POLAROGRAPHY OF ARSENIC

IV. THE ANODIC WAVE FOR TRIVALENT ARSENIC IN BASIC SOLUTIONS

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In basic solutions, trivalent arsenic is not reduced on a mercury capillary electrode [1], but yields an anodic wave with a half-wave potential of −0.25 V vs. the S.C.E. [2]. This wave has been the subject of study several times [3-7] and has been used in analytic determinations. It is considered that it corresponds to the oxidation of arsenite to arsenate. Direct proof of this assumption, however, is missing. This is important, for the possibility has not been excluded that the anodic wave corresponds to the oxidation of mercury with the formation of difficultly soluble mercury arsenite, rather than to the oxidation of arsenite ions.

Experiment shows that trivalent arsenic does not give anodic waves in neutral solutions (Fig. 1, curve 1). As the solution is alkalized, the cathodic wave disappears [1], and then an anodic wave appears and develops (curves 3-9). The shape of the anodic wave for various arsenic concentrations in 0.6 N LiOH is shown in Fig. 2. It is seen that at low arsenic concentrations the wave has the normal shape (curves 2-7), but with an increase in the concentration, a maximum (curves 8-12) develops at the limiting current plateau. A study of the dependence of the anodic wave currents on the height of the mercury column showed that the currents were diffusive.

The height of the anodic wave is about half that of the cathodic wave for As (3+) in a neutral solution. It thus corresponds to a transfer of three electrons per arsenite ion.

An experiment with a Kalousek switch is of decisive importance for determining the nature of the processes which correspond to the anodic wave. The fundamental idea behind this experiment is as follows. If trivalent arsenic is oxidized to pentavalent at the anodic wave potentials, the product should not yield a cathodic wave, since pentavalent arsenic is not reduced in basic media [8]. If, on the other hand, mercury is oxidized in the anodic wave, forming insoluble mercury arsenite, then a current for reduction of this compound should appear during cathodic polarization. This current would be similar to that for reduction of calomel and other difficultly soluble mercury salts.

The ordinary polarogram for trivalent arsenic in a basic electrolyte of 0.5 M LiOH (curve 1) and two polarograms with the Kalousek switch—by method III [9] (curve 2) and method IV (curve 3)—are shown in Fig. 3. During measurement by method III, the auxiliary potential corresponded to the maximum on the anodic wave, and the current was recorded at the switch to the fundamental potential. It is seen that a single anodic-cathodic wave is obtained in this case. During measurement by method IV, the auxiliary potential was equal to −0.4 V, and the current was recorded at the switch to the auxiliary potential. In this case a product reduction current appears on the curve with the switch in the range of potentials of the anodic wave (on the ordinary polarogram). The anodic wave thus corresponds to oxidation of mercury with the formation of difficultly soluble mercury arsenite.

In strongly basic media this process, the fastest of all, can be expressed by the equation

$$3Hg + 2AsO_3^{3-} = Hg_3(AsO_2)_2 + 6e$$

or

$$6Hg + 2AsO_3^{3-} = (Hg_2)_3(AsO_2)_2 + 6e,$$

according to which three electrons are required for each arsenite ion. If trivalent arsenic was present in basic solutions in the form of AsO_2 ions, anodic dissolution of mercury would be given by the equation

$$Hg + 2AsO_2^- = Hg(AsO_2)_2 + 2e$$

or

$$2Hg + 2AsO_2^- = Hg_2(AsO_2)_2 + 2e$$

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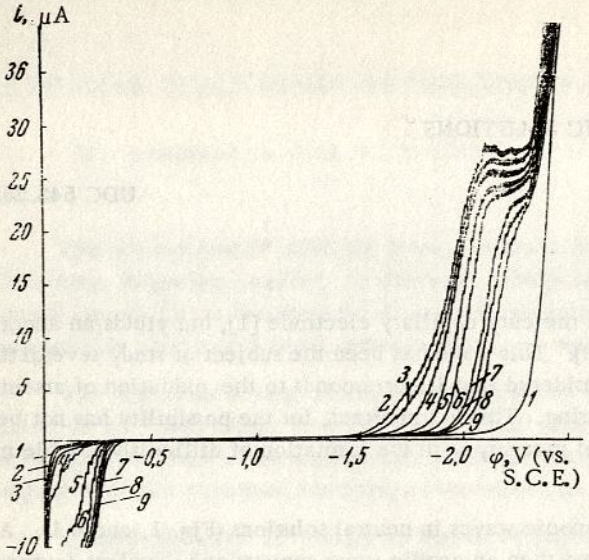


Fig. 1. Influence of alkalization on the polarogram of 10^{-3} M As (3+) in a basic electrolyte of 0.1 M LiCl. LiOH concentration: 1 and 2) 0; 3) $5.1 \cdot 10^{-4}$; 4) $1.5 \cdot 10^{-3}$; 5) $4.4 \cdot 10^{-3}$; 6) 0.014; 7) 0.055; 8) 0.11; 9) 0.22 mole/liter.

