ELECTROCAPILLARY CURVES OF INDIUM AMALGAMS

(UDC 541.13)

N. S. Polyanovskaya and A. N. Frumkin

M. V. Lomonosov Moscow State University

Translated from Élektrokhimiya, Vol. 1, No. 5,
pp. 538-545, May, 1965
Original article submitted November 28, 1964

The electrocapillary behavior of indium amalgams containing from 0.1 to 57.5% by weight In and the adsorption of inorganic anions and surface-active organic substances on the surface of the amalgams were investigated. The introduction of indium into mercury displaces the maximum of the electrocapillary curves in the direction of negative potentials. The dependence of the maximum interfacial tension on the indium concentration passes through a minimum. It was shown that with increasing negative potentials, there is a transition from positive adsorption of indium to negative adsorption. The electrochemical behavior of indium amalgams is compared with the behavior of thallium amalgams.

The electrocapillary properties of amalgams have been investigated by many authors. In early studies, devoted to dilute amalgams [1], coincidence of the potentials of the maximum interfacial tension on the electrocapillary curves of the amalgams and mercury was indicated, which led to the assumption of independence of the position of the electrocapillary maximum from the composition of the metallic phase. At the same time, for amalgams containing 40% of the alloy Bi + Pb + Sn, in the cited work Gouy found a shift and a decrease in the electrocapillary maximum. In the work of Frumkin and Gorodetskaya, who investigated the electrocapillary phenomena on concentrated amalgams of thallium, it was shown that the introduction of Tl into Hg produces a shift in the maximum of the electrocapillary curve, toward more negative potentials [2, 3]. A shift of the electrocapillary maximum in the negative direction in the case of cadmium amalgams is indicated in [4].

The purpose of this work was to study the electrocapillary properties of indium amalgams, selected as the object of investigation as a result of the high solubility of In in Hg (57.5% at 25°C according to [5]).

Experimental Section. Metallic indium, 99.99% pure, and triple-distilled mercury were used to produce the amalgams. The amalgams were prepared by dissolving In in Hg under acidified water. The In content in the amalgam was determined by complexometric titration of the hydrochloric solution of In [6] obtained in the solution of a weighed sample of the amalgam in concentrated HCl.

The electrocapillary curves were measured with Gouy's capillary electrode, described in [7], with a barometric tube 2 mm in diameter and a conical capillary, possessing a cross-sectional diameter of about 30 μ. To avoid oxidation of the amalgam in the side reservoir of the electrometer, its surface was covered with acidified double-distilled water and kept under cathode polarization at a current strength of $\approx$0.1 A. The determination of the electrometer constant k and the capillary depression of the amalgams was described in [8]. The density of the amalgams, the values of which are needed for the calculation of k, was determined with a pycnometer. The measurements were conducted at 21-22°C.

Figure 1 presents the electrocapillary curves of amalgams containing from 0.1 to 57.5% In in a solution of 1 N Na_2SO_4. The potentials are given according to a saturated calomel electrode. In order to continue the measurements as far as possible into the anodic and cathodic regions, which is hindered by the formation of surface oxides and by the liberation of hydrogen, respectively, each curve was taken successively in three solutions of different acidities: several extreme points in 0.01 N H_2SO_4, from more cathodic potentials to -1.5 V in 1 N Na_2SO_4

