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Abstract

Full Text

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POLAROGRAPHY AT HIGH PRESSURES

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The application of polarography to the investigation of electrode processes and chemical reactions at high pressures is of considerable interest. The present communication contains a description of the apparatus and method for polarography (with a mercury dropping electrode) at pressures up to 3000 kg/cm^2; it also gives the first results obtained by us in studying the influence of pressure on the polarographic behavior of several simple ions.

Fig. 1. Cell for polarography under pressure

The design of the apparatus used by us is shown in Fig. 1. The pressure is produced in the steel vessel 1 by oil supplied by a multiplier. In the side wall of the lower part of this vessel there is a three-cone electrical lead-in 4, serving to connect the electrodes of the polarographic cell with the electrometric circuit. The polarographic cell itself 3 and the mercury reservoir 6 are mounted on a steel frame-holder 8 with a steel cup 2. The cell consists of a glass cylinder into which, from above through ground joints, are inserted the capillary of the dropping electrode 9 and the salt bridge of the reference electrode 5. The lower, narrowed and serrated open end of the cell is immersed in mercury poured into cup 2. This mercury forms a seal which separates the solution under investigation from the compressing medium (oil) and at the same time serves as the bottom of the cell and its anode.

The capillary of the dropping electrode is provided with a small blade for the forced detachment of drops (^{1}), which ensures the preservation of a constant dropping period when the electrode potential is changed. Our experiments showed that the dropping period t of the electrode used practically does not change even when the pressure is raised from atmospheric pressure to 3000 kg/cm^2. The electrode had the characteristics $m = 1.147$ mg $\cdot$ sec^{-1}, $t = 0.19$ sec. The capillary of the electrode is connected by means of a vacuum rubber tube to the glass reservoir containing mercury 6. The small value of the mercury flow rate m and the sufficiently large cross-section of reservoir 6 (diameter

Fig. 2. Polarograms of a solution of TlCl and HCl in a KCl supporting electrolyte at pressures: 1 –1, 2 –1000, 3 –3000 kg/cm^2

Figure 2: Fig. 2. Polarograms of a solution of TlCl and HCl in a KCl supporting electrolyte at pressures: 1 –1, 2 –1000, 3 –3000 kg/cm^2

about 3 cm) ensure that the height of the mercury column remains practically unchanged during the experiment (2-3 hours).

The reference electrode is a saturated calomel electrode (s.c.e.) 5, the end of whose salt bridge (KCl solution) is closed with tightly rolled filter paper and an agar-agar plug.

The electrode has a mercury-filled siphon serving as a seal; the siphon is intended to equalize the pressure outside and inside the electrode.

The entire vessel 1 (Fig. 1) was placed in a water bath, in which a constant temperature ($25 \pm 0.1^\circ$) was maintained by means of an ultrathermostat.

The procedure for carrying out the experiments was as follows. Mercury was poured into cup 2 and the cell was placed in it. A pressure reservoir with mercury 6 was attached to holder 8, the dropping electrode 9 was inserted into the cell, after which oxygen from the air was removed from it by purging with nitrogen. Then the solution to be studied, previously purged with nitrogen, was poured into the cell under a current of nitrogen up to the top, and the reference electrode 5 was inserted. After this the holder with the cell was placed in the lower part of vessel 1, and the leads from the electrodes were soldered to the ends of the electrical input 4; then the stopcock under reservoir 6 was opened, the upper part (cap) was screwed onto the lower part of the vessel, the entire vessel was filled with oil and immersed in the thermostated bath. After the temperature had equalized (20-30 min), a control polarogram was recorded at atmospheric pressure. Then the pressure was raised to 1000 or 3000 kg/cm^2; after the temperature had equalized, polarograms were recorded under pressure.

Fig. 2. Polarograms of a solution of TlCl and HCl in a KCl supporting electrolyte at pressures:
1 –1, 2 –1000, 3 –3000 kg/cm^2

The polarographic measurements themselves were carried out in the usual manner: between the anode (mercury in cup 2) and the dropping electrode 9, a potential difference was produced by means of a voltage divider, and the current flowing in the circuit was measured with an M-95 microammeter (with a sensitivity of 5-10 μA over the whole scale). The potential of the dropping electrode was measured relative to the reference electrode with a P-4 potentiometer with an expanded measuring range (^{2}).

