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ELECTROCAPILLARY PHENOMENA IN THE Hg, Tl, Tl^+, H_2O SYSTEM

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The electrocapillary properties of thallium amalgams were studied by Frumkin and Gorodetskaya[1]. They found that thallium shifts the pzc of mercury in the negative direction. With increasing thallium concentration, its positive adsorption at the uncharged mercury/solution interface passes through a maximum and then becomes negative. As was shown by Kuznetsov *et al.*[2], the same concentration dependence of thallium adsorption is also observed at the mercury/vacuum interface. Frumkin and Gorodetskaya made a quantitative interpretation of the results obtained on the basis of the assumption that adsorbed thallium forms with mercury dipoles turned with their negative ends inside the metal. For Tl amalgams in 0.5 *M* Na_2SO_4 with a Tl content $\leqslant 10\%$ and at potentials, φ, lying within $-0.7 > \varphi > -1.1$ (NCE) this quantitative interpretation leads to the functional dependence

$$(c_{Tl})_{ads} = f_1(\mu_{Tl} + 0.22\varphi) \tag{1}$$

where $(c_{Tl})_{ads}$ is the concentration of Tl atoms in the surface layer and μ_{Tl} the chemical potential of Tl in the amalgam expressed in electrical units[1,3]. The same dipoles should arise during thallium adsorption at the mercury/vacuum interface. According to the measurements of Karpachev and Stromberg[4] the decrease in the work function upon transition from mercury to a 12% thallium amalgam, equal to 0.38 V, is very close to the shift of pzc in the direction of more negative potentials when passing from mercury to an amalgam of this composition.

Frumkin and Titievskaya[3] found that the maximum of the electrocapillary curve of mercury in thallium salts solutions shifts in the positive direction. They explained this shift by specific adsorption of thallium ions. Earlier, a similar shift of the dropping electrode potential was observed by Erdey-Gruz and Szarvas[5], who offered, however, no explanation for it. As was shown in ref. 3, the surface activity of thallium ions rises when passing from sulfate to nitrate solutions. For M KNO_3 + 0.01 *M* HNO_3 + *x M* $TlNO_3$ solution in the range of φ from -0.25 V to -0.45 V, the dependence of the decrease of the surface tension $\Delta\sigma$, caused by addition of Tl^+ ions to the solution, on the chemical potential of the ions μ_{Tl^+} was found to be of the form:

$$\Delta\sigma = f_2(\mu_{Tl^+} - 0.16\varphi) \tag{2}$$

If by means of Nernst's formula we pass from μ_{Tl^+} to μ_{Tl}, eqn. (2) transforms to

$$\Delta\sigma = f_2(\mu_{Tl} + 0.84\varphi)\,. \tag{3}$$

The value of the coefficient before φ in eqn. (1) can serve as a measure of polarity of the

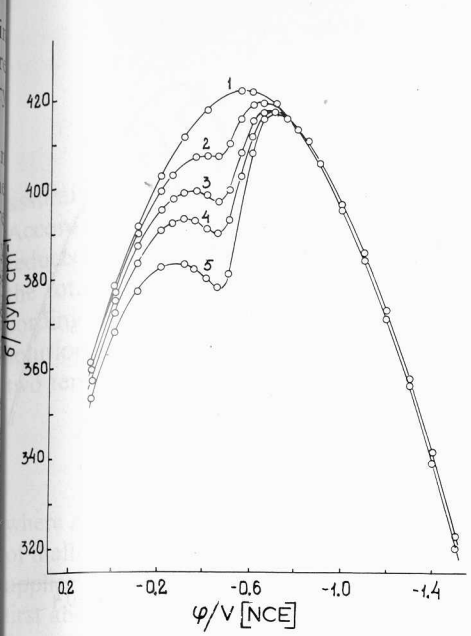
Tl–Hg bond. From the large difference in the values of the coefficients before φ i eqns. (1) and (3) it was concluded that the adsorption of Tl^+ ions observed at mo positive potentials cannot be treated as adsorption of Tl atoms dissolved in mercur which are in equilibrium with these ions[3,6].

An analysis of the regularities of the adsorption of Tl^+ ions and co-adsorptio of Tl^+ and NO_3^- ions was made by Delahay and coworkers[7,8]. It proved that th regularities characterizing the adsorption of Tl^+ ions from fluoride solutions a similar to those of the adsorption of surface-active anions. According to Delaha *et al.*, in the case of co-adsorption of Tl^+ and NO_3^- ions the plane in which the centre of Tl^+ ions are located lies closer to the mercury surface than the plane in which th centres of NO_3^- ions are localized (2 and 3.15 Å, respectively). These authors poi to the possibility of the ionic pairs Tl^+, NO_3^- being formed in the surface layer Whereas in TlF solutions the potential in the outer Helmholtz plane is alwa positive at positive surface charge ε, in the presence of both Tl^+ and NO_3^- ions, in certain range of positive ε values, this potential is negative. The results of a mod treatment of the co-adsorption of Tl^+ and NO_3^- ions differ from those obtained whe using the Hurwitz and Dutkiewicz–Parsons method[8]. It is not quite clear, howeve whether the use of the latter method is justified in this particular case. In refs. 9 and 1 when measuring the dependence of surface tension on electrode potential φ at th mercury/(0.2 *M* $TlNO_3$ + 0.8 *M* KNO_3) interface in a wide range of φ, a doubl humped curve was obtained, which was treated as a combination of two electr capillary curves: the electrocapillary curve of an ideally polarized mercury electro in a solution containing specifically adsorbed Tl^+ ions and that of an ideally polarize amalgam electrode. In ref. 11, from which Fig. 1 is taken, it was shown that the dep of the minimum located between the two maxima of these electrocapillary curv depends on the nature of the anion.