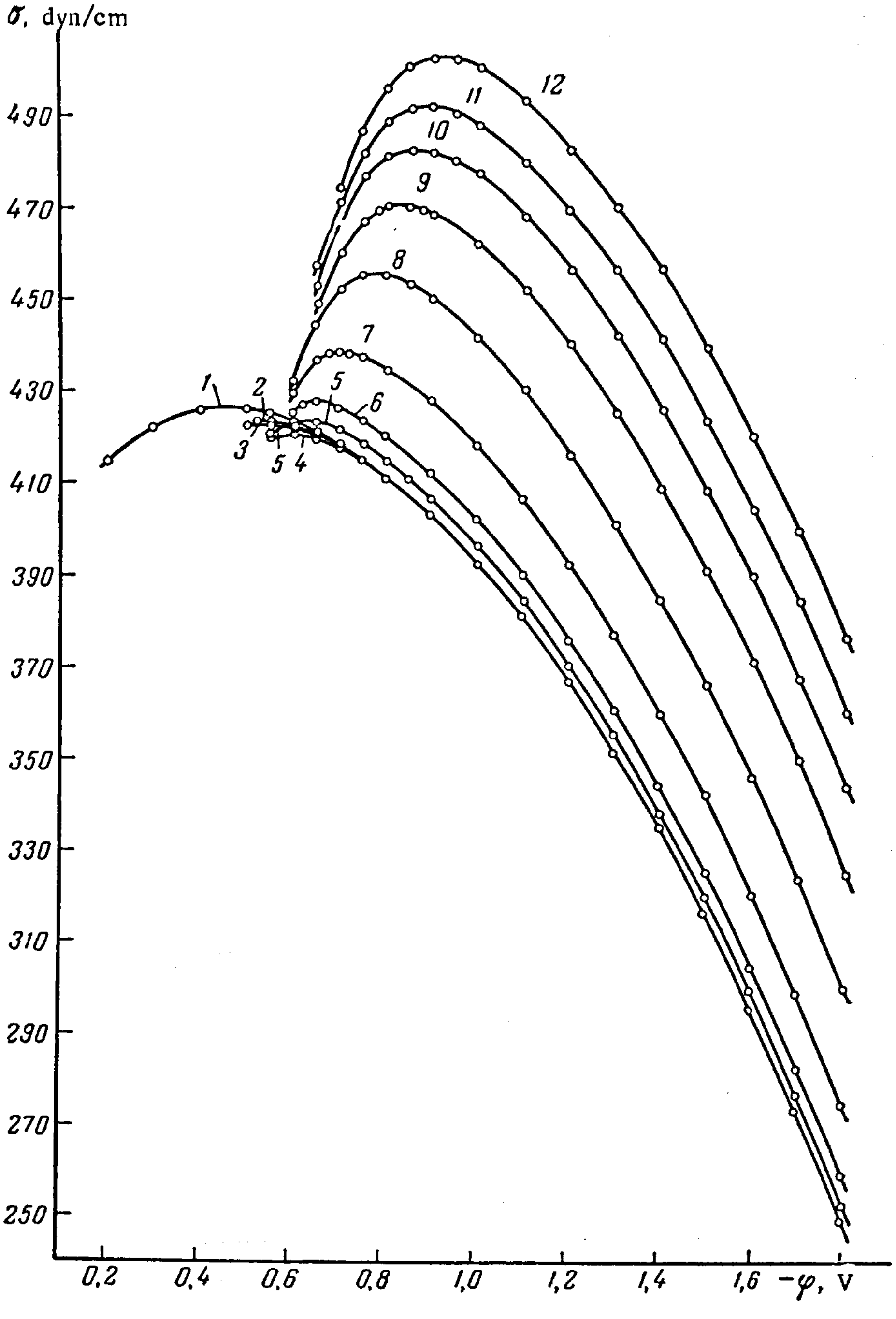

Fig. 1. Electrocapillary curves of In amalgams (%) in 1 N Na_2SO_4+ 0.01 N H_2SO_4 (KOH) and 1.01 N H_2SO_4; 1) 0; 2) 0.11; 3) 0.49; 4) 1.14; 5) 2.04; 6) 4.6; 7) 10.3; 8) 20.0; 9) 30.2; 10) 38.9; 11) 48.5; 12) 57.7.

+ 0.01 N H_2SO_4, and from −1.3 V to −1.9 V in 1 N Na_2SO_4+ 0.01 N KOH. Within the overlapping intervals of the potentials φ, the values of the interfacial tension σ fully coincide, which indicates the absence of any dependence of σ of the amalgams on the solution pH.

