PECULIARITIES ON THE POSITIVE BRANCH OF NONEQUILIBRIUM ELECTROCAPILLARY CURVES FOR MERCURY IN THE PRESENCE OF HALIDE IONS

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It had been shown by Gouy that halide ions are specifically adsorbed at the mercury/aqueous solution interface, and will strongly depress surface tension on the positive branch of the electrocapillary curve (ECC) [1]. In all subsequent work as well, electrocapillary measurements were made in the absence of supporting electrolyte. Only in [2, 3], mercury drop times were obtained as a function of potential in solutions containing nitrates and acetates in addition to the halides. These functions are ECC with two maxima.

We have obtained ECC for mercury in 1 N Na_2SO_4 containing KI, KBr, and KCl over a potential range from −1.00 to +0.35 V (sce). We used the Gouy capillary electrometer and the method of measuring the drop time of mercury flowing from a capillary (the latter only in the case of KI).

The ECC which represent the drop time as function of potential in 1 N Na_2SO_4 solutions containing different KI concentrations are presented in Fig. 1, where for the purpose of comparison, the currents recorded in the same solutions and with the same capillary are also given as functions of potential. It follows from Fig. 1 that in the range of potentials where in harmony with the equations

$$2I^- + 2Hg \rightleftharpoons Hg_2I_2 + 2e^- \qquad (1)$$

or

$$4I^- + Hg \rightarrow HgI_4^{2-} + 2e^- \qquad (2)$$

the dissolution rate of mercury is insignificant, the drop time in the presence of I^- is substantially smaller than in pure sulfate solution, which is in harmony with literature data on the specific adsorption of I^- at mercury [4]. However, in the range of potentials corresponding to the limiting current of mercury dissolution, where the I^- concentration at the electrode surface goes toward zero, it is found that the difference in drop times between solutions which do and do not contain I^- is decreasing. Probably the electrolysis products formed according to Eqs. (1) and (2) are less surface active than I^-. The HgI_4^{2-} concentration in the presence of Hg_2I_2 precipitate can be estimated. At the half-wave potential, this is about 10^{-7} N with an initial I^- concentration in the solution of $1 \cdot 10^{-3}$ N, a solubility product of Hg_2I_2 of $4 \cdot 10^{-29}$ [5], an instability constant of the complex HgI_4^{2-} of $5 \cdot 10^{-31}$ [5], and a ratio $[Hg_2^{2+}]/[Hg^{2+}] = 100$ [6].

At relatively high KI concentrations (over $2.5 \cdot 10^{-4}$ N), an increase in the drop time and increased scatter of the values is observed in this potential range. Increased scatter can be attributed both to nonuniform polarization of the drop surface and to the formation of an Hg_2I_2 precipitate. Similar effects were observed in [2].

The results obtained with the Gouy capillary electrometer qualitatively agree with the results of the drop-time measurements. However, the peculiarities due to the presence of a reversible redox system, the instability of the processes occurring, and the formation of insoluble Hg_2I_2 have a stronger influence in this case. In working with the Gouy capillary electrometer we had to confine ourselves to a potential range from −1.00 to +0.25 V, since at more positive potentials the mercury meniscus loses its mobility owing to Hg_2I_2 formation. It can be attributed to slow diffusion in the capillary that deviations from the

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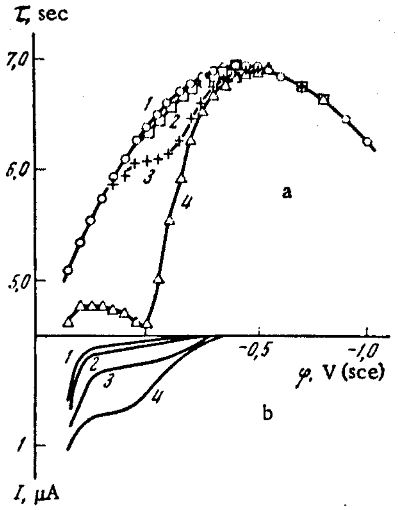