Salié and Lorenz[12], who considered the kinetics of the discharge of Tl^+ io and of the ionization of Tl atoms on the Tl amalgam surface in thallium salt solution came to the conclusion that the adsorption of the Tl^+ ion from nitrate and pe chlorate solutions involves a partial charge transfer to the metal surface, the transf coefficient λ being 0.7–0.8 (see also ref. 13). In ref. 11 an attempt was made to interpr the adsorption phenomena in the Hg, Tl, Tl^+, H_2O system on the basis of the electr capillarity theory of reversible systems developed in ref. 14. The possibility of thermodynamic treatment of the results obtained was, however, limited by the fa that most of the measurements of σ by the methods used in refs. 9 and 11, were pe formed under non-equilibrium conditions, *viz.* with current passing through th measuring system. This paper helps to remove the effect of this limitation.

EXPERIMENTAL

According to ref. 14, in order to get a complete idea of the adsorption phenom ena in reversible systems it is necessary to determine the σ, φ dependences at consta chemical potentials of the oxidized and reduced forms, respectively. In this paper t equilibrium values of σ were determined by means of a Gouy capillary electromet for thallium amalgams with Tl content c_{Tl} from 0.002 to 40 atomic % in *x M* $TlNO_3$ + $(1-x)$ *M* KNO_3 solutions, where x varied from 0.001 to 0.1 *M*. The electrometer w filled with amalgams using the technique employed earlier when working with liqu



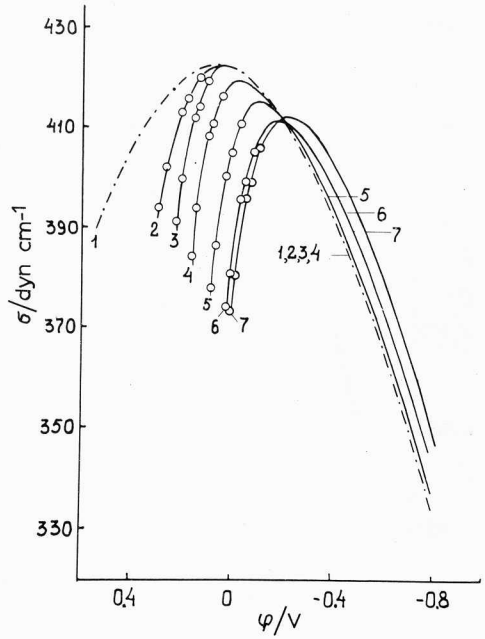


Fig. 1. Electrocapillary curves of mercury in solns.: (1) 1 *M* KNO_3, (2) 0.02 *M* $TlNO_3$ + 0.98 *M* KNO_3, (3) 0.05 *M* $TlNO_3$ + 0.95 *M* KNO_3, (4) 0.1 *M* $TlNO_3$ + 0.9 *M* KNO_3, (5) 0.2 *M* $TlNO_3$ + 0.8 *M* KNO_3 according to the data of ref. 11).

Fig. 2. σ, φ-Dependences corresponding to the condition μ_{Tl} = const. Thallium content c_{Tl} in amalgams in at.%: (1) 0, (2) 0.002, (3) 0.014, (4) 0.12, (5) 0.7, (6) 4.9, (7) 7.8.

gallium[15], which rules out the possibility of the contamination of the capillary by the oxidized amalgam. The measurements of σ were carried out without application of polarization at short circuit between the amalgam in the capillary and the amalgam of the same composition on the cell bottom. The temperature was 20°. The potential φ was measured against the reference electrode—9.9 % Tl amalgam in 0.1 *M* $TlNO_3$ + 0.9 *M* KNO_3. We assumed that the liquid junction potential at the interface between this solution and the other solutions used by us could be ignored. Before accumulating the amalgam on the bottom by dropping it from the capillary and measuring φ, the solution was thoroughly freed of traces of oxygen. The absence of current between the meniscus in the capillary and the amalgam on the bottom was verified by a microammeter with sensitivity 10^{-9} A. On varying the concentration of the $TlNO_3$ solution c_{Tl} from 0.001 to 0.1 *M* for each amalgam and measuring the equilibrium potential of the system and the value of σ corresponding to it, we obtained a set of σ, φ dependences complying with the condition μ_{Tl} = const. In the range of more negative potentials, which would correspond to the equilibrium values of $x \ll 0.001$ *M*, these were supplemented by data determined for each amalgam in a 1 *M* KNO_3 solution by the conventional method of measuring electrocapillary curves in 1 *M* KNO_3. The set of electrocapillary curves thus obtained is shown in Fig. 2. In this Figure and also in Figs. 3 and 4, the points measured under equilibrium conditions are shown by circles. The absence of points enclosed within circles indicates that the relevant part of the curve was obtained by polarization of the meniscus in the capillary. In Figs. 2–4 and