As can be seen from Fig. 1, the electrocapillary curves of concentrated amalgams in 1 N Na_2SO_4 cannot be continued into the anodic region to intersection with the curve of Hg on account of the loss of mobility of the meniscus in the capillary as a result of the formation of an oxide film on the surface of the amalgam. In a dilute amalgam (0.11%), measurements in a solution of 1 N Na_2SO_4 could be continued up to more positive potentials, since the oxide film evidently is not formed at these concentrations of In. As a result of the solution of In in this

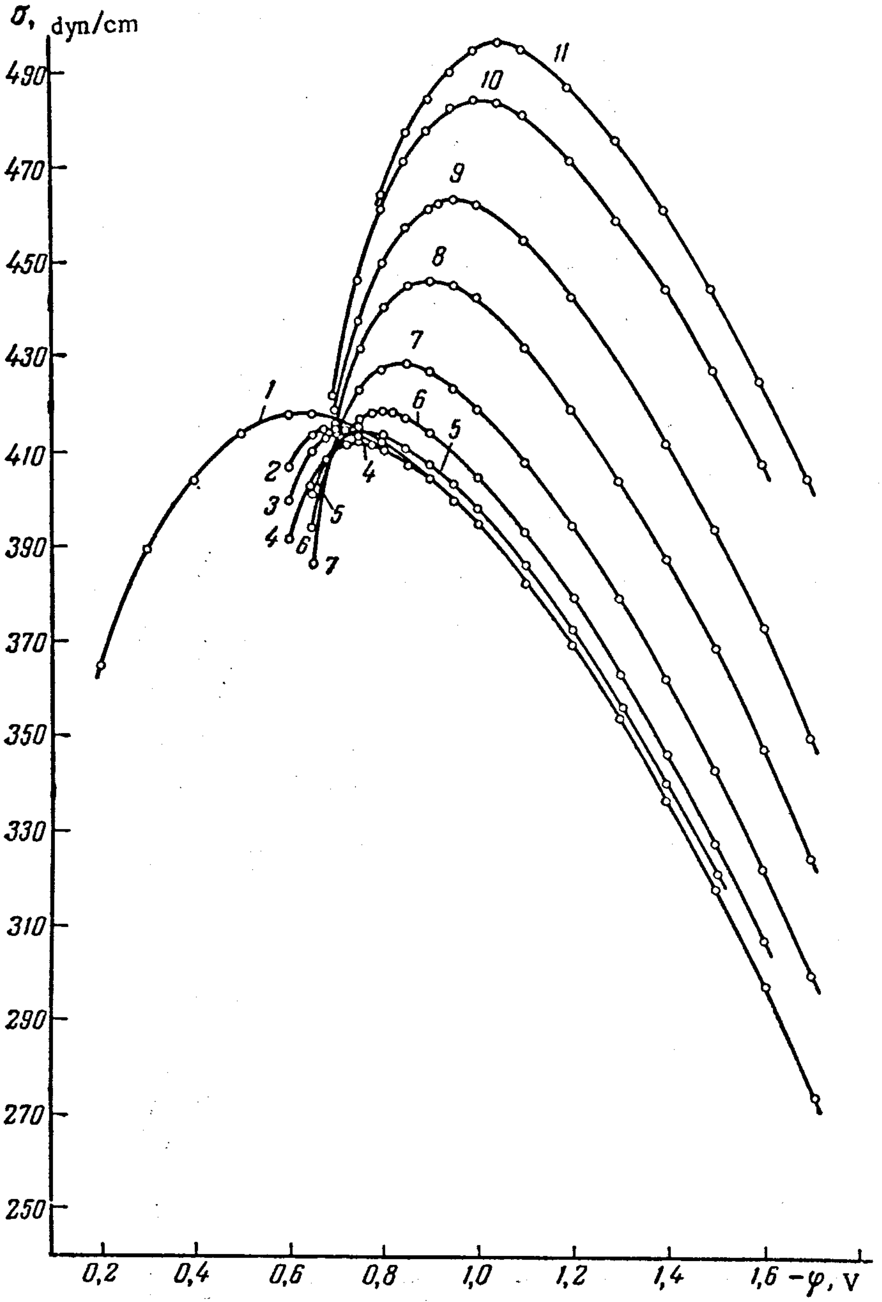

Fig. 2. Electrocapillary curves of In amalgams (%) in 1 N KBr+ 0.01 N H_2SO_4: 1) 0; 2) 0.11; 3) 0.49; 4) 1.14; 5) 2.04; 6) 4.6; 7) 10.3; 8) 20.0; 9) 30.2; 10) 48.5; 11) 57.5.

region, the amalgam curve approaches the normal electrocapillary curve of Hg in a solution of an inactive electrolyte. To continue the ascending branch of the electrocapillary curves, we took the curves of all the amalgams in a solution of 1 N KBr+ 0.01 N H_2SO_4 (Fig. 2).

As can be seen from Figs. 1 and 2, the introduction of In lowers σ of the amalgams in comparison with σ of mercury at low negative values of φ and increases them at higher −φ. The electrocapillary curves of the amalgams more dilute than 2.04% practically merge with the curve of Hg with increasing −φ, without intersecting it. The electrocapillary curves of more concentrated amalgams intersect with the curve of