POLAROGRAPHY OF ARSENIC.

I. TRIVALENT ARSENIC IN UNBUFFERED SOLUTIONS

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Two diffusion waves are formed against a background of lithium salts of As (3+); the second wave, corresponding to the reduction of AsO_2^- is converted to AsO_3^{3-} or $HAsO_3^{2-}$, which are not reduced, and the waves disappear. A new mechanism has been proposed to explain the appearance of two reduction waves of As (3+) in acid medium: As (3+) is reduced to As (3−), in the presence of which mercury undergoes anodic dissolution. The second wave arises when the reaction of ionization of mercury ceases. Alternating current measurements indicated that the process corresponding to the second wave is substantially more rapid than the first. In weakly and moderately acid solutions, nodissociated molecules of $HAsO_2$ are reduced, while in strongly acid medium (1-10 N) there is also a reduction of As^{3+} cations. The maxima on the second wave of As (3+) in acid medium are due to the catalytic evolution of hydrogen.

Compounds of trivalent arsenic exhibit a complex and interesting polarographic behavior. In acid solutions, As (3+) gives two waves [1-20], while under certain specific conditions, up to four waves have been observed [2-4]. A two-wave polarogram with two maxima on the second wave is the most characteristic [7-11]. According to the data of Meites [11], the first wave becomes an adsorption wave in the presence of a high arsenic concentration. There is a widespread opinion that it corresponds to three-electron reduction of As (3+) to elementary arsenic:

$$As(3+) + 3e \rightarrow As. \quad (1)$$

Meites believes that the formation of an adsorption film of elementary arsenic, which conducts electric current poorly, leads to inhibition of the electrode process within the interval of potentials of the first wave. At more negative potentials, arsenic undergoes a six-electron reduction, forming arsine

$$As(3+) + 6e \rightarrow AsH_3. \quad (2)$$

In the reduction of acid solutions of trivalent arsenic by zinc and cadmium amalgams, arsine and elementary arsenic were also found [21-24]. Arsine gives an anodic wave of eight-electron oxidation with $\varphi_{1/2} = +0.01$ V against a saturated mercury sulfate electrode (or +0.34 V against a saturated calomel electrode) [25].

Not one of the cited studies considered any other possible mechanism for explaining the experimental data. It can be imagined that within the entire inverval of potentials, trivalent arsenic undergoes reduction with the participation of six electrons, forming arsine (reaction 2), but at the potentials of the first wave, together with reaction 2, there is a reaction of anodic dissolution of mercury, forming mercury arsenide

$$3Hg + 2As(3-) = Hg_3As_2 + 6e. \quad (3)$$

The net process can be represented by the scheme

$$2As(3+) + 6e + 3Hg \rightarrow Hg_3As_2. \quad (4)$$

According to this scheme, in the reduction of one ion of As (3+), three electrons are formally consumed. When the potential at which reaction 3 stops is reached, a second wave arises on the polarogram. An analogous mechanism has been proposed for the reduction of the tellurite ion [26]. Since the second wave essentially corresponds to the anodic dissolution of mercury, this process should proceed reversibly or almost reversibly; the wave should be steeper than the wave corresponding to an entirely irreversible process, which corresponds to the literature data. This hypo-

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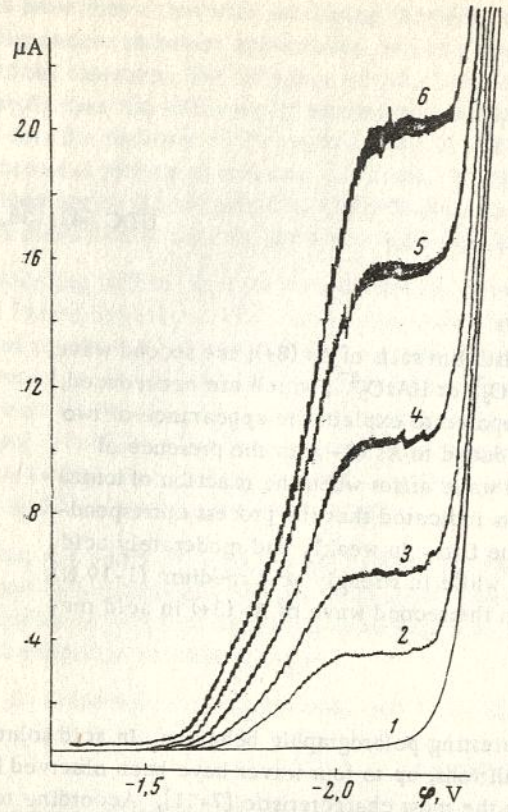