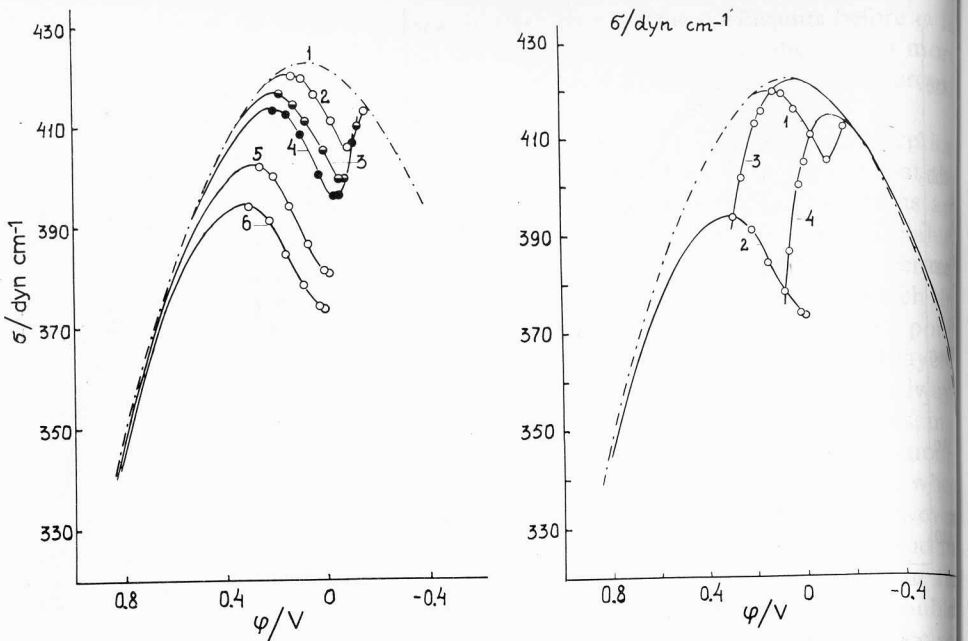


Fig. 3. σ, φ-Dependences corresponding to condition μ_{Tl^+} = const. Tl^+ concn. x in xM $TlNO_3+(1-x)$ KNO_3 solns.: (1) 0, (2) 0.001, (3) 0.005, (4) 0.01, (5) 0.05, (6) 0.1.

Fig. 4. Intersection of electrocapillary curves of first and second kinds: (1) $x=0.001$ M, (2) $x=0.1$ (3) $c_{Tl}=0.002$, (4) $c_{Tl}=0.7$. (-·-·-) Electrocapillary curve of mercury in 1 M KNO_3 soln.

6–7 the potentials are given *versus* the reference electrode: 9.9% Tl amalgam 0.1 M $TlNO_3+0.9$ M KNO_3. The values of φ and σ found by the procedure describ above were used in plotting a set of σ, φ curves complying with the condition μ_{Tl^+} const. (x=const.). For plotting the total electrocapillary curve of this kind the φ values, obtained in experiments with amalgams of the composition indicated abo were supplemented by the values of σ obtained by polarization of the mercu meniscus from an external current source in $TlNO_3$ solutions in the potential ran from the most positive potentials to those at which cathodic thallium deposit becomes appreciable. A 9.9% amalgam electrode in the working solution freed traces of oxygen was used as a reference electrode in these measurements. The potent of this electrode *versus* 9.9% amalgam in 0.1 M $TlNO_3+0.9$ M KNO_3 was determin in a separate experiment. The set of electrocapillary curves satisfying the conditi μ_{Tl^+} = const. is shown in Fig. 3. We shall call these curves electrocapillary curves of t first kind and the curves complying with the condition μ_{Tl} = const., electrocapilla curves of the second kind.

The values of σ, φ used in plotting the curves in Figs. 2 and 3 were strict equilibrium ones or were obtained under conditions where deviations from eq librium were negligible, owing to the small value of the equilibrium concentration one of the components of the redox system. Within the limits of the changes in t solution composition mentioned, the effect of the changes in the chemical potenti of water and of NO_3^- and K^+ ions on σ could be neglected and the results obtain could be treated using the equations deduced in ref. 14:

$$\left(\frac{\partial\sigma}{\partial\varphi}\right)_{\mu_{Tl^+}} = -Q' = \Gamma_{Tl} \quad (4)$$

$$\left(\frac{\partial\sigma}{\partial\varphi}\right)_{\mu_{Tl}} = -Q'' = -\Gamma_{Tl^+} \quad (5)$$

assuming the position of the interface to be determined by the condition $\Gamma_{Hg}=0$. According to ref. 14, Γ_{Tl} and Γ_{Tl^+} represent the Gibbs adsorptions of thallium in reduced and oxidized forms, respectively (expressed in electrical units); Q' and Q'' are the total electrode charges. Proceeding from the simplest double layer model according to which the adsorbed atoms are localized in the metal side and the ions in the solution side of the double layer, in ref. 14 we divided the quantities Γ_{Tl} and Γ_{Tl^+} into two terms

$$\Gamma_{Tl} = -\varepsilon + A_{Tl} \quad (6)$$

$$\Gamma_{Tl^+} = \varepsilon + A_{Tl^+}\,, \quad (7)$$

where ε is the free charge of the metal surface and A_{Tl} and A_{Tl^+} the surface excesses of thallium in reduced and oxidized forms, respectively. This approach proved to be applicable to the Pt, H, H^+ system and the shape of the electrocapillary curves of the first and second kinds of platinum could be readily interpreted[16].

The treatment of the electrocapillary curves of the Hg, Tl, Tl^+ system involves additional difficulties connected with the fact that Tl^+ ions, as well as the complexes formed by them with anions, unlike the H^+ ion, show significant specific adsorptivity on the metal phase surface. The existence of specific adsorptivity makes possible a gradual transition from the state, "adsorbed ion" to the state, "adsorbed atom". The possibility of this transition, which is not taken into consideration in this paper, does not affect, as was shown in ref. 14, the validity of the thermodynamic approach used here, but, quite naturally, must influence the model interpretation of the results obtained. As follows from ref. 14, the Γ_{Tl^+} ion adsorption at the charge transfer coefficient λ from the thermodynamic viewpoint is equivalent to co-adsorption of $(1-\lambda)\Gamma_{Tl^+}$ ions and $\lambda\Gamma_{Tl^+}$ atoms with concomitant increase of ε by the quantity Γ_{Tl^+}*.