Hg within a narrow interval of values of φ (−0.69 to −0.76 V in 1 N KBr). The point of merging of the curves of the dilute amalgams with the mercury curve lies in the capillary direction from the point of intersection. The position of the point of intersection depends on the composition of the solution.

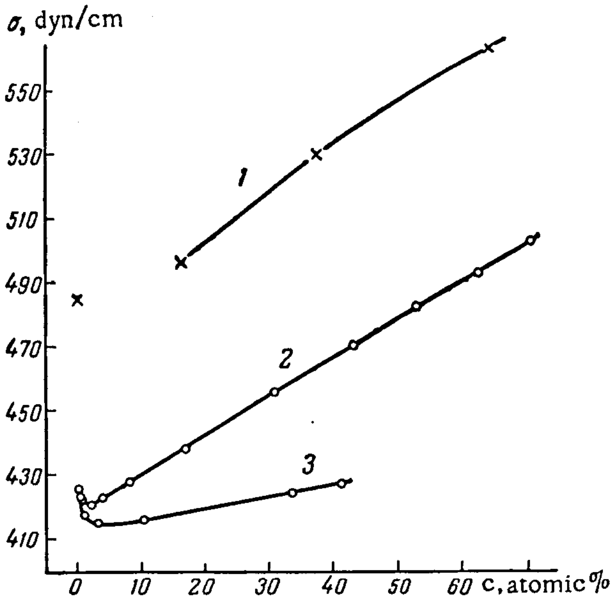

Fig. 3. Curves of σ versus c for amalgams of In and Tl: 1) In amalgam/vacuum; 2) In amalgam/1 N Na_2SO_4 (at maximum of electrocapillary curve); 3) Tl amalgam/1 N Na_2SO_4 (at maximum of electrocapillary curve, according to data of [2]).

The maximum interfacial tension σ_{max} first decreases with the introduction of In, then, passing through a minimum at an In concentration in the amalgam $c_{In} = 1.14\%$, gradually rises. The dependence of σ_{max} on c_{In} in a solution of 1 N Na_2SO_4 is presented in Fig. 3 (curve 2). For comparison, this same figure graphically presents the dependence of the surface tension of indium amalgams, measured under vacuum, on c_{In}, cited in [9] (curve 1), and the dependence of σ_{max} on the Tl concentration in thallium amalgams according to the data of [2] (curve 3). Curves 1 and 2 are almost parallel within a substantial range of concentrations; unfortunately, there are no data pertaining to amalgams with a lower indium concentration for the boundary with vacuum, which would make it possible to compare the shape of curves 1 and 2 in the region of the minimum in curve 2.