Fig. 1

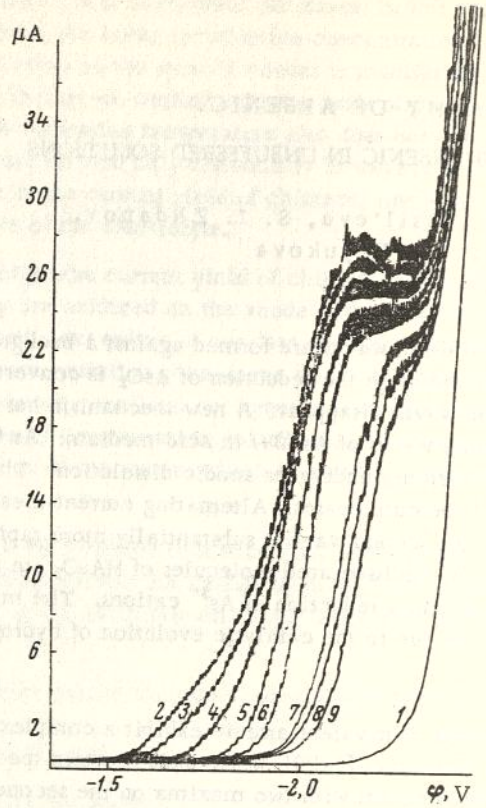


Fig. 2

Fig. 1. Polarograms of As (3+) against a background of 0.1 M LiCl. As (3+) concentration: 1) 0; 2) $1 \cdot 10^{-4}$; 3) $2 \cdot 10^{-4}$; 4) $3.8 \cdot 10^{-4}$; 5) $5.7 \cdot 10^{-4}$; 6) $7.4 \cdot 10^{-4}$ M. The potentials are given relative to mercury in 0.1 M LiCl.

Fig. 2. Influence of alkalinization on the waves of As (3+) against a background of 0.1 M LiCl. As (3+) concentration $1 \cdot 10^{-3}$ M; LiOH concentration: 1-2) 0; 3) $5.1 \cdot 10^{-4}$; 4) $1.5 \cdot 10^{-3}$; 5) $4.4 \cdot 10^{-3}$; 6) $1.4 \cdot 10^{-2}$; 7) $5.5 \cdot 10^{-2}$; 8) 0.11 and 9) 0.22 N. The As (3+) concentration was kept constant.

thesis is also supported by the fact that the second wave on the square-wave polarogram of trivalent arsenic possesses a better shape than the first [27]. This communication presents the results of a verification of our hypothesis.

According to some data [5], trivalent arsenic is not reduced in alkaline medium; in the opinion of the authors of [28] it gives a distinct wave, although actually only an earlier beginning of the rise in the background current was observed on the polarogram in the presence of arsenic. In general the relationship of the polarographic behavior of As (3+) to the structure of its particles in solutions of various compositions has been paid too little attention. And yet, depending upon the conditions, trivalent arsenic may exist in solutions in the form of anions of orthoarsenous (H_3AsO_3) and metaarsenous ($HAsO_2$) acids, neutral H_3AsO_3 and $HAsO_2$ molecules, and As^{+3} cations. Naturally the various particles of arsenic should be reduced at different potentials. Complexes may also be formed [17].