The experiments were carried out with two solutions: a) 1.00 mM TlCl and 0.75 mM HCl in 0.1 N KCl; b) 0.65 mM $CdSO_4$, 0.90 mM $ZnSO_4$ and 0.40 mM HCl

Fig. 3. Plots of lg i/i__pr − i waves of Cd^{2+} (A), Zn^{2+} (B) and H^+ (V) at different pressures: 1–1, 2–1000, 3–3000 kg/cm^2

Figure 3: Fig. 3. Plots of lg i/i__pr − i waves of Cd^{2+} (A), Zn^{2+} (B) and H^+ (V) at different pressures: 1–1, 2–1000, 3–3000 kg/cm^2

in 0.1 N KCl. The results of the experiments are given in Table 1 and in Figs. 2 and 3.

Consideration of the experimental data makes it possible to draw the following conclusions:

1) The half-wave potential of Tl^+ (relative to the N.C.E. at the same pressure) and the magnitude of the limiting current practically do not change with increasing pressure from atmospheric to 3000 kg/cm^2.
2) The half-wave potentials of Cd^{2+} and Zn^{2+}, with an increase in pressure to 3000 kg/cm^2, shift toward larger negative values (respectively by 35 and 41 mV); the magnitude of the limiting current increases somewhat when the pressure is raised from atmospheric to 1000 kg/cm^2.

Table 1

Changes in the polarographic characteristics of ions with pressure. $E_{1/2}$ values are given in volts relative to the N.C.E.; i_{pr}—in μa

Pressure, kg/cm^2	Tl^+ $E_{1/2}$	Tl^+ i_{pr}	Cd^{2+} $E_{1/2}$	Cd^{2+} i_{pr}	Zn^{2+} $E_{1/2}$	Zn^{2+} i_{pr}	H^+ ($C =$ 0.75 mM) $E_{1/2}$	H^+ ($C =$ 0.75 mM) i_{pr}	H^+ ($C =$ 0.40 mM) $E_{1/2}$	H^+ ($C =$ 0.40 mM) i_{pr}
Atm.	−0.459	1.53	−0.593	1.30	−0.998	1.77	−1.629	2.34	−1.633	1.21
1000	−0.459	1.54	−0.610	1.41	−1.018	1.89	−1.618	2.60	−1.625	1.34
3000	−0.459	1.53	−0.628	1.40	−1.039	1.85	−1.602	2.74	−1.609	1.42

3) The half-wave potential of the irreversible discharge of H^+, when the pressure is raised to 3000 kg/cm^2, shifts toward less negative values (by 24–27 mV); the magnitude of the limiting current increases over the entire pressure interval studied.

Fig. 3. Plots of $\lg i/i_{pr} - i$ waves of Cd^{2+} (A), Zn^{2+} (B), and H^+ (V) at different pressures: 1–1, 2–1000, 3–3000 kg/cm^2

4) The slope of the waves for all the ions studied practically does not change with pressure (see Fig. 3).

The change in the half-wave potential for a reversible system can be represented by the equation (3):

$$\left(\frac{\partial E_{1/2}}{\partial P}\right)_T = -\frac{\Delta V}{nF}, \tag{1}$$

where ΔV is the change in the volume of the system upon passage of a unit quantity of electricity, n is the number of electrons transferred in the electrode-reaction process, and F is the Faraday constant. For the electrode reaction

$$2\mathrm{Tl}^+ + 2\mathrm{Cl}^- + 7\mathrm{Hg} \rightarrow \mathrm{Tl}_2\mathrm{Hg}_5 + \mathrm{Hg}_2\mathrm{Cl}_2^*,$$