The potential of the maximum of the electrocapillary curve σ_{max} is shifted with increasing c_{In} in the direction of more negative potentials, reaching a value of −0.93 V in a solution of 1 N Na_2SO_4.* The descending branches of the amalgam electrocapillary curves for amalgams up to 20%, inclusively, pass parallel to the curve of mercury, beginning with −0.7 to −0.9 V. At higher c_{In} (30.2 and 38.9%), the area of parallelism is restricted, while at 48.5 and 57.5% of the amalgams within the potential interval that we investigated, a constant increase in the negative value of $\Delta\sigma = (\sigma_{Hg} - \sigma_{am})_{\varphi}$ is observed with increasing $-\varphi$.

Figure 4 presents the electrocapillary curves of 57.5% amalgam in solutions containing a number of surface-active substances. In a comparison of these curves with the electrocapillary curves in the same solutions, obtained on Hg, it is evident that the influence of surface-active inorganic anions and neutral organic molecules is of the same nature as on Hg, but is not as pronounced. Thus, the shift σ_{max}, produced by the I^- ion, from φ_{max} in Na_2SO_4 solution, is −0.35 V on Hg, while on a 57.5% In amalgam it is −0.21 V. In accord with this, there is some dependence of the adsorption effect on the amalgam concentration: as we pass from a 1.14% to 57.5% amalgam in KI solution, the shift of σ_{max} and φ_{max} from σ_{max} and φ_{max} in 1 N Na_2SO_4 decreases from 24 dyn/cm and −0.25 V to 20.8 dyn/cm and −0.21 V, respectively.

Discussion of Results. The indicated dependences of σ, σ_{max}, and φ_{max} on c_{In} and φ of the electrode and the composition of the solution are analogous to those found for thallium amalgams [2].

In [2] it was shown that the Gibbs thermodynamic theory of surface phenomena is applicable to an amalgam system containing Hg, Hg_2^{+2}, Tl, Tl^+, and other components. In the case of systems containing In, the Gibbs adsorption equation takes the form:

$$d\sigma = -\Gamma_{Hg} d\mu_{Hg} - \Gamma_{In} d\mu_{In} - \Gamma_{H_2O} d\mu_{H_2O} - \varepsilon d\varphi - \Sigma_i \Gamma_i d\mu_i, \quad (1)$$

where Γ_{Hg} and Γ_{In} are the summary adsorptions of Hg and In at the interface in the form of the atoms, and perhaps ions, respectively; Γ_{H_2O} and Γ_i are the adsorption of water molecules and other components found in the system; dμ is the change in the chemical potentials corresponding to the components; ε is the summary charge of the potential-determining ions, which disappear from solution when the amalgam/solution interface is increased by 1 cm^2.

---

*The values of φ_{max} in 1 N Na_2SO_4 for amalgams of different concentration, which we obtained, coincide satisfactorily with the data of [10], in which the points of zero charge of indium amalgams were determined as the potentials at which there is no current between dropping amalgam electrodes and amalgam electrodes at rest in a solution of 0.1 M $HClO_4$.