DISCUSSION

In the earlier interpretations of the electrocapillary curves of mercury in solutions of Tl salts and of Tl amalgams[1,3,6-9] the quantities A_{Tl} and A_{Tl^+} were not taken into account. The potentials of the maxima of the first kind were considered as being the potentials of the zero free charge of mercury shifted into the positive direction under the influence of specific adsorption of Tl^+ ions[3,6,9] and the potentials of the maxima of the curves of the second kind as being the potentials of the zero free charge of thallium amalgams[1]. However, as is clear from Fig. 4, the electrocapillary curves of the first and second kind intersect and at the intersection point, if A_{Tl} and A_{Tl^+} are

* The physical meaning of the charge transfer coefficient given to this quantity in the thermodynamic treatment is, however, not identical with the interpretation of this quantity by Lorenz. This difference which was overlooked in ref. 14 will be considered in more detail in a forthcoming publication.

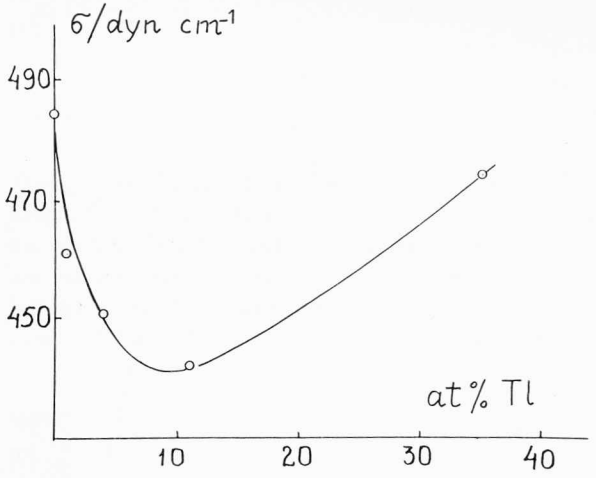


Fig. 5. Surface tension isotherm of thallium amalgams at 20° in vacuum (according to the data of ref. 2

not allowed for, the free charge of the mercury surface should have both negative an positive values at the same time. The appearance at more negative potentials of minimum and of the second ascending branch on the electrocapillary curve of th first kind* can also be explained only by taking account of A_{Tl}, *viz.* the negati thallium adsorption at its larger concentrations in the amalgam. This negati adsorption, as has been pointed out above, is observed in the Hg–Tl system at t metal–vacuum interface[2] (Fig. 5). Since at small Tl concentrations at the meta vacuum interface, Tl adsorption is positive, the drop of the electrocapillary curve the first kind after passing through the maximum can be associated not only with t transition from positive to negative ε values, but also with an initial increase of A with increasing μ_{Tl}. With further increase of μ_{Tl}, the positive thallium adsorpti changes to a negative one, which results in the appearance on the curves of the fi kind of a minimum corresponding to the potential of the zero total charge $-\Gamma_{Tl}$ $\varepsilon - A_{Tl} = 0$. This potential, however, cannot be considered as being a potential of t zero free charge. On the positive branch of the electrocapillary curves of the seco kind, the increase of σ when φ shifts in the direction of negative values (which tak place after intersection with the curves of the first kind at not too small values of t concentration of Tl^+ in solution c_{Tl^+} and also of Tl in the amalgam c_{Tl} (Fig. according to eqn. (7) leads to values of $\varepsilon + A_{Tl^+}$ that are too large (up to 71 μC cm to be considered as being free charge values of the amalgam surface covered wi adsorbed NO_3^- ions only. Hence, if follows that after discharge of the major porti of thallium ions in solution, adsorbed thallium in the oxidized form remains on t surface, as has already been stated in ref. 14. From eqns. (4)–(7) we obtain

$$\left(\frac{\partial\sigma}{\partial\varphi}\right)_{\mu_{Tl^+}} - \left(\frac{\partial\sigma}{\partial\varphi}\right)_{\mu_{Tl}} = \Gamma_{Tl} + \Gamma_{Tl^+} = A_{Tl} + A_{Tl^+} \,.$$

Thus, the change in the slope of the electrocapillary curves when passing from cur

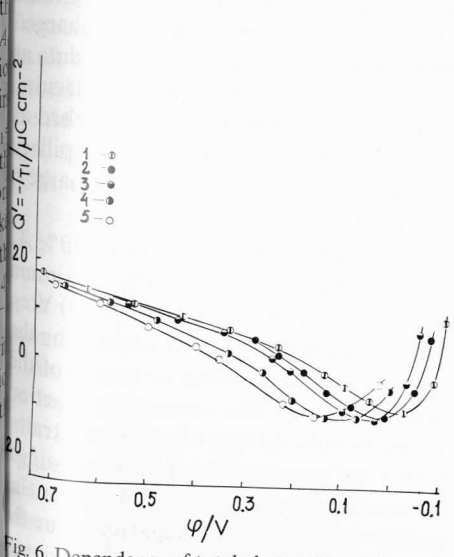
* The second ascending branches of curves 5 and 6 of Fig. 3 could not be measured on account of poor mobility of the meniscus in the capillary of the electrometer.

of the first kind to curves of the second kind at the point of intersection enables the total thallium adsorption depending on μ_{Tl^+} and μ_{Tl} to be readily calculated.

