THE ADSORPTION OF THALLOUS IONS AND THALLIUM ATOMS AT THE MERCURY–SOLUTION INTERFACE

A. FRUMKIN

Academy of Sciences, U.S.S.R., Institute of Physical Chemistry, Moscow

IT is usually assumed that inorganic cations show no marked specific adsorbability at the mercury–solution interface. Although this statement is not quite unambiguous, since the concept of specific adsorbability can be defined in different ways and, particularly in the case of the Cs^+ ion, there are some indications of an interaction with the mercury surface which is not purely coulombic (GRAHAME 1952; FRUMKIN, DAMASKIN, and NIKOLAJEVA 1957), it must be admitted that a typical specific adsorbability which might perhaps be compared with that of the Br^- anion has not hitherto been observed for inorganic cations. It will here be shown that the Tl^+ ion displays a decided specific adsorbability which is quite comparable with that of inorganic anions.*

FRUMKIN and GORODETZKAJA (1928) have recorded electrocapillary curves for thallium amalgams at potentials for which the anodic dissolution of thallium was negligible, so that the concentration of the amalgam remained constant. In N sodium sulphate solution, thallium lowers the mercury–solution interfacial tension, σ, if the potential, ϕ, is larger than $c. - 0.75$ V,† and raises σ for more negative potentials, so that the electrocapillary curve for the amalgam cuts that of mercury in the neighbourhood of this potential value. The maximum of the electrocapillary curve is displaced by thallium in the direction of more negative potentials. The results obtained could be explained on the assumption that thallium is adsorbed in the form of atoms, and that the Hg–Tl bond is polar, such that the positive end of the surface dipole is directed towards the solution. As a consequence of the polarity of the Hg–Tl bond, the energy of adsorption is potential dependent and becomes negative for sufficiently negative potentials. For the quantitative description of this situation, the concentration of thallium atoms in the surface layer, $(c_{Tl})_{ad.}$ can be represented as a function of the quantity $RT \log a_{Tl} + BF\phi$:

$$(c_{Tl})_{ad.} = f_1(RT \log a_{Tl} + BF\phi) \quad . \quad . \quad . \quad . \quad (1)$$

where a_{Tl} is the activity of thallium in the amalgam and B has the approximately constant value of 0.22 over the range $-1.1 < \phi < -0.7$ V. This

---

* Fuller details concerning the electrocapillary behaviour of the Tl^+ ion are given elsewhere (FRUMKIN and POLJANOVSKAJA 1958; FRUMKIN and TITIEVSKAJA 1957).

† Except when otherwise stated, all potentials are measured against the N.C.E.

relation holds for amalgams in which the thallium content does not exceed 10 per cent. The quantity B can be regarded as a measure of the polarity of the Hg–Tl bond. Indeed, if this were non-polar or, more accurately expressed, if the adsorption of thallium were not to alter the distribution of charge in the mercury–solution interface, B would have to be zero.

The electrocapillary curves which can be obtained with pure mercury in a solution of thallous ion, over a potential range such that no marked amalgam formation results from the discharge of thallous ions, represent the counterparts to those recorded by Frumkin and Gorodetzkaja. Electrocapillary curves so obtained by Frumkin and Titievskaja (1957) are shown in Figs. 1 and 2. It will be seen that the thallous ion displaces the maximum of the electrocapillary curve in the direction of more positive potentials and lowers σ by an amount which increases as the cathodic polarization increases,
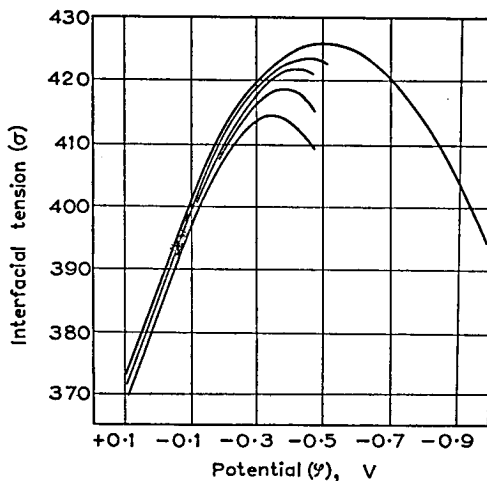

Fig. 1. Electrocapillary curves for mercury in solutions N in sulphuric acid and x N in thallous sulphate. Curves from top to bottom: $x = 0$, 0·01, 0·025, 0·05 and 0·1.

as one would expect for a surface-active cation. Determination of the potential of the charge null-point by means of a dropping electrode gave values which were in good agreement with the results of the electrocapillary measurements.

