A STUDY OF THE POLAROGRAPHIC BEHAVIOUR
OF TRIVALENT ARSENIC IN CONCENTRATED PHOSPHORIC ACID

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The electrochemical behaviour of trivalent arsenic in concentrated phosphoric acid (85%) has been studied at the dropping mercury electrode. It was found that trivalent arsenic is reduced in two or, in some cases, three waves. The first wave, $E_{1/2} = -0.45$ V (S.C.E.), is diffusion controlled and corresponds to the three-electron reduction, As(III) $+ 3 e^- = $ As(0). The electrode reaction is irreversible; its apparent rate constant at the standard potential has the value $k^\circ = = 1 . 10^{-9}$ cm s^{-1}, and the charge transfer coefficient $\alpha = 0.22$.
   The second wave, $E_{1/2} = -0.66$ V (S.C.E.), is substantially steeper and somewhat lower than would correspond to a three electron reduction, *i.e.* As(0) $+ 3 e^- + 3 H^+ = $ AsH$_3$. Gaseous arsenic(III) hydride was proved chemically. The reduction of the limiting current was explained by the participation of the chemical reaction As(III) $+$ AsH$_3 = 2$ As(0) $+ 3 H^+$ which consumes arsenic(III) ions at the electrode, the concentration of which is given by their diffusion rate. The third wave, with $E_{1/2} \sim -0.8$ V (S.C.E.), appears at higher arsenic concentrations than $1 . 10^{-3}$M and is perceptible only in the presence of surface active substances. The sum of the second and the third waves is somewhat less than would correspond to a three electron reduction. As is shown by experiments on a stationary mercury cup electrode and by microscopic observation of a dropping mercury electrode, a film of red-brown arsenic, which covers the surface of the electrode, is formed at higher concentrations of trivalent arsenic. This arsenic film, in some cases in the presence of a surface active substance, evidently causes a shift of the electrode reaction to more negative potentials and thus gives rise to the appearance of a third wave.

The polarographic behaviour of As(III) has already been studied by several authors[1−4]. These authors worked in a 1M-HCl medium and observed two reduction waves which they assigned to the stepwise reduction. As(III) $\rightarrow$ As(0) $\rightarrow$ AsH$_3$. Their investigations centred primarily on study of the first wave, however, results are varied.
   A more careful study was carried out by Meites[5]. He characterized the first wave as the irreversible reduction of As(III) to elemental arsenic and, on the assumption of the adsorption of metallic arsenic on the surface of the mercury drop, calculated the thickness of the layer of elemental arsenic. He further describes an unusual double maximum on the limiting current of the second wave, which can be suppressed by surface active substances. More recently published communications[6−8] also attempt to explain the anomalous behaviour of As(III) in various media. They describe one to four cathodic waves which they use primarily for analytical purposes. However, they do not throw any light on the actual electrode mechanism.

EXPERIMENTAL

Reagents. The chemical preparations used were of purity p.a. and produced by Lachema Brno. Further used was NaAsO$_2$ (Erba, Italy). Silver diethyldithiocarbamate was prepared according to[9].

Apparatus. Polarographic measurements were made on the polarograph Polariter PO 4, Radiometer (Denmark). For measurements with controlled drop time, the mechanical drop tapper DLT-1 and the electrode B-405 from the same firm were connected to the PO 4. *i-t* curves were recorded photographically with a string-mirror galvanometer (Stylo A 80) from the firm, Kipp en Zonen, with a swing time of 1/60 s and a sensitivity of 3·00 . 10^{-8} A/mm/90 cm.

Microscopic observations were made with the help of a workshop binocular microscope. As indicator electrodes were used: *a*) a dropping mercury electrode (m = 2·3 mg s^{-1}, t_1 = 3·6 s at h = 64 cm); *b*) a stationary mercury cup electrode (area = 0·75 cm^2); *c*) a rotating carbon disk (area 0·7 cm^2); *d*) a rotating platinum disk (area 0·4 cm^2). For the study, a Kalousek vessel with a mercurous sulphate electrode was used. Its potential was checked using a standard thallium ion test solution. Potential values were recalculated with respect to (s.c.e.).