Table 1 lists some results obtained by graphical differentiation of the curves in Figs. 2 and 3 at the points of their intersection. In each space of the Table in the upper line on the left and on the right are given the values of the Gibbs adsorptions of the thallium atom $\Gamma_{Tl} = -\varepsilon + A_{Tl}$ for the condition μ_{Tl^+} = const., and that of the

TABLE 1

At.% Tl in amalgam	*Molarity of Tl^+ in soln.*				
	0.001	0.005	0.01	0.05	0.1
0.002	1.1; 4.7 5.8	1.0; 10 11	0.8; 15 16	0.7; 23 24	1.0; 29 30
0.014	3.8; 8.5 12	5.2; 13 18	4.2; 18 22	7.2; 33 40	7.6; 42 50
0.12	6.8; 10.5 17	8; 17 25	9.0; 20 29	10.5; 46 56	10; 71 81
0.7	8.7; 12.5 21	10; 20 30	11; 26 37	10.5; 40 50	8; 56 64
4.9	2.7; 13 15.5	4.6; 19 24	3.0; 27 30	4.5; 40 44	3.4; 40 43
7.8	−10; 14 4	−6.6; 22 15.5	−7.0; 28 21		



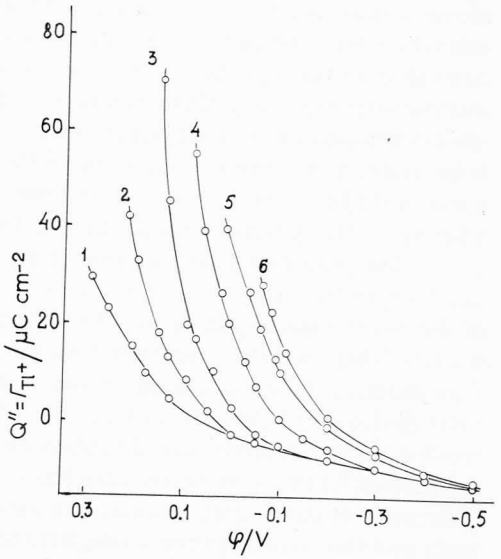


Fig. 6. Dependence of total charge $Q' = -\Gamma_{Tl}$ on φ along the electrocapillary curve of the first kind for the system xM $TlNO_3 + (1-x)M$ KNO_3 at x: (1) 0.001, (2) 0.005, (3) 0.01, (4) 0.05, (5) 0.1 M.

Fig. 7. Dependence of total charge $Q'' = \Gamma_{Tl^+}$ on φ along the electrocapillary curve of the second kind at hallium concns. in amalgams c_{Tl}: (1) 0.002, (2) 0.014, (3) 0.12, (4) 0.7, (5) 4.9, (6) 7.8.

thallium ion $\Gamma_{Tl^+} = \varepsilon + A_{Tl^+}$ for the condition $\mu_{Tl} = \text{const.}$, respectively. The botto line gives the values of the total thallium adsorption $\Gamma_{Tl} + \Gamma_{Tl^+} = A_{Tl} + A_{Tl^+}$.

Figure 6 shows the dependence of the value of $Q' = -\Gamma_{Tl}$ on φ for various valu of c_{Tl^+} and Fig. 7 the dependence of $Q'' = \Gamma_{Tl^+}$ on φ for various Tl contents.

The value of Q' is positive on the ascending branch of the electrocapillary cur of the first kind. When φ shifts in the negative direction it passes through zero t negative values, the slope of the Q', φ curve increasing. This can be explained by a increase of the specific adsorption of Tl^+ ions or by the influence of the term A_{Tl} i eqn. (6). According to eqns. (4) and (6), the transition from positive A_{Tl} values t negative values leads, however, to the appearance of a minimum and of an ascendi branch on the Q', φ curves. The Q'', φ curves (Fig. 7) show high initial values of th total charge. At sufficiently negative φ, the Q'', φ curves merge, *i.e.* the electrocapilla curves of the second kind become parallel, as was already observed in ref. 1.

Using the data obtained in this paper and in refs. 1, 3 and 19 as well as the resul of investigation of the electric double layer of mercury on the ascending branch the electrocapillary curve in thallium fluoride and nitrate solutions carried out b Delahay and coworkers, it is possible to draw some conclusions about the change the interface structure in the mercury–thallium system upon transition from positi to negative potentials. These conclusions, however, are beyond the framework of th thermodynamic approach and are not unambigous.

In developing the scheme described in this paper, we proceeded from the fo lowing assumptions, which seem to us to be sufficiently substantiated.

In the potential range corresponding to the ascending branch of the electr capillary curve of the first kind, adsorbed thallium is present in the ionic side of th double layer, in fluoride solutions probably as simple Tl^+ ions. In nitrate solution in the surface layer Tl^+ ions are bound with adsorbed NO_3^- anions forming ion pairs Tl^+, NO_3^- or polar $TlNO_3$ molecules. It seems to us that negatively charg complexes of the type $Tl(NO_3)^{2-}$ may also be formed, although we have no data our disposal regarding their existence in the solution bulk. The $TlNO_3$ molecul ionic pairs and anion complexes, unlike simple Tl^+ ions, can also be adsorbed large positive potentials. The slope of the ascending branch of the electrocapilla curve of the first kind—$\partial\sigma/\partial\varphi$, is determined by the positive value of the free charge whereas in this potential range A_{Tl} can be neglected.