EXPERIMENTAL SECTION

The polarograms were recorded with a Radiometr electronic polarograph (Denmark) and an LP-55A photorecording polarograph (Czechoslovakia). A cell of simple design, the anodic and cathodic spaces in which were separated by a porous glass No. 3 diaphragm, was used. The anode was mercury in 0.1 M LiCl or a saturated calomel electrode, the salt bridge of which was lowered into the anodic compartment of the cell with a 0.1 M solution of LiCl. The freely dropping capillary with a height of the mercury column h = 50 cm possessed the following characteristics: m = 2.14 mg/sec and t = 1 sec at the potential −2.15 V in 0.1 M LiCl relative to the mercury bottom, i.e., at the potential of the plateau of the limiting current of As (3+) in neutral medium.* The solution of As (3+) was prepared

* There were no maxima of the second kind under these conditions.

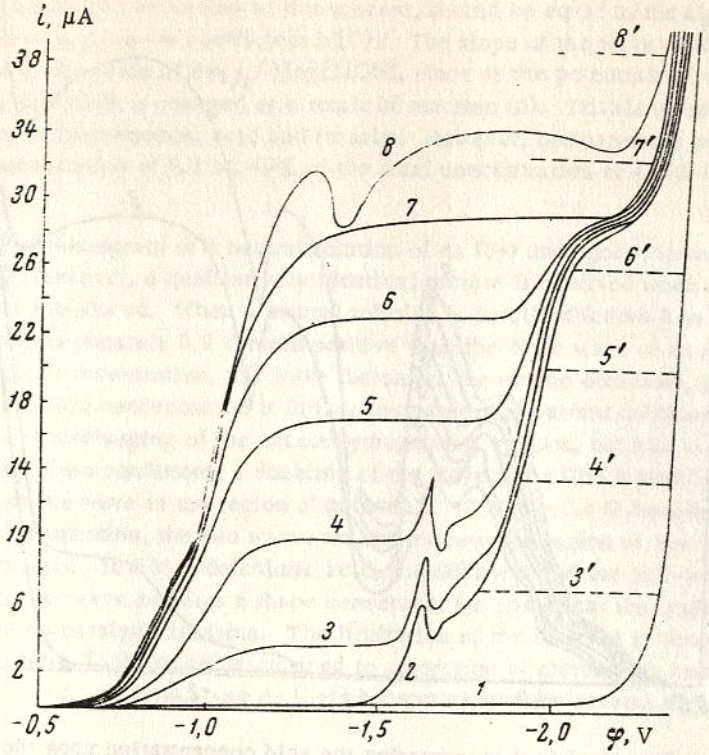


Fig. 3. Influence of acidification on the polarogram of As (3+) against a background of 0.1 M LiCl. As (3+) concentration: 1) 0; 2-8) $1 \cdot 10^{-3}$ M. $HClO_4$ concentration: 1 and 2) 0; 3) $7.3 \cdot 10^{-4}$; 4) $1.5 \cdot 10^{-3}$; 5) $2.2 \cdot 10^{-3}$; 6) $2.8 \cdot 10^{-3}$; 7) $3.5 \cdot 10^{-3}$; 8) $4.3 \cdot 10^{-3}$ M. The segments 3'-8' show the limiting currents of the discharging of H^+ ions in the absence of As (3+).

by dissolving spectrally pure As_2O_3 in a small excess of LiOH solution. After the As_2O_3 was dissolved, the solution was neutralized with hydrochloric or perchloric acid to pH ~ 7. The background solutions were prepared in twice-recrystallized and calcined salts in double-distilled water [32, 33]. The acids were purified by redistillation; lithium hydroxide was especially pure, prepared according to a special order. Oxygen was displaced from the solutions with pure argon or purified nitrogen. In an investigation of the influence of the composition of the solution upon the polarogram of arsenic, its concentration and the concentrations of the other components of the solution were maintained constant. For this purpose, the added solution, for example, of acid, contained simultaneously both arsenic and the other nonvariable components of the solution in the same concentration as the solution in the cell.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

1. Neutral Solutions. Against a background of lithium in neutral medium, trivalent arsenic forms two closely situated waves with $\varphi_{1/2} = -1.68$ and -1.93 V relative to the mercury bottom in 0.1 M LiCl (Fig. 1). The second wave is substantially higher than the first and more pronounced. An analysis of the dependence of the limiting current upon the height of the mercury column indicated that both waves are diffusion waves. The total limiting current is proportional to the arsenic concentration. It can be used for analytical purposes.