experiment shows that $(\partial E_{1/2}/\partial P)_T \approx 0$, and, consequently, $\Delta V \approx 0$. Substituting the values of the molar volumes of the substances into the reaction equation, while replacing the unknown values for $2\mathrm{Tl}^+ + 2\mathrm{Cl}^-$ by twice the molar volume of $\mathrm{TlCl}_{\mathrm{tv}}$, we find that the volume of the substances on the left-hand side of equation (1) is about 3 cm^3/mol less than the corresponding value for the right-hand side. It was noted above that $\Delta V \approx 0$; therefore the obtained difference in volumes should be regarded as equal to the change in volume upon dissolution, in 0.1 N potassium chloride solution, of two moles of TlCl with formation of $2\mathrm{Tl}^+ + 2\mathrm{Cl}^-$. The data available in the literature (5) for the densities of TlCl solutions in aqueous KCl are, unfortunately, insufficiently accurate. Thus, calculation from these data shows that

* Thallium amalgam has the composition $\mathrm{Tl}_2\mathrm{Hg}_5$ (4).

The dissolution of TlCl in 0.05 N and 0.2 N KCl solutions is accompanied by some expansion, whereas in 0.1 N and 0.5 N KCl there is a slight contraction of the solution.

The very careful investigations of Cohen and Piepenbrock (6) show that the dissolution of TlCl in 1.0 N KOH, also containing KCl, is accompanied by an increase in volume of 8 cm^3/mol. Thus, it is highly probable that the dissolution of TlCl in 0.1 N KCl is accompanied by a small increase in volume, of the order of 1.5 cm^3/mol. It should be noted that the formation of thallium amalgam from thallium and mercury also occurs with an increase in volume (4).

In contrast to the Tl^+ wave, the values $(\partial E_{1/2}/\partial P)_T$ for the Cd^{2+} and Zn^{2+} waves have rather appreciable negative values. The discharge of these ions is accompanied by an increase in volume owing to destruction of the hydrate shells, which accounts for the positive value of ΔV in equation (1).

The effect we observed of a decrease in the hydrogen overvoltage under pressure is of considerable interest and requires further detailed study. The difference in $E_{1/2}$ of the hydrogen waves in two experiments (the last columns of Table 1) is associated with the well-known phenomenon of the shift of $E_{1/2}$ of these waves toward positive potentials with increasing concentration of H^+ in a solution containing indifferent electrolyte. Let us now consider the question of the influence of pressure on the value of the limiting diffusion current. The diffusion current is determined by the Ilkovič equation:

$$i_{\text{pr}} = 607\, m^{2/3} t^{1/6} C n D^{1/2}, \tag{2}$$

where C is the concentration of the depolarizer, D is its diffusion coefficient, and the factor 607 contains the value of the density of mercury d to the power 2/3. Combining m and d, in equation (2) one may substitute for them the quantity $\omega^{2/3}$, where ω is the volume of mercury flowing per unit time from the capillary of the dropping electrode. Analysis of the operation of electrodes with paddles shows that, at a high degree of forced dropping (when the period of forced dropping of the electrode is many times smaller than the dropping period observed for the given capillary in the absence of the paddle), the size of the drops does not depend on the surface tension of mercury at the mercury-solution interface and is determined only by the angle of inclination of the paddle and its distance from the mouth of the capillary. As noted above, the dropping period t proved to be practically independent of pressure. Consequently, under the conditions studied, pressure does not noticeably affect the value of ω either.

Thus, in equation (2) the only quantities that change with pressure are the concentration C (increasing with pressure) and the diffusion coefficient D, which decreases with pressure. Let us now replace the product $CD^{1/2}$ in (2) by the proportional quantity $v^{-1}\eta^{-1/2}$ (where v is the specific volume and η the viscosity of the solution). According to Bridgman' s data (^{7}), changes in v and $\eta^{1/2}$ with pressure compensate each other to a considerable extent. Thus, for water at 30°, the quantity $v \cdot \eta^{1/2}$ changes by only 0.3% when the pressure is increased from atmospheric to 3000 kg/cm^2. Therefore, one should have expected a very slight change in i_{pr} under the conditions we studied.

Indeed, for Tl^+ ions the value of the limiting current in the pressure range up to 3000 kg/cm^2 at 25° remains practically unchanged. However, this situation is not confirmed for the other ions studied: the observed changes in i_{pr} are far beyond the limits of experimental error, and the causes of these changes require further study.

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