The potential of the minimum on the differential capacity curve of 40% amalgam in 0.01 *M* NaF (−0.925 V *vs.* NCE[19]) almost coincides with the maximu of the electrocapillary curve of 41.5% Tl amalgam in 0.5 *M* Na_2SO_4 (−0.930 V NCE[1]). This probably indicates that in the case of concentrated Tl amalgams th maximum of the electrocapillary curve determines the zero value not only of th total, but also of the free charge. The pseudocapacity of the ionization reacti hinders the determination of the differential capacity minimum for less concentrat amalgams[19], but following the conclusions of ref. 1, we can suppose that this assum tion remains valid, even if approximately, for amalgams with lower Tl content well, and that therefore the amalgam surface at potentials more negative than t maximum of the electrocapillary curve of the second kind has a negative charg Therefore our task is to consider the various possibilities of the transition from t positively charged mercury surface on the ascending branch of the electrocapilla curve of the first kind to the negatively charged amalgam surface on the descendi

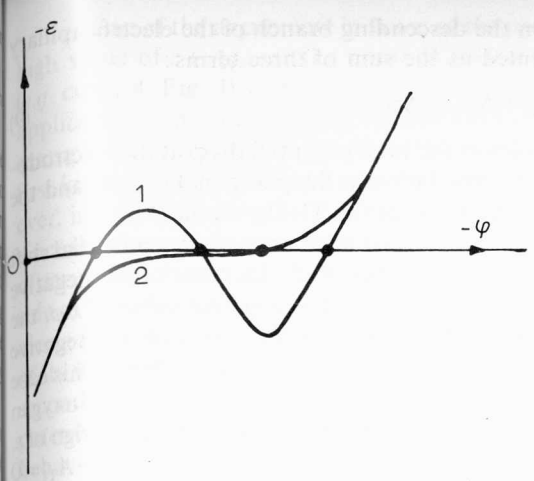


Fig. 8. Schematic diagram of dependence of ε on φ when passing from Hg to Tl amalgams through point of intersection of electrocapillary curves of the first and second kinds.

branch of the curve of the second kind, crossing the point of intersection of these curves. We have to choose between the two possible dependences of the free charge density on the electrode potential, which are shown schematically in Fig. 8. The choice between these two versions depends on the magnitude of the contribution of A_{Tl} to Γ_{Tl}. Some idea of the value of A_{Tl} could be obtained from the data on Tl adsorption at the metal–vacuum interface (Fig. 5), although in ref. 2 no measurements were carried out for dilute amalgams. Moreover, the concentration of the dipoles arising during thallium adsorption in the amalgam surface layer at the interface with the electrolyte can differ from their concentration at the metal–vacuum interface as the result of interaction with the electric field of the double layer. As these dipoles are turned with their negative (probably mercury) end inside the metal, their adsorption should increase in the presence in the solution surface layer of dipoles of opposite sign, which can arise, for example, as the result of adsorption of the ionic pairs Tl^+A^-, whose negative end faces the solution.

Let us consider first the version corresponding to curve 1 in Fig. 8, which takes account of the possibility of a significant dependence of Γ_{Tl} on A_{Tl} and, as it seems to us, enables one to interpret correctly the dependence of Γ_{Tl} and Γ_{Tl^+} on φ upon transition from the electrocapillary curve of the first kind to the curve of the second kind through the point of their intersection in the case of not too small Tl^+ and Tl concentrations. When passing from the ascending branch to the maximum and the descending branch of the electrocapillary curve of the first kind, thallium begins to enter the metal side of the double layer and there arise dipoles oriented with their negative end inside the metal. The appearance of these dipoles gives rise to a potential difference χ in the metal surface layer. At negative ε it has the same sign as the potential difference φ_1 between the metal surface and the plane in which the thallium ions centres are located. In the potential range indicated, this plane must be located closer to the metal surface than the plane of NO_3^- ions, since otherwise it would be impossible to account for the shift of the maximum of the electrocapillary curve of the first kind in a positive direction in the presence of Tl^+ in solution.

The shift of the potential $\Delta\varphi$ on the descending branch of the electrocapilla curve of the first kind can be represented as the sum of three terms:

$$\Delta\varphi = \Delta\chi + \Delta\varphi_1 + \Delta\varphi_2 = X\,\Delta c^{a}_{Tl} + \Delta\varphi_1 + \Delta\varphi_2 \qquad (9)$$

where X is the contribution of the dipoles to the total potential drop at the electrod solution interface, φ_2 the potential difference between the plane of Tl^+ ions and th solution bulk and c^{a}_{Tl} the surface concentration of the Tl–Hg dipoles*.

Let us see how the quantities contained in eqn. (9) change upon a potential shi in the negative direction, which increases c_{Tl} and hence c^{a}_{Tl}. Increase of the negati value of Xc^{a}_{Tl} can lead to a situation where, in spite of the negative value of $\Delta\varphi$, th value of the free charge ε becomes zero and with further shift of φ in the negati direction becomes positive. A similar change of sign of the free charge (but in this ca from positive to negative) is observed when dipoles formed by adsorbed oxyg appear on the surface of platinum metals[21-23]. As the result of the change of sign of the minimum on the curve of the first kind complying with the condition $\varepsilon - A_{Tl} =$ occurs at a more positive potential than the potential at which A_{Tl} becomes zer In this case, at the point of intersection of the electrocapillary curves of the first an second kinds the free surface charge is positive. Change to the positive charge lea in the case of adsorption of the ionic pairs Tl^+, A^- to their reorientation and a proach of the anionic end to the electrode surface. This conclusion is consistent wi the steep slope of the curve of the second kind at the point of intersection. Near th point of intersection, the slope of the curve of the first kind, determined by the val of $\varepsilon - A_{Tl}$, *i.e.* the difference of two positive quantities, should be small. The slope of t curve of the second kind is determined by the value of $\varepsilon + A_{Tl^+}$, *i.e.* the sum of tw positive quantities. As follows from the comparison of the behavior of thallium io in the presence of various anions[11], the value of A_{Tl^+} on the ascending branch of t curve of the second kind depends on the nature of the anion. High values of A_{Tl^+} see to be determined by adsorption on the surface, along with the NO_3^- ions, of the ion pairs Tl^+, NO_3^- or neutral complexes $TlNO_3$, oriented with their anionic en towards the metal (and perhaps also of anions of type $Tl(NO_3)_2^-$). The assumption the adsorption of neutral particles $TlNO_3$ would be similar to that of Barker according to which the high activity of the Pb^{2+} ion in the presence of Br^- is the res of the adsorption by mercury of the neutral $PbBr_2$ molecules**. Passing further alo the curve of the second kind, the value of A_{Tl^+} decreases, owing to the potential sh in the negative direction, which at $\mu_{Tl} = \text{const.}$ leads to a drop in the concentration thallium-containing ions in the solution, and finally A_{Tl^+} becomes zero. As a res eqn. (5) assumes the usual form of the electrocapillary curve equation with $-\varepsilon$ in right-hand side.

