nickel concentration in solution, obtained for more dilute (a) and less dilute (b) nickel solutions, on the second mercury drop; shunt 1/3; rate of cathodic stirring 234 rev/min. 1—height of the nickel peak obtained on the second mercury drop after anodic polarization of the first drop.

During oxidation of nickel from its amalgam by the method described, an anodic nickel peak was found on the polarograms before the onset of mercury oxidation (Fig. 1), with a half-peak potential of about −0.27 V (SCE). The result of the experiments is a calibration curve (Fig. 2), showing that the height of the anodic oxidation peak of nickel is proportional to the nickel concentration in solution up to a value of $8 \cdot 10^{-5}$ mole/l. With further increase in concentration, the height of the nickel peak in solution remains constant. Since in the course of pre-electrolysis the second drop does not come into contact with the solution, it may be assumed that oxidation of nickel from the liquid phase of the amalgam takes place. This means that, at a nickel concentration in solution above $8 \cdot 10^{-5}$ mole/l, under the selected experimental conditions a saturated amalgam is obtained not only in the first drop but also in the depth of the capillary. At such concentrations nickel can also be detected in the third drop (Fig. 1).

In order to exclude the possibility of oxidation of nickel from surfaces adjacent to the electrode, an experiment was carried out on anodic oxidation of nickel from the second drop also after the first had been subjected to anodic polarization (Fig. 1). It was found that in this case the height of the anodic peak of nickel oxidation from the second drop is the same as in the case of dropping the first drop without anodic polarization of it (see Fig. 2).

Fig. 3. Dependence of the diffusion coefficient of a metal in mercury on the radius of the metal atom (from the work of Cooper and Furman ([10])). Points denote our data; the triangle denotes the data of K. Zh. Sagadieva ([11]).

From the results of anodic oxidation of nickel from the second drop, the solubility and diffusion coefficient of nickel in mercury were calculated. The concentration of nickel in the amalgam was calculated coulometrically from the quantity of electricity (Q) expended in the anodic oxidation process: $Q = i_0/2.303\,K$ ([6]). As shown in ([7]), polarographic peaks of anodic oxidation of a metal from an amalgam can be used to determine i_0 and K.

For calculation of the diffusion coefficient, the Ševčík equation ([8]) was used, whose applicability to amalgam polarography was shown earlier ([9]).

For comparison, the diffusion coefficient of zinc was found by the same method; its value proved to be $2.03 \cdot 10^{-5}$ cm^2/sec, which agrees with the values reported in the literature by other authors ([11]).

For nickel, the values we calculated for the solubility and diffusion coefficient in mercury proved to be $1.1 \cdot 10^{-4} \pm 0.7$ g-atom/l and $1.9 \cdot 10^{-5} \pm 0.2$ cm^2/sec, respectively. This value falls on the straight line expressing the dependence of the diffusion coefficients of metals in mercury on the atomic radius ([10]), shown in Fig. 3.

During the cathodic reduction of nickel on a stationary mercury drop, contrary to the assertion of Mindowicz ([2]), diffusion of nickel into the mercury occurs. The peaks observed under the selected conditions correspond to the anodic oxidation of nickel from the liquid phase of the amalgam.

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