THE REDUCING PROPERTIES OF MERCURY

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During studies of electrochemical processes which occur on mercury or amalgam electrodes, due attention is not usually given to the side reactions which accompany the main electrode process. In particular, little attention is given to the direct interaction of mercury with materials reduced on the cathode, and to its anodic oxidation together with the other metals present in the amalgam. Underestimation of side reactions may sometimes lead to a one-sided interpretation of the mechanism of the electrode processes. This interpretation has, in our opinion, been made in attempts to explain the steplike waves in works published on polarography by Shvaer and Sukhi on reduction of selenite and tellurite [1], by Issa on reduction of permanganate [2], and by others on reduction of multivalent ions [3, 4]. Formation of steplike waves is also observed during the reduction of ions having only one degree of oxidation. Their appearance in this case is explained by reduction [5, 6] of complexes with different instability complexes. However, the possibility is not excluded that formation of a complex wave is determined by the superposition of the anodic process of the oxidation of mercury on the cathodic process of the reduction of the ions. The appearance of sparingly soluble materials as the result of side reactions may complicate the polarograms even more [7].

During reduction of metals by amalgams, participation of mercury in the reduction reaction is usually not taken into account either.

The reducing property of mercury is determined by the chemical nature of the anions present in solution and adsorbed on its surface. This was pointed out as long ago as 60 years by Paschen [8].

The effect of anions on the potential of mercury can be seen from Table 1.

A comparison of these results with the values of the solubility products of the corresponding mercury salts, and also with the instability constants of the mercury complexes, graphically shows the connection between the depolarization potential of mercury by one ion or another and the solubility (or stability) of the compounds formed between mercury and the corresponding ion. The lower the solubility the greater the negative potential. The existence of such a relationship permits one to carry out quantitative polarographic determination of certain anions [9, 10].

The kinetics and the mechanism of the anodic oxidation of mercury has been studied to a comparatively small extent. Wakkad [11] has given an equation which expresses the relation between the rate at which mercury dissolves and the extent to which the electrode is polarized. All other values being constant, the equation given by Wakkad takes the form

$$V = \text{const} + \frac{RT}{\alpha ZF} \ln I,$$

where V is the difference between the electrode potential and the equilibrium potential; I is the current density; Z is the number of electrons; and F is the Faraday number.

TABLE 1

Normal Oxidation Potentials of Mercury (Normal Hydrogen Electrode) in Various Media

Electrode reaction	E_0, volt	Electrode reaction	E_0, volt
$Hg + H_2O - 2e \rightarrow HgO + 2H^+$	+0,926	$2Hg + 2CNS^- - 2e \rightarrow Hg_2(SCN)_2$	+0,22
$2Hg + SO_4^{2-} - 2e \rightarrow Hg_2SO_4$	+0,615	$2Hg + 2Br^- - 2e \rightarrow Hg_2Br_2$	+0,139
$2Hg + CrO_4^{2-} - 2e \rightarrow Hg_2CrO_4$	+0,41	$2Hg + H_2O - 2e \rightarrow Hg_2O + 2H^+$	+0,123
$Hg + 2IO_3^- - 2e \rightarrow Hg + (IO_3)_2$	+0,40	$2Hg + 2I^- - 2e \rightarrow Hg_2I_2$	−0,041
$2Hg + CO_3^{2-} - 2e \rightarrow Hg_2CO_3$	+0,32	$Hg + 4CN^- - 2e \rightarrow Hg(CN)_4^{2-}$	−0,37
$2Hg + 2Cl^- - 2e \rightarrow Hg_2Cl_2$	+0,268	$Hg + S^{2-} - 2e \rightarrow HgS$	−0,70

Thus, the relationship between the logarithm of the current strength and the potential, during anodic dissolution of mercury, is expressed by a straight line. However, according to this author, this relation is only preserved at very low current densities.