* The quantity c^{a}_{Tl} should be differentiated from A_{Tl}: the former is always positive and rises monot ically with increasing Tl concentration in the amalgam; the latter is a surface excess and with increasing concentration passes through a maximum and then becomes negative, which means that at sufficie high Tl content in the amalgam, the Tl concentration in the amalgam bulk increases faster than in the surf layer.

** The question whether it is necessary to explain the steep slope of the electrocapillary curve of second kind also by a certain specific interaction of Tl^+ with the positively charged surface, as Mott Watts-Tobin[18] do for the anodic end of the electrocapillary curve of mercury (appearance of Hg^+ ions the mercury surface), can be settled only after measurements of the quantity $(\partial\sigma/\partial\varphi)_{\mu_{Tl}}$ in the presenc fluorides have been carried out.

One of the arguments in favor of the correctness of the picture presented is the high value of $\varepsilon + A_{Tl^+}$ at the point of intersection of the curves of the second kind (*e.g.* curve 4, Fig. 4) with the curves of the first kind. This argument is however inapplicable to the curves of the second kind of amalgams with low Tl content, as for example curve 3, Fig. 4, especially in the case of their intersection with the curves of the first kind of mercury in solutions with low Tl^+ concentration (curve 1, Fig. 4). However, in this case as well the value of ε is probably positive at the intersection point, since this lies very near to the maximum of the curve of the first kind, *i.e.* to the potential of zero total charge, in which owing to the existence of the term A_{Tl} in the right-hand side of eqn. (6) ε has a positive value, even if a small one. Thus, in this case, if we move along the curve of the first kind from positive to negative potentials up to the point of its intersection with the curve of the second kind and then along the curve of the second kind, the value of ε should be positive up to a potential which lies close to the potential of the maximum of the curve of the second kind. Thus we approach the behavior of the mercury surface in solution without Tl^+ ions. This case is shown schematically in curve 2 of Fig. 8.

Since at the maximum of the electrocapillary curve of the second kind $\varepsilon + A_{Tl^+} = 0$ and A_{Tl^+} is a positive quantity, $\varepsilon < 0$. In other words, the potential of the zero free charge should be somewhat more positive than the electrocapillary curve maximum. The difference in the position of the zero points of free and total charges, which, as has been pointed out above, practically disappears in the case of concentrated amalgams, can be appreciable in the case of more dilute ones, since the concentration of Tl^+ ions in the solution which is in equilibrium with Tl amalgam at the potential of the electrocapillary curve maximum, increases significantly with decreasing amalgam concentration until a certain limit is reached[1,20], *e.g.* from $\sim 2 \times 10^{-6}$ *M* for the 41.5% amalgam to $\sim 10^{-3}$ *M* for the 1% amalgam (in the presence of 0.5 *M* Na_2SO_4). With further decrease in concentration, the equilibrium value of c_{Tl^+}, and hence that of $c^{a}_{Tl^+}$, drops. According to the data of this study, in the presence of *M* $TlNO_3$ the values of c_{Tl^+} are 2.7×10^{-5}; 5.3×10^{-5}; 2×10^{-4}; 1×10^{-4}; 3×10^{-5} *M* for 4.86; 0.68; 0.12; 0.014; 0.002 at.% Tl amalgams, respectively.

It should be noted that in the interpretation in this paper of the differences in the pzc values for electrocapillary curves both of the first and second kinds, as in earlier work, no account was taken of the potential difference arising at the boundaries between bulk metal phases, *i.e.*, the Galvani potential at the mercury/thallium amalgam boundary, which in the case of concentrated amalgams may be appreciable. The absolute value of χ can therefore be greater than the value obtained from measurements of the Volta potentials or of the shift of pzc without taking account of the Galvani potential at the boundary between the bulk metallic phases. This fact can be of importance when considering the difficulties associated with the extrapolation of the values of χ obtained from experiments with amalgams to the 100% surface coverage with Tl–Hg dipoles[1].

Finally, it was of interest to compare the transition from the electrocapillary curves of the first to those of the second kind under equilibrium conditions with the non-equilibrium double-humped curves obtained earlier. The result of such a comparison is shown in Fig. 9. The top curve (curve 1) has been obtained by means of a capillary electrometer during cathodic polarization of the 0.1 *M* $TlNO_3 + 0.9$ *M* KNO_3 solution, as described in refs. 9–11. The electrocapillary curves of the first and second