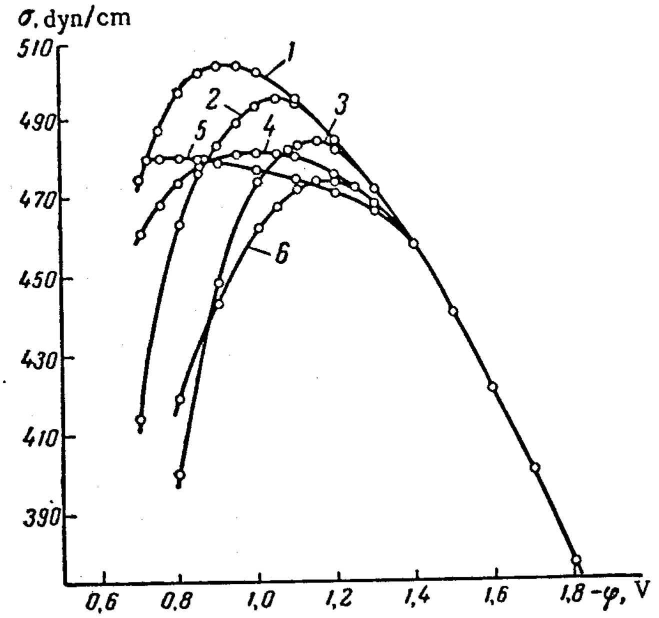

Fig. 4. Electrocapillary curves of a 57.5% In amalgam in solutions: 1) 1 N Na_2SO_4 + 0.01 N H_2SO_4 (KOH); 2) 1 N KBr + 0.01 N H_2SO_4; 3) 1 N KI + 0.01 N H_2SO_4; 4) 1 N Na_2SO_4 + 0.4 M hydroquinone; 5) 1 N Na_2SO_4 + 0.01 N H_2SO_4 + 0.14 M isoamyl alcohol; 6) 1 N Na_2SO_4 + 0.5 M thiourea.

In the case of sufficiently dilute solutions and constancy of the concentrations of the components i, we have: $d\mu_{H_2O} = 0$ and $d\mu_i = 0$, and Eq. (1) is converted to

$$d\sigma = \varepsilon d\varphi - \Gamma_{In} d\mu_{In} - \Gamma_{Hg} d\mu_{Hg}. \tag{2}$$

By the selecting the position of the interface, we can set $\Gamma_{In} = 0$ or $\Gamma_{Hg} = 0$. In the first case:

$$d\sigma = \varepsilon d\varphi - \Gamma_{Hg} d\mu_{Hg}, \tag{2a}$$

in the second:

$$d\sigma = \varepsilon d\varphi - \Gamma_{In} d\mu_{In}. \tag{2b}$$

from (2b), it follows that

$$\Gamma_{In} = -\left(\frac{\partial\sigma}{\partial\mu_{In}}\right)_{\varphi}. \tag{3}$$

The mutual position of the amalgam and mercury curves indicates the adsorption of indium on the amalgam-solution interface, which is a function of the potential. From Eq. (3), considering the mutual arrangement of the curves, it follows that upon transition to more negative φ, there is a transition of the positive adsorption of indium to negative adsorption. The point of intersection of the curves corresponds to zero adsorption of indium. From the thermodynamic theory of electrocapillary phenomena on amalgams, set forth in [2], it follows that in the case of dilute amalgams, the potential of intersection of the electrocapillary curves φ_1 is related to the potential of zero charge of mercury φ_0 by the function

$$\varphi_1 = \varphi_0 + W_0 / [C(\varphi_N - \varphi_0)S].$$

Here W_0 is the work of adsorption in the adsorption of dissolved metal on an uncharged mercury surface; C is the double layer capacitance; φ_N is the zero charge potential of the surface, covered by adsorbed indium; S is the area per mole of adsorbed indium in the surface layer. The decrease in the quantity $|\varphi_1 - \varphi_0|$ with increasing c_{In} may be partially explained by an increase in the double-layer capacitance as the point of intersection on the