RESULTS

For the study of the polarographic behaviour of trivalent arsenic were used solutions containing 1 . 10^{-4} to 1 . 10^{-2}M As(III) in 85% H$_3$PO$_4$. Low concentrations of tri-valent arsenic, $\left(1 . 10^{-4}\right.$ to 1 . 10^{-3}M$\left.\right)$ in 85% H$_3$PO$_4$ in the absence of surface active substances, gave two waves during polarographic recording; the height of the second wave is somewhat less than that of the first. As the concentration of arsenic appro-aches the value 1 . 10^{-3}M, a maximum appears on the limiting current of the second wave, its height increasing with the concentration of depolarizer. After supression of the maximum with methylene blue or gelatine, and at arsenic concentrations greater than 10^{-3}M, this maximum is converted into a separate and more negative wave (third wave) with a well defined limiting current. At higher arsenic concentra-tions $\left(> 3 . 10^{-3}\text{M}\right)$, it is more convenient to use the maximum supressor Triton-X-100 (Fig. 1). To verify the character of the currents of individual waves, the dependence
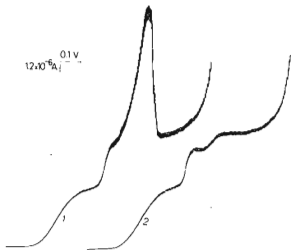

12×10^{-6}A| 0·1 V

Fig. 1

The Polarographic Curves of As(III)
1 3 . 10^{-3}M As(III), 85%, H$_3$PO$_4$; 2 + 1·5 .
. 10^{-4}M Triton X-100, from —0·2 V (s.c.e.).

of the limiting currents on concentration, reservoir height, temperature, drop time, and i–t curves were studied. The dependence of the limiting current i_1 on the concentration c at various drop times (0.5, 2, 4, 6, 8 s) and on the reservoir height at temperatures, $t = 20$, 30, 40, 50 and $60°C$ were followed. These dependences for individual waves and for their sum are linear with the exception of the i_1–c dependence for the limiting current of the third wave, which is less at higher concentrations than that required for linearity. The temperature coefficients calculated for the temperature range $20-50°C$ have the values 1.9% for the first wave, 2.5% for the second wave, and 11% degree for the third wave.

Basically the same results are also attainable in more dilute H_3PO_4 solutions ($80—40\%$). They show only increased limiting current with decreased viscosity of the medium, and the half-wave potentials are shifted to more negative values. In even more dilute acid, it is possible to observe a larger number of poorly defined waves.

Logarithmic analysis of the dependence of the limiting currents on drop time yielded straight lines for the individual waves, whose slopes have the values $x = 0.18$ for the first, $x = 0.27$ for the second, $x = 0.5$ for the third wave, and $x = 0.3$ for the sum of the three waves.

The *method of the dependence of the instantaneous current on time* (i–t curves) was further used to explain the character of the limiting current. For the measurements was used a horizontal capillary, on which the effect of concentration polarization transfer is excluded to a substantial extent. From the registration of curves at the potential of the foot of the wave (-0.35 V), were obtained parabolas with the exponent $x' = 0.5$. In the limiting current region of the first and second waves, the value of the exponent of the i–t curves is $x' = 0.18$. In the potential region corresponding to the current of the third wave, the i–t curves are anomalous. Waves appear on the parabolas and become oscillations with increasingly negative potential (Fig.

Fig. 2

i–t Curves Registered Using a Horizontal Capillary

$3 . 10^{-3}$M-As(III), 85% H_3PO_4, $1.5 . 10^{-4}$M Triton X-100; *1* —0.6 V (s.c.e.); *2* —0.85 V (s.c.e.); t_1 5s.