Cousens, Ives, and Pittman [12-14] have studied the mechanism of the anodic oxidation of mercury. They subjected a mercury electrode to polarization by an interrupted direct current of low value. In the breaks between the individual current impulses, micropolarization tests were carried out (forward and reverse) in order to determine the extent of the reversibility of the electrode. They found that a mercury electrode in a hydrochloric acid solution behaves itself irreversibly, even after passing a fairly large amount of electricity through it, when a precipitate of Hg_2Cl_2 is formed. The irreversibility was confirmed by the existence of a hysteresis loop between the ascending and descending branches of the polarization curve. But, after a long interval between such impulses, the electrode became reversible again. It was established that the changes which occur in the potential of the mercury electrode with changes in the amount of electricity passed through the solution are not linear; this follows from the fact that the curve passes through a maximum. The potential of the maximum is several millivolts more positive than the potential of the reversible calomel electrode. It was also found that in order to reach the potential of the calomel electrode, it is necessary to expend a considerably greater amount of electricity than the theoretical amount. Their research led the authors to the conclusion that the primary electrode reaction during anodic polarization of mercury in hydrochloric acid solutions (current density 0.25 $\mu a/cm^2$) is the formation of mercuric ions. Calomel is then formed as the result of a secondary reaction: $Hg^{2+} + Hg^0 \rightarrow Hg_2^{2+}$. At very low current densities generation of Hg_2^{2+} and Hg^{2+} in equilibrium concentration should also occur, since the electrode in this case deviates only insignificantly from the equilibrium state. Application of higher current densities does not alter the mechanism of the process. However, the rapid covering of the mercury surface by Hg_2Cl_2 leads to passivation of the electrode and to a discharge of chlorine ions. Subsequently, the liberated chlorine oxidizes the Hg_2Cl_2 and depassivizes the electrode.

The presence in solution of ions or molecules which are capable of being reduced on the dropping-mercury electrode may complicate or modify the over-all electrode process. It is known that the reduction potentials of many anions on the dropping-mercury electrode are shifted towards more negative values as compared with their potentials on solid electrodes, particularly platinum ones. This may be explained on the grounds that at those potentials at which anions are reduced on a platinum electrode, anodic oxidation of mercury occurs at the same time on a mercury electrode. As a result of the superposition of the latter process on the reduction of the anions, the cathodic wave may disappear completely, when the oxidation current of mercury exceeds the cathodic current for the reduction of the anions. In actual fact, in this case direct interaction of mercury with the reduced anions will occur. In all cases when the rate at which mercury is oxidized anodically is higher than the rate at which the anions are reduced, the cathodic wave for the reduction of the anions will be absent, and will only appear at those potentials at which the anodic oxidation of mercury ceases. The wave obtained at these potentials will correspond either to the direct reduction of the given ion, or the reduction of mercury ions formed as a result of the interaction of metallic mercury with reducing ions. Opinion on this point differs. Thus, Simpson and Evans [15] assume that in the anodic region metallic mercury in reducing ions of the noble metals gives an equivalent amount of mercury ions, e.g.:

$$2Au^{3+} + 6Hg \longrightarrow 2Au^0 + 3Hg_2^{2+}$$

TABLE 2

Interaction of Mercury with Ions in Neutral and Alkaline Solutions*

Composition of the supporting electrolyte	MnO_4^-		CrO_4^{2-}		$S_2O_8^{2-}$		MoO_4^{2-}		Fe^{3+}		Cu^{2+}	
	reaction product	potential, volt	reaction product	potential, volt	reaction product	potential, volt	reaction product	potential volt	reaction product	potential, volt	reaction product	potential, volt
NH_4Cl	MnO_2 Hg_2Cl_2	+0,64	The mercury forms a sludge	+0,33	SO_4^{2-} Hg_2Cl_2	+0,65	0	+0,34	Fe^{2+} Hg_2Cl_2	+0,35	0	+0,37
NH_4Cl NH_4OH	O	+0,41	The mercury forms a sludge	+0,30	SO_4^{2-} Hg_2O	+0,31	0	+0,35	—	—	0	+0,33
$(NH_4)_2SO_4$	MnO_2 Hg_2SO_4	+0,66	The mercury forms a sludge	+0,51	Hg_2SO_4	+0,68	0	+0,40	0	+0,40	0	+0,51
KSCN	—	—	0	+0,21	—	—	The solution becomes blue-green	+0,13	$Hg(SCN)_2$ Decolorized no precipitate	+0,30	—	—
KI	—	—	0	—0,06	—	—	The solution becomes blue	—0,09	$Hg(I)_4^{2-}$ No precipitate	—0,03	—	—
NaOH	MnO_4^{2-} Hg_2O	+0,45	0	+0,15	SO_4^{2-} Hg_2O	+0,33	—	+0,12	—	—	—	—

* Supporting electrolyte concentration 0.5 M, concentration of the various ions 0.05 M. (1) signifies that the reaction was not studied because of the interaction of the ions with the supporting electrolyte; (0) signifies absence of interaction between the ions and mercury.