% In	N_2	N_1	a_1	lg a_1	$\Delta\sigma$	$\overline{\Gamma}_{Hg}$
2,04	0,0351	0,9649	0,0026	—0,017	—3,7	$3{,}85\cdot10^{-9}$
4,6	0,078	0,922	0,0074	—0,043	—9,3	$3{,}84\cdot10^{-9}$
10,3	0,167	0,833	0,026	—0,118	—25,5	$3{,}84\cdot10^{-9}$
20,0	0,304	0,696	0,1255	—0,330	—50,4	$2{,}71\cdot10^{-9}$
30,2	0,431	0,569	0,310	—0,562	—76,2 *	$2{,}39\cdot10^{-9}$
38,9	0,527	0,473	0,501	—0,755	—95,0 *	$2{,}23\cdot10^{-9}$
48,5	0,622	0,378	0,772	—1,012	—111,7 *	$1{,}96\cdot10^{-9}$
57,5	0,703	0,297	0,995	—1,231	—127,7 *	$1{,}84\cdot10^{-9}$

* $\varphi = -1{,}8$ V.

electrocapillary curve of the amalgam moves from its descending branch to its ascending branch. It is possible, however, that the hypothesis of constancy of the quantities W_0 and $\varphi_N - \varphi_0$ within the amalgam concentration range considered is not justified. The displacement of φ_1 from more negative values to more positive values with increasing amalgam concentration is also observed in the case of thallium amalgam, but it is more pronounced in the case of indium.

Using Eq. (2a), we can calculate the positive adsorption of Hg, or, which is the same, the negative adsorption of In at large negative φ, as was done in [2] for Tl amalgams. Since $\mu = \mu_0 + RT \ln a$, from Eq. (2a) it follows that

$$\overline{\Gamma}_{Hg} = \frac{1}{RT}\frac{\Delta\sigma}{2.303 \lg a_1}, \tag{4a}$$

where a_1 is the activity of Hg in the In amalgam, $\overline{\Gamma}_{Hg}$ is the average value of Γ_{Hg} within the interval of mercury activities from 1 to a_1, while $\Delta\sigma$, as was indicated above, is a constant for each of the amalgams up to 20%, inclusively, beginning with the potentials −0.7 to −0.9 V, and possesses the values cited in the table.

The value of log a_1 was calculated using the values of the activity of In in indium amalgams a_2 at 20°, taken from [11], by the method of Lewis and Randall [12], according to which −log a_1/N_1 from the area of the curve of N_2/N_1 versus log a_2/N_2, where N_1 and N_2 are the molar fractions of Hg and In. In addition, we calculated log a_1 with the aid of the values of a_2, obtained by Butler in the selection of a different standard state of the metal in mercury [13]. The values of log a_1, calculated according to the data of the two studies, are in good agreement.

The data needed for the calculation of the values of Γ_{Hg} according to Eq. (4) and the calculated $\overline{\Gamma}_{Hg}$ are cited in the table.

For the first three amalgams cited in the table, we obtained an average value of Γ_{Hg} equal to $3.84 \cdot 10^{-9}$ mole/cm^2. This value indicates the existence of a layer $3.84 \cdot 10^{-9} \cdot 200.6/13.55 = 5.68 \cdot 10^{-8}$ cm thick, the concentration of indium in which is small in comparison with the volume concentration, on the surface of amalgams with c_{In} from 2.04 to 10.3%, inclusively, at more negative φ. In the case of thallium amalgams, the thickness of this layer is equal to $6.1 \cdot 10^{-8}$ cm, i.e., very close to the value calculated for In.

For 20% and more concentrated amalgams, the negative adsorption of In in the surface layer is reduced, as it follows from the table. This is even more sharply manifested if we calculate from the curve $\Delta\sigma$ versus log a_1 not the average values of $\overline{\Gamma}_{Hg}$ but the values of Γ_{Hg}, corresponding to a definite value of a_1. For amalgams with 50% In, $\Gamma_{Hg} \approx 1.2 \cdot 10^{-9}$, i.e., it is reduced approximately three-fold in comparison with the value in dilute solutions. The negative work of adsorption of indium evidently is not large enough to entirely prevent the penetration of indium into the surface layer of the amalgam with increasing indium activity in the volume of the amalgam. It may be that higher values of Γ_{Hg} might have been observed if the measurements were continued to more negative potentials. We should also keep in mind that in concentrated amalgams most of the mercury is found in the form of intermetallic compounds with indium. The formation of an intermetallic compound $InHg_3$ at an In content in the amalgam of 16.8% (26 atomic %) is indicated in [14].