Fig. 1

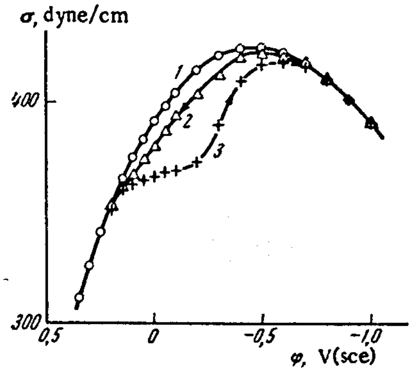

Fig. 2

Fig. 1. The drop time (a) and the current passing (b) as functions of potential: 1) N Na_2SO_4; 2) the same, + 2 · 10^{-5} N KI; 3) + 1 · 10^{-4} N KI; 4) + 2.5 · 10^{-4} N KI.

Fig. 2. Electrocapillary curves in the presence of iodides: 1) 1 N Na_2SO_4; 2) the same, + 5 · 10^{-4} N KI, recorded at an unrenewed mercury surface while changing the potential in the anodic direction; 3) + 5 · 10^{-4} N KI, recorded at an unrenewed mercury surface immediately after curve 2 while shifting the potential in the cathodic direction.

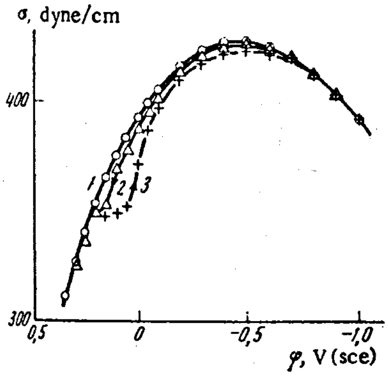

Fig. 3. Electrocapillary curves in the presence of bromide: 1) 1 N Na_2SO_4; 2, 3) the same, + 1 · 10^{-3} N KBr, and recorded under the regimes of curves 2 and 3 of Fig. 2, respectively.

customary shape of the ECC for KI are observed at higher KI concentrations with the Gouy capillary electrometer than in drop-time measurements.

The techniques were used for recording the ECC with the Gouy capillary electrometer. In the first case, the electrode surface was renewed prior to each reading, while the surface tension (σ) was determined 2 min after surface renewal. In the second case the meniscus surface in the capillary was renewed only at a potential of −1.00 V, two minutes later σ was measured, then the potential was shifted by 0.10 or 0.05 V steps up to the value +0.25 V, and back from +0.025 V to −1.00 V, and at each new potential value a reading was taken 2 min after its application.

In the potential range where anodic mercury dissolution in the presence of I^- can be neglected, the ECC recorded at renewed and unrenewed mercury surfaces (in the latter case, with the potential changing in the direction of positive values) practically coincide. In the potential range where the anodic process occurs at a noticeable rate, these curves diverge, and do so more strongly the higher the KI concentration in the bulk of the solution. The σ values obtained on the unrenewed surface when changing the potential in the cathodic direction are always lower than those obtained on the renewed surface (Fig. 2, curve 3). Moreover, at KI concentrations above 10^{-3} N one observes on the $\sigma - \varphi$ curve at the unrenewed surface a greater depth of the minimum occurring because of the reversibility of reaction (1). As the potential is shifted in the anodic direction, there is an increase in the amount of Hg_2I_2 with time. But when the potential is shifted in the cathodic direction (after attaining a value of +0.25 V), the I^- concentration at the electrode will increase because of reduction of the accumulated Hg_2I_2. As diffusion from the capillary is slow, the I^- concentration in the solution volume contained in it for some time will remain higher than in the rest of the solution. Thus the ECC appears as if it were shifted toward more negative potentials relative to that obtained at the renewed mercury surface and to that at the unrenewed surface when shifting the potential in the anodic direction.

Similar effects which, because of weaker specific adsorption and more positive potentials for mercury dissolution are correspondingly less clearly developed, are found in the presence of Br^- (Fig. 3) and Cl^-. The peculiar features of the ECC in the presence of halide ions can be analyzed using the concepts developed in [7-9].