The constant of the diffusion current of the sum of the waves is equal to 26.3 μA/millimole. According to the Ilkovic equation, assuming that six electrons participate in the reduction (n = 6), we obtain $D = 1.92 \cdot 10^{-5}$ cm^2/sec. This value is close to the values of the diffusion coefficients of ions of the AsO_2^- type (for example, for NO_2^- at 25°, $D = 1.92 \cdot 10^{-5}$ cm^2/sec*) and substantially exceeds the values for ions of the H_2AsO_3- type (less than 10^{-5} cm^2/sec, for example, for $H_2AsO_4^-$, $D = 0.9 \cdot 10^{-5}$ cm^2/sec). As will be evident from the following, it is most probable that precisely AsO_2^- ions are reduced in neutral unbuffered medium.

The first wave evidently corresponds to the reduction of some other arsenic particles, which do not exist in rapid equilibrium with AsO_2^- ions.

* This and other values of the diffusion coefficients were calculated from the table data for the ion mobilities.

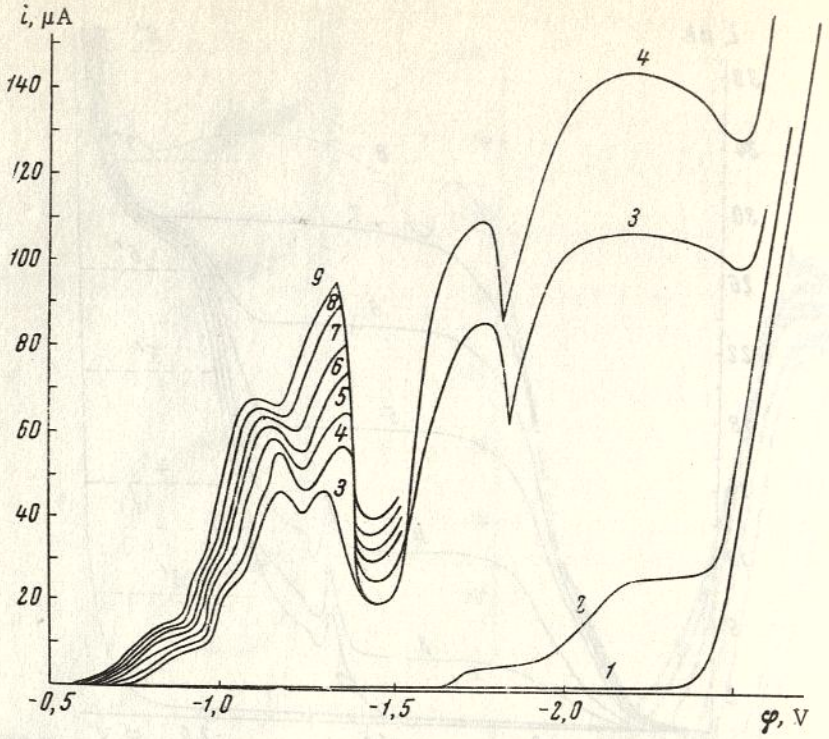


Fig. 4. Influence of further increasing the acid concentration upon the polarogram of As (3+) against a background of 0.1 M LiCl. As (3+) concentration: 1) 0; 2-9) $1 \cdot 10^{-3}$. $HClO_4$ concentration: 1 and 2) 0; 3) 0.013; 4) 0.018; 5) 0.035; 6) 0.08; 7) 0.15; 8) 0.27; 9) 0.48 M.