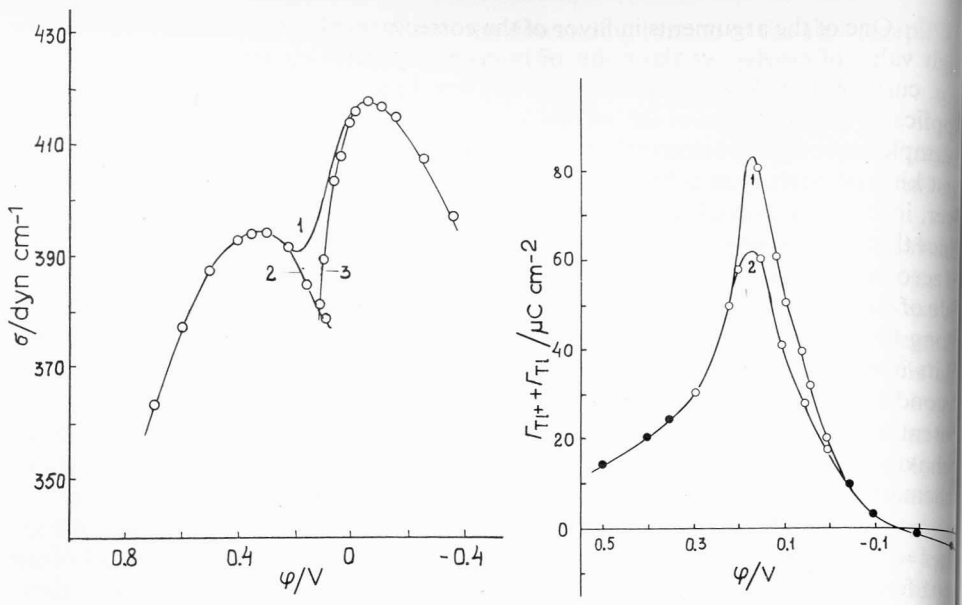


Fig. 9. σ, φ-Dependences in the Tl, Tl^+, Hg, H_2O system: (1) electrocapillary curve of mercury in 0.1 M $TlNO_3$+0.9 M KNO_3 (according to the data of ref. 11); (2) electrocapillary curve of the first kind in th 0.1 M $TlNO_3$+0.9 M KNO_3 system; (3) electrocapillary curve of the second kind for a thallium concn. i the amalgam $c_{Tl} \approx 0.4\%$.

Fig. 10. Dependence of total Tl adsorption on φ. (1) Along curve 1 of Fig. 9, (2) along upper parts of curves 3 of Fig. 9, (○) determined from eqn. (8); (●) determined from eqn. (10).

kind shown by circles have been chosen from the curves obtained in this wor because their maxima coincide with the first and the second maxima of the double humped curve, respectively. As is clear from Fig. 9, the ascending branch of the curv of the first kind completely merges with the corresponding ascending branch of th double-humped curve. A small shift of the descending branch of the double-humpe curve as compared with the descending branch of the curve of the second kind, n noticeable on Fig. 9, is due to trivial reasons discussed in refs. 6 and 9. Of interest is th significant difference in the values of σ obtained in both cases in the potential rang close to the point of intersection of the curves of the first and second kinds. Th proves, in particular, that it is impossible to determine the value of total adsorptio according to eqn. (8) from the values of $\partial\sigma/\partial\varphi$ measured under non-equilibriu conditions. This must be kept in mind when drawing conclusions from the double humped electrocapillary curves, obtained by determining the dependence of the me cury drop time on potential in solutions containing reducible substances, often cite in the polarographic literature.

Curve 2 of Fig. 10 gives the dependence of the total thallium adsorptio $\Gamma_{Tl}+\Gamma_{Tl^+}=A_{Tl}+A_{Tl^+}$ on φ along the double humped σ, φ curve of Fig. 9; curve the corresponding dependence when passing from the electrocapillary curve of th first kind of Fig. 9 to that of the second kind. The $\Gamma_{Tl}+\Gamma_{Tl^+}$ values were determine from eqn. (8) and in the potential range in which the necessary $(\partial\sigma/\partial\varphi)_{\mu_{Tl^+}}$ an $(\partial\sigma/\partial\varphi)_{\mu_{Tl}}$ data were not available, from the Gibbs equation in the form

$$\Gamma_{Tl}+\Gamma_{Tl^+} = -\left(\frac{\partial\sigma}{\partial\mu_{Tl}}\right)_{\varphi} = -\left(\frac{\partial\sigma}{\partial\mu_{Tl^+}}\right)_{\varphi} \quad (10)$$

Of special interest is the maximum of total thallium adsorption in the neighbourhood of the intersection potential, especially pronounced in the case of curve 1.

To make more precise the schemes suggested here and in particular to determine how they should be modified to account for partial charge transfer, it is necessary to determine the electrocapillary curves of the first and second kinds in the presence of other anions and also neutral adsorbable molecules. It would be of interest to measure the differential capacity of mercury in thallium salt solutions at low electrolyte concentrations in order to determine in what measure the maximum of the electrocapillary curve of the first kind in the Hg, Tl, Tl^+ system determines the position of the potential of zero free charge. It would be essential also to determine thallium adsorption and work function at the amalgam/vacuum interface in a wide concentration range. Since this programme will take time, we thought it expedient to present the results so far obtained in spite of the tentative nature of some of the conclusions.

CONCLUSIONS

The electrocapillary curves of the Hg, Tl, Tl^+, H_2O system have been measured in the presence of a KNO_3 excess at μ_{Tl^+} = const. and μ_{Tl} = const., respectively, in a wide range of concentration of Tl^+ ions and of Tl in thallium amalgam. It is shown that the results obtained can be interpreted on the basis of Lippman's equation for reversible redox systems. According to this interpretation, of essential importance are the surface excesses of Tl^+ ions in solution A_{Tl^+} and of Tl atoms in the metal phase A_{Tl}. Unlike A_{Tl^+}, which increases monotonically with increasing μ_{Tl^+}, A_{Tl} with increasing μ_{Tl} passes through a maximum, then decreases and becomes negative. On the basis of all the experimental data on the Hg, Tl, Tl^+, H_2O system, we can conclude that in addition to the potentials of the free zero charge lying near the maxima of the electrocapillary curves of the first and second kind, there can exist a third potential of the free zero charge in the intermediate region, at which the free surface charge passes from negative to positive values when the potential shifts in the negative direction. This phenomenon is associated with the appearance of a dipole potential in the surface layer of the metal phase when thallium atoms enter into it.

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