Denoting the components of the redox system in such a way that $O \equiv Hg_2I_2$ ($Hg_2I_4^{2-}$) and $R \equiv I^- + Hg$, we shall apply Eq. 46a of [9] (cf. also the remark concerning [10]) to the present case as

$$\frac{\partial\sigma}{\partial(-\varphi)} = \alpha Q' + (1-\alpha)Q'', \tag{3}$$

where $\alpha = [O]/([O]+[R])$ is the mole fraction of the ox-component in the layer near the electrode (but not that in the adsorbed layer), Q' is the total charge density at constant chemical potential of the ox-component, and Q" is the total charge density at constant chemical potential of the red-component in the redox system. Equation (3) only applies qualitatively, since nonstationary processes occur in the system, and the condition $[O] + \gamma[R] = \text{const}$ (cf. [8, 9]) is not fulfilled because insoluble Hg_2I_2 is produced. From Eq. (2) it follows that

$$\frac{\partial\sigma}{\partial(-\varphi)} = \varepsilon + (1-\alpha)A_0 - \alpha A_R, \tag{4}$$

since Q' and Q" are connected with the free charge density ε of the electrode and with the surface excesses of the red- and ox-components A_R and A_0 via the relations $Q' = \varepsilon - A_R$ and $Q'' = \varepsilon + A_0$.

At the most positive potentials $\alpha = 1$, i.e., the concentration of R near the electrode and, thus, A_R as well are zero at the limiting current of the wave corresponding to mercury dissolution. Under these conditions the derivative $\partial\sigma/\partial(-\varphi) = \varepsilon > 0$, which signifies normal growth of σ with decreasing positive φ. This segment of the ECC often is poorly defined because of the unreliability of the σ values measured, for the reasons indicated above. As φ shifts in the negative direction, α decreases and strongly adsorbing iodide ion appears in the layer next to the electrode, whereupon A_R strongly increases. If, under these conditions, the term αA_R increases faster than the sum $\varepsilon + (1-\alpha)A_0$ (which seems to be the case here), then the derivative $\partial\sigma/\partial(-\varphi)$ decreases, goes through zero, and becomes negative. This corresponds to the left-hand maximum and to the first descending branch of the ECC. As the potential is further shifted in the negative direction, then due to the decrease in the term αA_R which is caused by the beginning I^- ion desorption, the derivative $\partial\sigma/\partial(-\varphi)$ goes once more through zero (minimum on the ECC), and then begins to rise (second ascending branch of the ECC). The positive value of the sum $\varepsilon + (1-\alpha)A_0 - \alpha A_R$ on the second ascending segment is determined by the positive value of ε together with a decreasing value of αA_R. However, at even more negative potentials, owing to the decrease and change in sign of ε, the derivative $\partial\sigma/\partial(-\varphi)$ again goes through zero (right-handmaximum). The continuation of the ECC corresponds to the normal decrease of σ with increasing negative values of φ.

LITERATURE CITED

1. M. Gouy, Ann. Chim. Phys., 29, 236 (1903).
2. I. M. Kolthoff and C. S. Miller, J. Amer. Chem. Soc., 63, 1405 (1941).
3. K. Hasebe and T. Kambara, Rev. Polarography (Kyoto), 19, 44 (1973).
4. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, and B. N. Kabanov, The Kinetics of Electrode Processes [in Russian], Izd. Mosk. Un-ta, Moscow (1952).
5. Short Handbook of Physicochemical Quantities [in Russian], Khimiya, Leningrad (1967), p. 118.
6. J. M. Kolthoff and C. S. Miller, J. Amer. Chem. Soc., 63, 2732 (1941).
7. A. N. Frumkin, O. A. Petrii, and B. B. Damaskin, Élektrokhimiya, 6, 614 (1970).
8. A. Frumkin, O. Petrii (Petry), and B. Damaskin, J. Electroanal. Chem., 27, 81 (1970).
9. A. N. Frumkin, O. A. Petrii, and B. B. Damaskin, in: Double Layer and Adsorption at Solid Electrodes [in Russian], Vol. 2, Tartu University (1970), p. 5.
10. G. P. Girina, A. N. Frumkin, and L. G. Feoktistov, Élektrokhimiya, 11, 762 (1975).