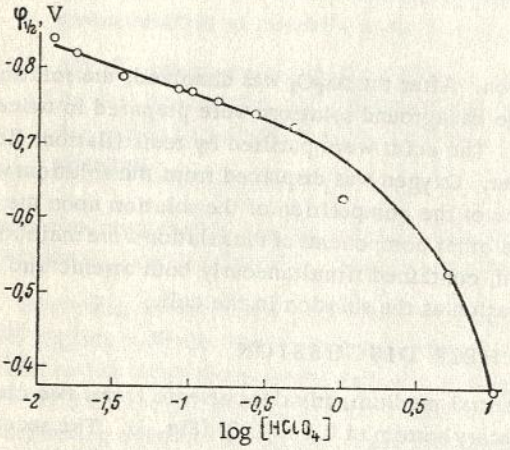


Fig. 5. Dependence of $\varphi_{1/2}$ of the first wave of As (3+) on the logarithm of the perfluoric acid concentration. As (3+) concentration $1 \cdot 10^{-3}$ M.

2. Alkaline Solutions. In alkaline solutions with alkali concentration above 0.2 M, there are no reduction waves of As (3+). In the case of gradual alkalinization of a neutral unbuffered solution of As (3+), the following is observed (Fig. 2): the first weakly pronounced wave disappears even in the presence of slight alkalinization. The single wave remaining is shifted in the cathodic direction all the way up to complete fusion with the reduction wave of the background. A graph of the dependence of $\varphi_{1/2}$ upon log [LiOH] within the range of LiOH concentrations from 10^{-2} to 0.3 M is linear; moreover, $\partial \varphi_{1/2} / \partial \ln [LiOH] \approx 100$ mV.

If we assume that a singly charged anion AsO_2^- is reduced in neutral medium:

$$AsO_2^- + 6e + 5H_2O \rightarrow AsH_3 + 7OH^-, \qquad (5)$$

then this process is evidently entirely irreversible, and the half-wave potential should not depend upon the pH, since water molecules and hydroxyl ions participate only in the subsequent conversions of the product of decelerated discharging of the AsO_2^- ion. The experimentally established dependence of $\varphi_{1/2}$ upon the alkali concentration therefore indicates that AsO_2^- ions arise as a result of a preceding chemical reaction with the participation of hydroxyl ions. It is natural to assume that the AsO_2^- ions exist in equilibrium with ions of orthoarsenous acid, for example:

$$AsO_2^- + 2OH^- = AsO_3^{3-} + H_2O \qquad (6)$$

or

$$AsO_2^- + OH^- = HAsO_3^{2-}, \qquad (7)$$

which is shifted to the right with increasing alkali concentration. Highly charged anions evidently are incapable of reduction within the range of potentials accessible to measurement.

The value of $\partial\varphi_{1/2}/\partial \log [LiOH]$, according to this scheme, should be equal to the slope of the straight line in a plot of $\log [i/(i_d - i)]$ versus φ, i.e., the coefficient b [29]. The slope of the wave of As (3+) in unbuffered solutions cannot be compared with the value of $\partial\varphi_{1/2}/\partial \log [LiOH]$, since at the potentials of various portions of the wave, the pH of the layer near the electrode is changed as a result of reaction (5). Trivalent arsenic exists in aqueous solutions primarily in the form of metaarsenous acid and its salts. However, orthoarsenous acid arises in alkaline media. Thus, at a OH^- ion concentration of 0.2 M, 40% of the total concentration of As (3+) is comprised of $HAsO_3^{2-}$ ions [30].