2,3). For this reason, the curves cannot be evaluated. At even more negative potentials, the $i-t$ curves again become smooth with the exponent $x' = 0.25$. Calculation of the number of electrons consumed in the electrode reaction by coulometric measurement at a constant potential did not give satisfactory results. From a comparison of the heights of the arsenic waves with the heights of the waves of various ions (Tl, Pb, Fe, Cd, Cu), in identical media, it was found that the first wave corresponds to a three electron reduction, and that the sum of the second and third waves also approaches three electrons.

The logarithmic analysis of the waves gave a slope of 90 mV for the first and 40 mV for the second wave. Considering that the third wave was measured in the presence of surface active materials, which can change the course of the electrode reaction, the results of the logarithmic analysis of this wave were not taken into account.

A further method used to clarify the electrode reactions of trivalent arsenic in concentrated phosphoric acid was *cyclic voltammetry* with a hanging mercury electrode. During the registration of the polarization curves from $+0.1$ to -1.1 V (s.c.e.), *i.e.* in the region of As(III) reduction, the curve showed a deformed peak whose position corresponds to the first reduction wave obtained by the polarographic method. At a potential of -0.75 V, a second peak appears, whose potential value corresponds approximately to the half-wave potential of the second wave. On the reverse scan of the curves from the hydrogen ion reduction potential to positive values, the curves have an anomalous course since the current on the return registration is higher than during polarization from positive to negative potentials. This course would suggest the reduction of an adsorbed product. On repeated cyclic polarization with the same mercury drop in the potential range $+0.1$ to -1.1 V, the reduction peak of trivalent arsenic was not found. Similar results were found with the use of a rotating platinum disk electrode (600 rev./min).
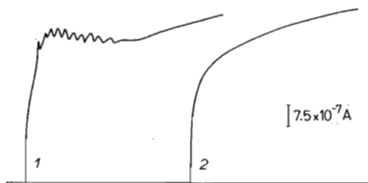

FIG. 3

$i-t$ Curves Registered Using a Horizontal Capillary

$3 . 10^{-3}$ M–As(III), 85% H_3PO_4, $1.5 . 10^{-4}$ M Triton X-100; *1* —0.875 V (s.c.e.); *2* —0.95 V (s.c.e.); t_1 5s.

During the study of the voltammetric curves using a rotating carbon disk electrode (600 rev./min), two cathodic waves were found. However, no conclusions can be drawn from these experiments because of changes in the character of the electrode surface by the arsenic deposited during the polarization. The high viscosity of the medium prevented oscillopolarographic measurements.

An attempt to confirm the assumed adsorption processes led to the use of the *method of electrocapillary curves* constructed from drop time measurements. Electrocapillary curves with maxima considerably shifted to negative values were found, even at high As(III) concentrations $(1 \cdot 10^{-2}\text{M})$, no adsorption processes were manifested. The curve is almost coincident with the electrocapillary curve of the pure electrolyte. In the vicinity of the dropping mercury, a brown turbidity is formed. At potentials corresponding to the limiting current of the second and third waves, this phenomenon was observed even in the near vicinity of the capillary orifice. The obtained brown-coloured arsenic was attendant in such large quantities that it is not possible to presume its origin from the electrode reaction alone. The phenomenon of formation of elemental arsenic was also noted during some further experiments when the electrode was polarized for a longer period than that corresponding to the registration of a single polarization curve. During the electrolysis of $5 \cdot 10^{-3}\text{M}$ As(III) in 85% H_3PO_4 on a stationary mercury cup electrode at a potential of -0.6 V, corresponding to the limiting current of the first wave, brown flakes of elemental arsenic appeared during the electrolysis. At the potential of the limiting current of the second wave $(-0.7$ V) and with the same experimental arrangement, bubbles of gas were formed in addition to the brown flakes in the close vicinity of the electrode. The gaseous product was collected in a glass bell placed above the cup electrode and hence was subsequently removed with a hypodermic syringe and transfered to a silver
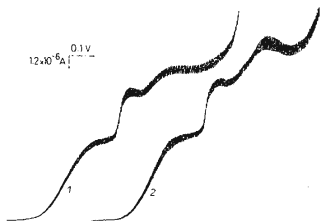