TABLE 3

Interaction of Mercury with Certain Ions in Acid Solution

Ion	HCl 1–6N		H_2SO_4 1–6 N	
	reaction products	reduction potential, volt	reaction products	reduction potential, volt
MnO_4^-	Mn^{2+}, Hg_2Cl_2 MnO_2	+0,22	Mn^{2+} Hg_2SO_4, MnO_2	+0,70
CrO_4^{2-}	Cr^{3+}, Hg_2Cl_2	+0,20	Cr^{3+}, Hg_2SO_4	+0,57
MoO_4^{2-}	Mo^{V}, Mo^{III}, Hg_2Cl_2	+0,16	Does not react	+0,37
VO_3^-	V^{4+}, Hg_2Cl_2	+0,30	» »	+0,42
SeO_3^{2-}	HgSe, sludge	+0,11	» »	+0,19
TeO_3^{2-}	HgTe*	+0,17	» »	+0,18
Fe^{3+}	Fe^{2+}, Hg_2Cl_2,sludge	+0,19	» »	+0,68
Cu^{2+}	Cu_2Cl_2, Hg_2Cl_2,sludge	+0,19	» »	+0,36
IO_3^-	Hg_2Cl_2, ClI	+0,21	» »	+0,31
$S_2O_8^{2-}$	Hg_2Cl_2, SO_4^{2-}	+0,27	Hg_2SO_4	+0,70

*The reduction proceeds in concentrated hydrochloric acid solutions (> 4N).

while the cathodic wave corresponds to the reduction of mercury ions:

$$Hg_2^{2+} + 2e \longrightarrow 2Hg$$

Kivalo, Laitinen [16] and other authors [17] are of the same opinion. But in a number of cases [2-4, 18, 19] the cathodic waves are explained by the direct reduction of ions ($S_2O_8^{2-}$, MoO_4^{2-}, MnO_4^-, etc.) on the dropping-mercury electrode. A correct interpretation of the mechanism of electrode processes requires that the whole complex of reactions accompanying polarography should be taken into account. In a particular case, e.g., reduction of tellurium, it is necessary to take into account the depolarization of mercury by tellurite and telluride ions and the formation of precipitates between mercury and these ions.

Thus, a study of the interaction of mercury with a number of ions in the presence of various depolarizers is of undoubted interest. A solution of this question would enable one to give a more correct interpretation of the nature of the polarographic waves and to evaluate the extent to which mercury participates in the reduction of metal ions.

In the work described here, we studied the reduction of copper (II), iron (III), selenite, tellurite, permanganate, dichromate, molybdate, iodate, vanadate, persulfate, and arsenate ions by metallic mercury in various media.

Indications are given in the literature [20-25] on the interaction of mercury with a number of ions. Some of these reactions have been used during the titrimetric determination of oxygen-containing anions for their reduction. However, the reactions indicated have for the most part been carried out in hydrochloric acid solutions. In addition, reduction was effected without any measurements of the potential of mercury. Measurement of this potential during the reduction process is very important, since it permits one to explain the change in the reducing properties of mercury with changes in the experimental conditions.

The supporting electrolytes which we used were neutral, alkaline, and acid materials which shift the oxidation potential of mercury; they included: sulfuric and hydrochloric acids, the ammonium salts of these acids, an ammonia–ammonium chloride mixture, potassium thiocyanate, potassium iodide, and sodium hydroxide.

The reactions were studied by shaking a solution containing the test ions and the appropriate supporting electrolyte with mercury. Shaking was carried out either in a separating funnel or in a special 50 ml vessel

TABLE 4

Cementation of Tellurium by a Cadmium Amalgam

HCl concentration M	Cd isolated in the solution, g	Te found in the precipitate, g	Yield of Te with respect to Cd, %
1	0,3850	0,3366	144,7
2	0,3853	0,3312	142,3
3	0,3805	0,3312	144,7
4	0,3870	0,3360	144,7
5	0,3800	0,3368	142,3

Note: Amount of tellurium taken for cementation 0.3310 g; amount of cadmium taken for cementation 0.410 g.

provided with a mechanical stirrer and an attachment for measuring the potential of the mercury. After a 15-20 min shaking the mercury was removed from the solution, any precipitates which might have been formed being filtered off, and the precipitate and solution analyzed separately for their content of reaction products. The precipitates were also analyzed spectrographically. The experimental results are given in Tables 2 and 3.