3. Acid Solutions. The polarogram of a neutral solution of As (3+) undergoes interesting changes when the solution is gradually acidified; moreover, a qualitatively identical picture is observed when hydrochloric, perchloric, sulfuric, or phosphoric acid is introduced. When a neutral solution is acidified (curve 3 in Fig. 3), a new wave arises on the polarogram, situated approximately 0.9 V more positive than the basic wave of As (3+) in neutral medium (curve 3). With increasing acid concentration, this wave increases; the second decreases, but the sum of their heights remains unchanged. When the acid concentration is further increased, the current continues to increase not only at potentials at which the wave of discharging of the excess hydrogen ion appears, but also at less negative potentials (see curve 8 in Fig. 3). Under these conditions, a doubling of the wave of As (3+) is noted. In more concentrated acid solutions, the doubling of the wave in the region of potentials -0.8 to -0.9 V becomes more distinct (Fig. 4), since with increasing acid concentration, the two waves are shifted into the region of less negative potentials, but the first wave becomes more rapid. In 5 M hydrochloric acid, the difference of the half-wave potentials of the waves of As (3+) reaches 0.5 V; the first wave acquires a shape convenient for analytical use; moreover, on it, in contrast to the second wave, there are no catalytic maxima. The limitation of the increase in the wave of As (3+) with the concentration, described by Meites [11], which he ascribed to adsorption of elementary arsenic, was not observed in our experiments, although we used solutions whose As (3+) concentrations were several times as high as those used by Meites.

As a result of the presence of two maxima, the second wave of As (3+) is poorly expressed. With increasing acid concentration, chiefly the second maximum is developed (Fig. 4). In the intermediate interval of acid concentrations (0.01-0.02 M), polarograms of As (3+) with three maxima of arsenic are obtained (curves 3 and 4 in Fig. 4). In the case of a higher acid concentration, the third maximum, preceding the wave of discharging of H^+ ions, becomes so large that it is no longer recorded. In a consideration of the experimental data presented, three questions must be considered, namely: the easier reduction of As (3+) in acid medium, doubling of the wave of As (3+) in acid medium, and the maxima on the second wave of As (3+).

1. The abrupt facilitation of the reduction of As (3+) in the case of acidification of the solution is undoubtedly associated with a change in the mechanism of the electrode process: the reduction of the AsO_2^- anion at first is replaced by a reduction of the nondissociated metaarsenous acid. The removal of the negative charge from the discharging particle, according to the general rule, substantially facilitates the course of the reduction process.

The half-wave potential of the first wave of As (3+) in acid medium, as has already been noted, depends upon the acid concentration. The value of $\partial\varphi_{1/2}/\partial \log [H^+]$ is 67 mV within the range of $[H^+]$ from 0.01 to 0.5 M (Fig. 5). This value is typical of most irreversible electrode reactions of reduction with preceding single protonation. If the acid being reduced is sufficiently strong, then the limiting current of the wave, arising in weakly acid medium, is determined by the diffusion of hydrogen ions. In the reduction of weak acid, the limiting current is below this value, as a result of an at least partial replacement of the diffusion of free hydrogen ions by the slower diffusion of oxygen molecules. In Fig. 3 the level of the limiting current of hydrogen ions in the absence of As (3+) is shown by the dashed lines 3'-8'; the H^+ ion concentration was the same as in the case of curves 3-8. It is evident that the reduction of As (3+) in acid medium corresponds to the reduction of a weak acid. It may be that part of this effect is also due to the consumption of hydrogen ions for shifting of equilibria of the type of 6 and 7 as well.

In strongly acid solutions, trivalent arsenic is partially converted to the state of a simple triply charged cation [30]. This explains the increase in the solubility of As_2O_3 in strongly acid solutions, beginning with 3-5 M. In one of the early studies [4], it was hypothesized that in strongly acid solutions the first wave corresponds to the reduction of As^{3+} cations. Such a substantial increase in the number of positive charges on the particle being reduced (in comparison with the $HAsO_2$ molecule) should lead to a substantial facilitation of the process. Figure 5 shows that precisely in the region of high acid concentrations, when we might assume the formation of As^{3+} cations, there is a strong shift of $\varphi_{1/2}$ in the direction of positive values. In 10 N perchloric acid, it becomes equal to -0.37 V against Hg in 0.1 M LiCl. This result shows that in strongly acid solutions, actually, discharging of As^{3+} cations takes on great importance.