The decrease in the interfacial tension, $\Delta\sigma$, caused by the thallous ion is greater in the presence of nitrate ions than in the presence of sulphate ions. The adsorption of thallous ions is therefore influenced not only by the interaction with the mercury surface, but also by the anions adsorbed on this surface. The fact that $\Delta\sigma$, particularly in nitrate solutions, does not vanish as the positive charge on the mercury surface increases is in agreement with this. Similar conditions are met in the investigation of the adsorption of organic cations, e.g. $N(C_3H_7)^+$ (Gouy 1906), although only in the presence of anions such as Br^-, which display a marked specific adsorbability. In the case of solutions containing the nitrate ion, the observed

dependence of the quantity $\Delta\sigma$ upon potential, and upon the concentration of thallous ion, $c_{Tl}+$, can be represented by the equation:

$$\Delta\sigma = f_2(RT \log c_{Tl}+ - 0.16F\phi) \qquad . \quad . \quad . \quad . \quad (2)$$

over the potential range from -0.25 to -0.45 V, where f_2 denotes a function of the quantity in brackets.
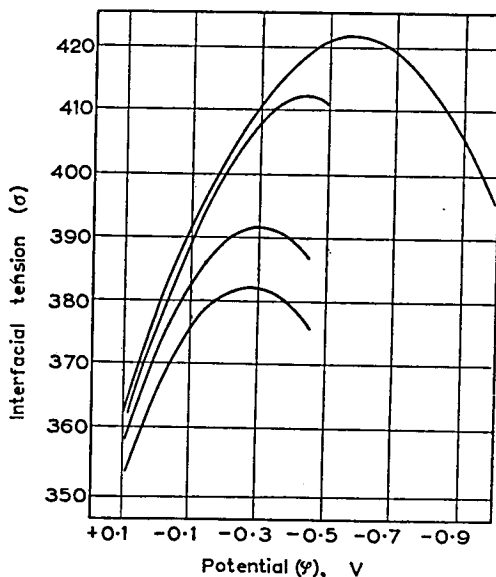

FIG. 2. Electrocapillary curves for mercury in solutions N in potassium nitrate, 0.01 N in nitric acid and x N in thallous nitrate. Curves from top to bottom: $x = 0, 0.01$, 0.1 and 0.2.

The mercury which is in contact with the thallous salt solution must contain a definite concentration of thallium, which can easily be computed from the equilibrium potential of the thallium amalgams. This concentration is small over the potential range in which the electrocapillary measurements were made; for example, it amounted to c. $10^{-3.8}$ per cent at the maximum of the electrocapillary curve for a solution N in sulphuric acid and 0.1 N in thallous sulphate, which lies at $\phi = -0.33$ V.

One could now attempt to interpret the observed decreases in σ by the adsorption of the thallium atoms dissolved in the mercury, assuming that for positive potentials thallium also occurs as atoms at the boundary. However, this assumption contradicts the following facts. With the aid of the expression:

$$RT \log c_{Tl}+ = RT \log a_{Tl} + F\phi + \text{const.}$$

eqn. (2) can be brought to the form:

$$\Delta\sigma = f_2(RT \log a_{Tl} + 0.84 F\phi) \qquad . \quad . \quad . \quad . \quad (3)$$