Fig. 4

The Polarographic Curves of As(III)

1 $3 \cdot 10^{-3}$M-As(III), 85% H_3PO_4, $1.5 \cdot 10^{-4}$M Triton X-100; *2* solution bubbled 30 min with AsH_3, registration after standing 30 min, from -0.2 V (s.c.e.).

diethyldithiocarbamate solution. A red-coloured solution is an indication of arsenic(III) hydride. Coincident results were also obtained when the electrode was polarized to a potential corresponding to the limiting current of the third wave $(-0.9$ V$)$. The amount of arsenic hydride liberated during the same polarization time as in the preceding experiment was much larger.

Microscopic observation of the mercury drop was carried out at an As(III) concentration of $5 \cdot 10^{-2}$M. When the electrode is at the potential corresponding to the limiting current of the first wave, it is possible to observe a red-brown coloration, being, apparently, elemental arsenic, which, with the growth of the drop, turns a deep red. With polarization of the drop to more negative potentials, bubbles of gas are formed at the capillary orifice and the drop is simultaneously covered with metallic arsenic. From the potential of the limiting current of the second wave can clearly be seen the breaking up of the coloured surface layer; on the surface pieces of elemental arsenic move about freely. The drop displays a twisting motion and undergoes a considerable deformation of its spherical shape. On bubbling a solution of trivalent arsenic in 85% phosphoric acid with gaseous arsenic hydride, the colourless solution becomes light brown from the liberated elemental arsenic. During registration of $i-E$ curves of this solution, the limiting current of the third wave shows an increase. This growth is accompanied by the formation of a small maximum (Fig. 4).

DISCUSSION

From the results obtained, it follows that, during the polarographic reduction of trivalent arsenic in 85% phosphoric acid, besides the electrode reaction, a number of further chemical reactions also occur.

The situation is still somewhat complicated in that it is not known in what form the arsenic exists in the solution in which the measurements were carried out. It can be assumed that, in a medium of concentrated phosphoric acid, arsenic will act as a base, *i.e.* will dissociate to As^{3+}. Free arsenic ions are capable of existing only in strongly acid solutions. It was not possible to ascertain from the accessible literature whether such species also exist in phosphoric acid or whether they form various solvated complexes. For a clearer picture, the waves will be discussed individually.

The shape of the first reduction wave at -0.45 V (s.c.e.) can be described by the equation for an irreversible electrode reaction:

$$E = E^0 - \frac{RT}{\alpha nF} \ln \frac{i}{i_d - i} + \frac{RT}{\alpha nF} \ln 0.886 \frac{k^0 t_1^{1/2}}{D^{1/2}} . \qquad (1)$$

Hence, if the charge transfer coefficient, α, is independent of potential, it is possible to calculate the apparent rate constant of the electrode reaction for the first

wave. The diffusion coefficient was calculated from the Ilkovič equation for the mean diffusion current; the value of the normal potential is given by Latimer[10] as $E° = +0.247$ V (s.h.e.) The values: $E_{1/2} = -0.235$ V (s.h.e), $T = 293$ K, $n = 3$, $t_1 = 4.22$ s^1, $D = 2.75 . 10^{-7}$ cm^2 s^{-2}, $\alpha = 0.22$, were substituted into Eq.:

$$E_{1/2} = E° + \frac{RT}{\alpha nF} \ln 0.886 k° \sqrt{\frac{t_1}{D}}, \qquad (2)$$

giving for the apparent rate constant at the standard potential the value $k° 1 . 10^{-9}$ cm s^{-1}.

The correction of the rate constant for its dependence on the electrode double layer was not carried out since the values of the potential in the diffusion part of the double layer, φ_2, are not known for the medium studied.