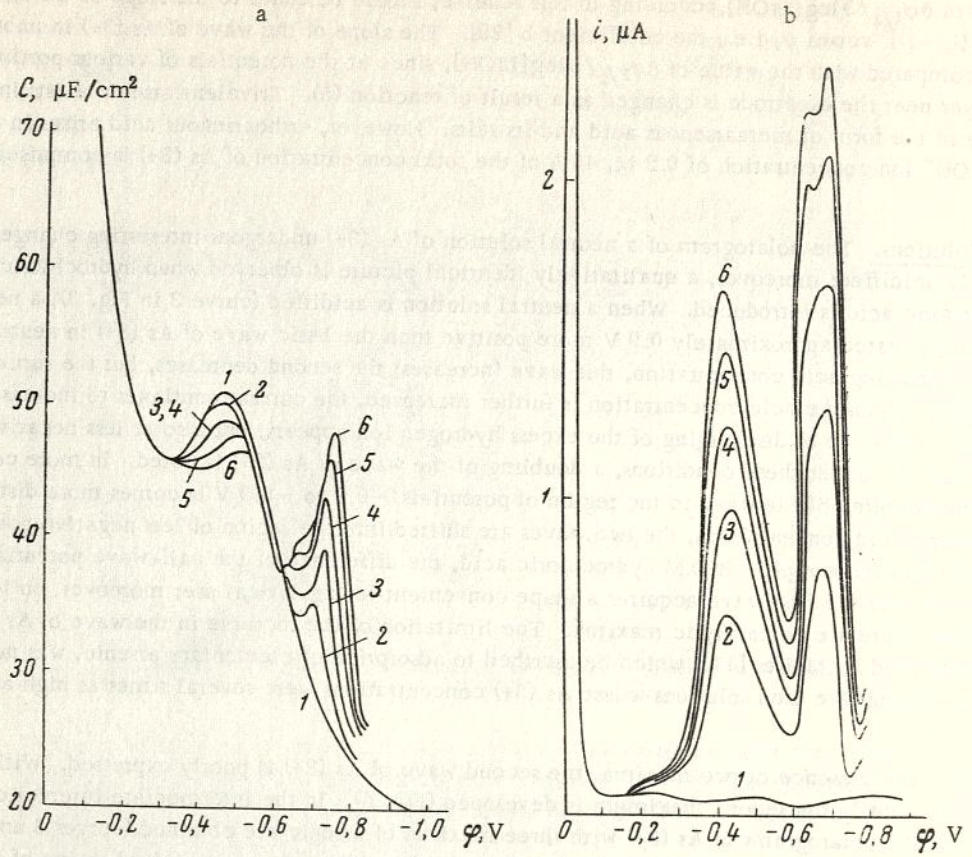


Fig. 6. Vector polarograms of solutions of As (3+) in 1N HCl. As (3+) concentration: 1) 0; 2) $3 \cdot 10^{-4}$; 3) $5 \cdot 10^{-4}$; 4) $7 \cdot 10^{-4}$; 5) $9 \cdot 10^{-4}$; 6) $1.1 \cdot 10^{-3}$ M. Amplitude of the variable voltage 8 mV. Lag 1.6 sec. a) Reactive component, calibrated in units of capacitance per cm^2; b) active component.

2. We assume that the doubling of the wave of As (3+) in acid medium is associated not with stepwise reduction of As (3+) first to metallic As and then to AsH_3, but with the occurence of a reaction of ionization of mercury, forming mercury arsenide (reaction 3).

In order for this reaction to be accomplished at the potentials of the first wave of As (3+) in acid medium, mercury arsenide must be a difficultly soluble compound. Then its appearance would lead to a sharp decrease in the mercury ion concentration. There are no data on the solubility of mercury arsenide in the literature. However, there is information indicating that gaseous AsH_3 reacts rapidly with a saturated solution of $HgCl_2$ (and with other mercury salts as well), forming various products, including Hg_3As_2 [30]. It should be kept in mind that under the conditions of the appearance of the first wave of As (3+), mercury arsenide arises (if it actually does arise) according to a reaction of mercury ions not with AsH_3, but evidently with As (3−) even before the formation of AsH_3 molecules, which may substantially accelerate this reaction.