From eqns. (1) and (3), it follows that $B = 0.84$, whereas the experiments with amalgams gave $B = 0.22$. Hence, if one wished to interpret the adsorption of thallium at positive potentials as atomic adsorption, a significantly larger polarity would have to be attributed to the Hg–Tl bond than that obtained from the experiments with amalgams. One can arrive at the same conclusion, i.e., that there is a real difference in the mechanism of adsorption in the two potential regions investigated, by a somewhat different path. The quantity σ in a solution N in sulphuric acid and 0.1 N in thallous sulphate when $\phi = -0.33$ V is lowered by 7.5 dyn/cm in comparison with a N sulphuric acid solution at the same potential. According to Frumkin and Gorodetzkaja, the same value for $\Delta\sigma$ is obtained in N sodium sulphate for $\phi = -0.7$ V with a thallium concentration of c. 2.1 per cent, which corresponds to $a_{Tl} = 2.8 \times 10^{-2}$ (LEWIS and RANDALL 1921). If one calculates from eqn. (1) the activity of thallium which should correspond to $\Delta\sigma = 7.5$ for $\phi = -0.33$ V, using the value 0.22 for B, which holds over the range $-0.7 > \phi > -1.1$ V, one obtains $a_{Tl} \sim 10^{-3}$. The concentration of thallium should therefore be c. 0.1 per cent, whereas the value obtained experimentally is $10^{-3.8}$ per cent (see above), almost three powers of ten smaller.

Measurement of the electrocapillary curves by FRUMKIN and TITIEVSKAJA (1957) was stopped at $\phi = -0.45$ V, owing to the onset of amalgam formation. Since the potential of a 0.1 per cent thallium amalgam in contact with a solution 0.2 N in thallous nitrate, 0.8 N in potassium nitrate and 0.0077 N in nitric acid is -0.489 V, the thallium concentration in the mercury in contact with this solution for $\phi = -0.45$ V is c. 0.014 M. Peculiar phenomena are encountered if one extends the measurement of interfacial tension to more negative potentials despite the onset of amalgam formation. Performing these measurements with a Gouy capillary electrometer leads to no difficulties, and the ohmic drop in the capillary tube does not exceed 2.8 mV in the case of a solution of the composition specified above, as will be shown subsequently. The result of such measurements is shown in Fig. 3. It will be seen that a second maximum occurs at more negative potentials, which appears surprising, but which can be interpreted without difficulty.

For increasing cathodic polarization, the concentration of thallium in the mercury in contact with the solution rises, following an exponential law initially. Simultaneously, the layer of solution at the mercury boundary is impoverished of Tl^+; consequently a continuous transition occurs from the system Hg–Tl^+ solution to the system Hg+Tl in a Tl^+ free solution.

When $\phi = -0.517$ V, the volume concentration of thallium becomes the same in both phases; thus this potential can to a certain extent be considered to be the boundary between the regions wherein each system exists. For increasing cathodic polarization, the concentration of thallous ions in the solution in the vicinity of the mercury surface becomes arbitrarily small, while the concentration of the thallium amalgam in the neighbourhood of the interface, c_{Tl}^s (not to be confused with the concentration of adsorbed thallium in the surface layer, $(c_{Tl})_{ad.}$), approaches a limiting value $(c_{Tl}^s)_{lim.}$, which is determined by the bulk concentration of thallous ions as well as by

the conditions in the capillary tube of the electrometer for the diffusion of thallous ions in the electrolyte solution and of thallium atoms in the mercury. By comparison of the values $\phi_{max.}$ and $\Delta\sigma_{max.}$, which correspond to the second maximum in Fig. 3, with the data given by FRUMKIN and GORO-DETZKAJA (1928) for thallium amalgams, it can be concluded that for sufficiently negative potentials the concentration of thallium in the amalgam formed in the immediate vicinity of the boundary is *c.* 0·45 per cent or
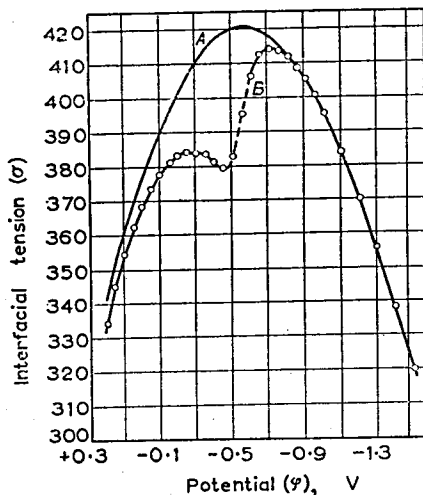

FIG. 3. Dependence of the interfacial tension upon potential: Curve A, mercury in N potassium nitrate solution; curve B, mercury in a solution 0·8 N in potassium nitrate, 0·2 N in thallous nitrate and 0·0077 N in nitric acid. $t = 19°C$.