As is evident from the results given in Table 2, in nonacidified solutions mercury can reduce permanganate, persulfate, and iron(III) ions, and, apparently, molybdate,* while reduction of iron ions only occurs in the presence of strong depolarizers (halide and thiocyanate ions). Iodide ions, as is known, are themselves capable of reducing iron, elemental iodine being formed. On shaking a mixture of iodide and iron (III) solutions with mercury, the iodine is decolorized and reduction of iron proceeds to completion.

In contrast to other ions, permanganate ions are reduced by mercury even in strongly alkaline solutions. Ions such as selenite, tellurite, vanadate, iodate, copper (II), and arsenate do not interaction with mercury in any of the solutions indicated in Table 2. The behavior of mercury in each concrete case is in good agreement with the values of its potentials.

In acid solutions (Table 3) a number of additional ions are included in the reduction reaction: selenite, tellurite, chromate, iodate, vanadate, copper (II).

It should be noted that selenite, tellurite, vanadate, iodate, iron (III), copper (II) ions are only reduced in hydrochloric acid solutions, they are not reduced in sulfuric acid solutions. Here, presumably, the difference in the depolarizing effect of chloride and sulfate ions becomes apparent. Arsenate ions do not interact with mercury even in acid solutions.

The list of ions capable of being reduced by mercury, obviously, is not limited to the ions listed here. But even the small amount of experimental evidence given in Tables 1 and 2 is sufficient to indicate clearly the reactivity of mercury with respect to a whole series of ions. These results enable one to affirm that during polarography of the ions which we have studied, there will occur interaction between them and mercury with formation (in most cases) of sparingly soluble compounds. This interaction should lead to a drop in, and frequently even to complete disappearance of, the diffusion current of the materials being reduced. The true value of the reduction current is only attained at potentials at which oxidation of mercury ceases. In this connection, during the polarographic process one might expect the appearance of step-shaped waves even in the absence of a stepwise reduction of the materials being polarographed.

As an example of the participation of mercury in the reduction of metal ions by the amalgams of more-negative metals one can induce the reduction of copper by cadmium and amalgam.

In a previous study of this process, we established that copper is reduced by a cadmium amalgam (0.5% Cd) at a definite, almost constant, potential (−0.4 volt) to the metal. After a certain time interval there is observed a potential jump to positive values. After the potential jump the reduction process continues, but in this case univalent copper and not copper metal is formed. It might be assumed that in the reduction of copper to the univalent state only cadmium participates. But the results of experiments on the reduction of copper by mercury (Table 3) showed that mercury is capable, at a given potential value, of reducing copper in hydrochloric acid solutions. Analysis of the solution and precipitate formed during the cementation of copper by the amalgam, showed that mercury and cadmium at a given positive potential can simultaneously participate in the reduction of copper.

* On shaking a molybdate solution in a supporting electrolyte of KSCN and KI with mercury, the color of the solution changes to blue-green and blue, respectively. When no mercury is present this is not observed. We did not establish the extent of the reduction.

Simultaneous participation of mercury in the reduction reaction was also observed during the cementation of tellurium (IV) by a cadmium amalgam in hydrochloric acid solutions (Table 4). The yield of tellurium with respect to cadmium exceeded 100% as a result of its reduction not only by cadmium, but also by mercury. Under these conditions mercury reduced tellurium (IV) at negative potentials (−0.13 volt) (normal hydrogen electrode). As soon as all the cadmium had been removed from the amalgam, there was observed a steplike change in the potential of the amalgam to more positive values, but reduction of tellurium by mercury did not cease even at this positive potential value.

SUMMARY

A study has been made of the reduction of a number of ions by metallic mercury in various solutions containing ions which can shift the potentials of the anodic oxidation of mercury.

It has been shown that permanganate and persulfate ions are reduced by mercury in neutral, alkaline, and acid solutions; iron (III) and molybdate in nonacidified and acid solution. Selenite, tellurite, vanadate, iodate, chromate, copper (II) are only reduced in acid solutions, a very strong effect on the reduction being displayed not only by the acidity of the solution, but also by the presence of other anions which shift the potential of the anodic oxidation of mercury.

The mercury potentials during the reductions have been measured. The value of the mercury potential depends on both the nature of the depolarizer and on the nature of the ion being reduced.

It has been shown that during the cementation of copper and tellurium by a cadmium amalgam, mercury participates simultaneously with the cadmium in the reduction reaction.

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