In [30] it was noted that the polarographic data contradict the data on the reduction of arsenous acid on other metals. According to the polarographic data, in the reduction of arsenous acid, it might seem, metallic mercury should be readily obtained. Actually, it is obtained only under very specific conditions (low current density and prolonged slow electrolysis). In the case of intensive electrolysis, practically always only AsH_3 is obtained [30].

The indicated discrepancy is eliminated if we assume that actually metallic mercury is not an intermediate product of the stepwise reduction of arsenous acid, but arises as a result of a secondary reaction of AsH_3 with arsenous acid. Since this reaction proceeds slowly [30], the production of As should be promoted precisely by prolonged electrolysis with low current densities.

Figure 6 shows the vector polarograms of As (3+) against a background of 1N hydrochloric acid. On the curves of the dependence of the active component of the alternating current upon the potential (Fig. 6b) there are two peaks, corresponding to the two waves of As (3+) on the usual polarogram. The first peak is lower and broader than the sec-

ond. The width of the half-peak (σ) is about 150 mV, which far exceeds the value characteristic of the reversible process (i.e., $\sigma = 88/n$ mV [31]). On the curves of the dependence of the reactive component of the alternating current upon the potential (Fig. 6a), only a small decrease in the background curve, due most likely to weakly pronounced adsorption, is observed in the region of the potentials of this peak. There is no peak of the pseudocapacitance of the reaction on these curves. Consequently, the electrode process on the first wave of As (3+) in acid medium is entirely irreversible. The second peak in Fig. 6b is higher and narrower than the first. To it corresponds a pronounced peak in Fig. 6a. Consequently, the process corresponding to the second wave proceeds so rapidly that it is detected on the vector polarogram by the presence not only of the polarization resistance, but also of a pseudocapacitance of the reaction. It is rather improbable that the process of six-electron reduction, which is postulated for the second As (3+) in acid medium, would proceed rapidly. On the contrary, it is more probable that these data correspond to the mechanism with anodic dissolution of mercury and the formation of mercury arsenide. For the discharging-ionization of mercury, high rates of the process are practically always observed.

The second peak in Fig. 6 is nonsymmetrical. It is steeper on the cathodic side. The upper part of the peak is distorted in the presence of an increased arsenic content. This phenomenon, like the decrease in the background curve in Fig. 6a, at potentials of the first peak, is evidently due to the adsorption of mercury arsenide. Information on the reversibility of the process can be obtained by analyzing the cathodic branch of the peak, since it is less distorted by the adsorption of mercury arsenide. For this purpose it is necessary to construct a vertical line up to intersection with the cathodic branch of the peak, to measure the width of the narrow peak thus obtained at half its height, and to double. For curve 6 we found a value $\sigma = 35$ mV, which is far closer to $88/n$ mV than in the case of the first peak. Thus, the proposed mechanism of the production of As (3+) in acid medium finds some experimental confirmation.

3. The maxima on the second wave of As (3+) in acid medium are catalytic. These maxima cannot be attributed to discharging of polarographic waves, associated with the tangential motions of the surface of the mercury drop, since they were also observed in the absence of such motions [7-10]. It may be assumed that at least one of the three catalytic maxima that As (3+) gives in acid medium is due to the catalytic reduction of perchloric acid by arsenic to a lower valence state. However, this hypothesis must be discarded as not corresponding to the experimental data, since qualitatively analogous phenomena are also observed in other mineral acids.

It remains to be assumed that these maxima are due to the catalytic evolution of hydrogen. Precisely three types of particles may be catalytically active: arsenous acid, arsine, and elementary arsenic, which arises in greater or lesser amounts (depending upon the acidity of the solution) according to the reaction of As (3+) with AsH_3 [30]. The overvoltage in the liberation of hydrogen on arsenic is far lower than on mercury [34]. To what degree this hypothesis corresponds to the facts and what concrete processes are associated with one maximum or another will be the subject of our further investigations.

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