For lower arsenic concentrations, the first reduction wave of trivalent arsenic was followed by a second wave, which is roughly $10-15\%$ lower and has a half-wave potential of $E_{1/2} = -0.60$ V (s.c.e.). At higher concentrations, $> 1 . 10^{-3}$M As(III), at which a third wave appears, as will be discussed later, this lowering compared to the first wave is even more marked (up to one third). As further experiments showed, this lowering can be caused by a chemical reaction in the neighbourhood of the electrode, which competes with the electrode reaction occurring at the potential of the second wave. With arsenic concentrations increased over $6 . 10^{-4}$M, a maximum is formed on the wave. This maximum may be formally classified as an eddy maximum of the first kind; however, after applying the given potential to the electrode, no streaming of the solution in the neighbourhood of the electrode was observed. Only the formation of the brown turbidity was seen at the capillary orifice, even with the naked eye.

A similar phenomenon was described by Hans and Stackelberg[11], who noticed the formation of a sharp maximum on the limiting current of the reduction wave of tellurate. At the potential of this maximum, a brown turbidity is formed at the surface of the drop, corresponding to metallic tellurium, which is supplied by a chemical reaction in the vicinity of the electrode from telluric ions, originating from the electroreduction reaction, and tellurate ions diffusing from the bulk solution. Similar to that done by Hans and Stackelberg, the cause of the current maximum on the reduction wave of trivalent arsenic should be sought in the mechanism of the electrode process.

If the second reaction corresponds to reduction to arsenic hydride, *i.e.* to the reaction

$$As(0) + 3 e + 3 H^+ = AsH_3 \qquad (A)$$

gaseous arsenic hydride should be formed in the potential region of the second wave. The formation of bubbles of gas was observed microscopically. The gaseous product was collected in large quantities and it was shown that it is arsenic hydride. The fact that this wave is somewhat lower than would correspond to three electrons according to the above equation can be attributed to the chemical reaction

$$As(III) + AsH_3 = 2 As(0) + 3 H^+ . \tag{B}$$
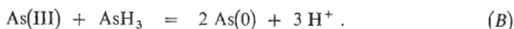
To verify the participation of this chemical reaction, an experiment was carried out, during which a colourless solution containing trivalent arsenic turned light brown with the formation of elemental arsenic after being bubbled with gaseous arsenic hydride. The possibility of this reaction is mentioned in the literature[12,13].

The third wave can be observed only at concentrations greater than $1 . 10^{-3}$M As(III). In solutions without surface active materials, it is entirely obscured by a maximum. After suppression of the maximum, it appears in the form of a drawnout, irreversible wave with $E_{1/2} \simeq -0.8$ V (s.c.e.).

Experimental criteria show that the limiting current of the third wave is not diffusion controlled alone, and that its size is affected by the rate of a chemical reaction. Registration of i–t curves in the given potential region indicates further complications. On the i–t curves, oscillations appear, and for this reason, they cannot be easily evaluated. The oscillations are apparently the result of the breakup of the surface layer of metallic arsenic on the electrode. Microscopic observations at large concentrations of trivalent arsenic confirmed that a red-brown layer is formed on the drop, and breaks up, moves freely about the mercury surface, and that considerable deformation of the spherical drop shape takes place. The origin of a gas is perceptible at the capillary orifice. The gaseous product, arsenic hydride, was demonstrated in the same way as with the second wave. The formation of a brown turbidity was also observed at potentials corresponding to the third wave. After bubbling a solution containing trivalent arsenic in 85% phosphoric acid, the colourless solution turned light brown with the formation of elemental arsenic, and, during the registration of the polarization curves of this solution, it was ascertained that this lead to a considerable increase in the limiting current of the third wave. A maximum is formed on the wave (Fig. 4). It is now possible to assume that, besides the electrode reaction, chemical reactions also occur, the possible chemical reaction is again reaction (B). Electrolytically produced arsenic hydride (second wave) reacts with trivalent arsenic ions arriving by diffusion from the solution to the electrode. The metallic arsenic thus produced is again reduced to arsenic hydride, however in a further individual wave which is due to the adsorption of arsenic metal in the form of a film.

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Translated by M. Štulíková.