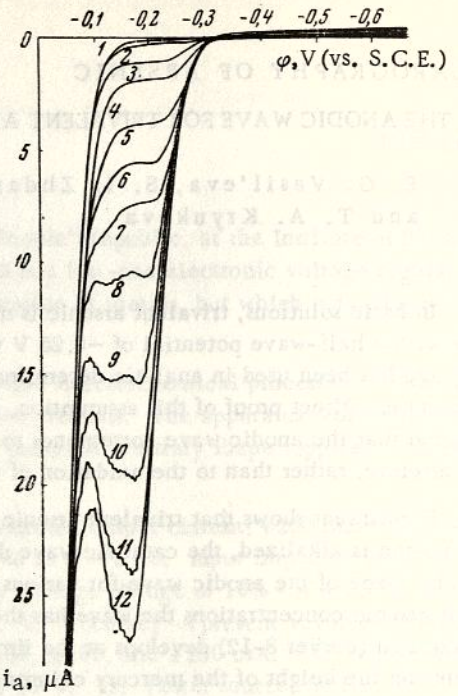


Fig. 2. Anodic wave of As (3+) in a basic electrolyte of 0.6 N LiOH As (3+) concentration: 1) 0; 2) $2 \cdot 10^{-5}$; 3) $1.2 \cdot 10^{-4}$; 4) $2 \cdot 10^{-4}$; 5) $3.9 \cdot 10^{-4}$; 6) $5.7 \cdot 10^{-4}$; 7) $7.4 \cdot 10^{-4}$; 8) $9.1 \cdot 10^{-4}$; 9) $1.26 \cdot 10^{-3}$; 10) $1.53 \cdot 10^{-3}$; 11) $1.80 \cdot 10^{-3}$; 12) $2.06 \cdot 10^{-3}$ M.

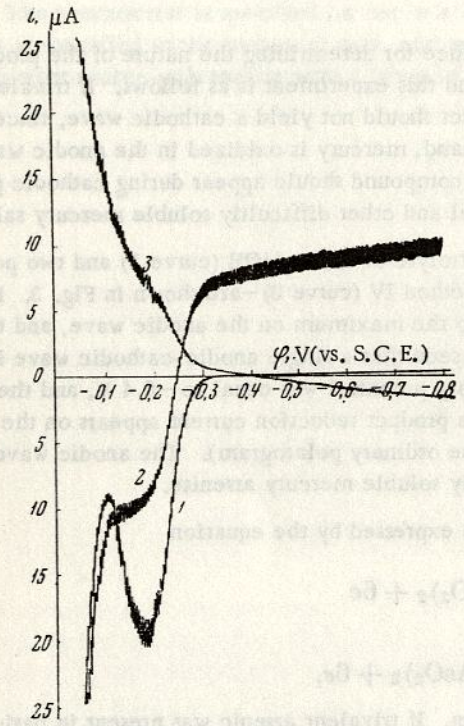


Fig. 3. Experiment with a Kalousek switch. Solution composition: 0.5 N LiOH + 10^{-3} M As (3+). 1) Ordinary polarogram; 2) polarogram with Kalousek switch, method III; 3) the same, but with method IV (see text).

and the anodic wave would be lower. This result confirms the assumption of the transition of AsO_2^- to AsO_3^{3-} during the alkalization of the solution as a reason for the disappearance of the cathodic wave [1].

By comparing the half-wave potentials of the series of anions which form difficultly soluble salts with mercury (Cl^-, Br^-, I^-, S^{2-}) with the solubility products of these salts and inserting in this series the value for the anodic wave of arsenite, one can estimate the solubility product for mercury arsenite. It turns out to be on the order of 10^{-35}: i.e., significantly lower than the solubility product for mercury iodide ($3.7 \cdot 10^{-29}$), but larger than that for HgS ($4 \cdot 10^{-53}$).

The nature of the maximum on the anodic wave for As (3+) has not been examined in this paper. Its appearance may be connected with the appearance of a layer of mercury arsenite on the electrode surface.

LITERATURE CITED

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