On the whole, the electrocapillary behavior of indium amalgams is similar to the behavior of thallium amalgams, and, just as in the latter case, may be interpreted on the basis of the assumption of a dipole character of the Hg−In bond in the surface layer of the amalgam [15, 3]. The existence of such a dipole, turned with its positive end toward the volume of the solution, leads to a dependence of the work of adsorption on the potential and to a transition from positive adsorption of indium to negative adsorption as the potential is shifted toward more negative values.

However, there are quantitative differences between the electrocapillary properties of indium and thallium amalgams (cf., Fig. 3). The small surface activity of In in the amalgam, which affects the magnitude of the shift of $\varphi_{\max}$ in the negative direction from $\varphi_{\max}$ on Hg, is one such difference of In amalgams from Tl amalgams. For a 33.9% Tl amalgam, the shift of $\varphi_{\max}$ is equal to −0.44 V, while for the 20% In amalgam equal to it in concentration in atomic percent, this quantity reaches only −0.29 V. An equal shift in $\sigma_{\max}$, equal to −0.45 V, is observed for amalgams of In and Tl, possessing concentrations of 70.27 and 41.04 atomic percent, respectively.

Another difference is the far higher values of $\sigma_{\max}$ of concentrated In amalgams in comparison with $\sigma_{\max}$ for the same concentrations of Tl amalgams (Fig. 3, curves 2 and 3), which indicates a higher interfacial tension of metallic In at the boundary with the solution in comparison with the interfacial tension of Tl. According to the data of [16], the value of $\sigma_{\max}$ of metallic In, determined in an electrolyte melt at 450°C, is equal to 523 dyn/cm.

LITERATURE CITED

1. V. Rothmund, Z. Phys. Chem., 15, 1 (1894); G. Gouy, Ann. Phys. (9), 6, 25 (1916); Christiansen, Drud. Ann., 16, 382 (1905).
2. A. Frumkin and A. Gorodetzkaja, Z. Phys. Chem., 136, 451 (1928).
3. A. Frumkin, Surface Phenomena in Chemistry and Biology, Pergamon Press (1958), p. 189.
4. A. Frumkin and N. Polyanovskaya, Zh. Fiz. Khimii, 32, 157 (1958).
5. L. Kozin, Transactions of the Institute of Chemical Sciences, Kazakh SSR [in Russian], 9, 101 (1962).
6. R. Prshibil, Complexones in Chemical Analysis [in Russian], Moscow (1960), p. 130.
7. B. Damaskin and N. Nikolaeva-Fedorovich, Handbook for Problems of Special Practices in Electrochemistry [in Russian], Izd. MGU (1963), p. 47.
8. A. Frumkin, N. Polyanovskaya, and N. Grigor'ev, Dokl. AN SSSR, 157, 1455 (1964).
9. D. Olsen and D. Johnson, J. Phys. Chem., 67, 2529 (1963).
10. J. Butler and A. Makrides, Trans. Faraday Soc., 60, 1664 (1964).
11. L. Kozin, Transactions of the Institute of Chemical Sciences, Academy of Sciences, Kazakh SSR [in Russian], 9, 81 (1962).
12. G. Lewis and M. Randall, Chemical Thermodynamics [Russian translation] (1936), p. 211.
13. J. Butler, J. Phys. Chem., 68, 1828 (1964).
14. L. Kozin, Transactions of the Institute of Chemical Sciences, Kazakh SSR [in Russian], 9, 71 (1962).
15. A. Frumkin and A. Titievskaya, Zh. Fiz. Khimii, 31, 485 (1957).
16. V. Kuznetsov and L. Zagainova, Zh. Fiz. Khimii, 35, 1640 (1961).