0·3 M, and is therefore of the same order of magnitude as that of the bulk concentration of thallous ions in the solution. The concentration of the K^+ and NO_3^- ions, $c^s_{K^+} = c^s_{NO_3^-}$, which appear in the neighbourhood of the mercury surface when the thallous-ion concentration falls to zero, is given by $(c^o_{K^+})^{\frac{1}{2}}(c^o_{NO_3^-})^{\frac{1}{2}} = 0.895$ N, where $c^o_{K^+}$ and $c^o_{NO_3^-}$ represent the corresponding bulk concentrations (EUCKEN 1907). The position of the experimentally determined descending branch, which is displaced by *c.* 0·01 V in the direction of more negative potentials compared with the descending branch for N potassium nitrate, corresponds to that which one would expect for a 0·45 per cent thallium amalgam in a *c.* 0·9 N potassium nitrate solution when one considers the potential drop in the capillary tube of the electrometer. The latter is $(RT/F)\ln(c^o_{K^+})^{-\frac{1}{2}}(c^o_{NO_3^-})^{\frac{1}{2}} = 2.8$ mV (EUCKEN 1907).

As shown by Fig. 3, in a system containing mercury and thallium two charge null-points occur, which are separated by 0·44 V. It must be noted, however, that changing the experimental fact that two maxima occur in the electrocapillary curve into the assertion that two charge null-points exist is to some extent conventional: because, if we interpret the left-hand maximum

N

(Fig. 3, curve B) as a charge null-point, we do not add the charges of the adsorbed thallous ions to the charge of the metal surface, whereas in considering the right-hand maximum (Fig. 3, curve B) the charges on the thallium atoms, which form the positive end of the Hg–Tl dipoles, are included in the charges on the mercury surface (these charges are compensated by the negative charges of the mercury atoms contained in these dipoles). The reason for the difference in the treatment of the two cases rests upon the assumption that in one case the thallium is found in the surface layer in the form of ions, and in the other case as atoms.

Thallous ions are not only adsorbed on mercury, but also on platinum. This can be proved by means of a method which has recently been developed in the Electrochemical Laboratory of Moscow University (OBRUCHEVA 1958). The surface of a platinized platinum electrode in N sulphuric acid, which has been brought to a potential within the range 0·3 to 0·7 V (against the hydrogen electrode), contains mainly ions of the double layer, and only a few adsorbed hydrogen or oxygen atoms. If one adds to this solution, in which is immersed a similar electrode carrying no current, a solution containing a specifically adsorbed ion, taking extreme care to exclude atmospheric oxygen, a displacement of the potential occurs in the cathodic or anodic direction which indicates the adsorption of the corresponding ion. Thus if the concentration of potassium bromide is brought to 0·1 N, the potential of the platinum electrode is displaced from 0·6 to 0·25 V. Addition of thallous sulphate displaces the potential in the anodic direction; as the concentration of thallous ion reaches 0·1 N, the potential displacement amounts to 0·6 V for an initial potential of 0·3 V. The adsorption of thallous ion causes an extensive change in the form of the charging curve, indicating a marked decrease in the adsorbability of hydrogen atoms.

With the aid of this method, it can be shown that Cd^{2+}, Pb^{2+} and Zn^{2+} cations also show specific adsorbability on a platinum electrode, albeit to a different extent.

REFERENCES

EUCKEN, A. (1907) Z. phys. Chem. **59**, 72.
FRUMKIN, A. and GORODETZKAJA, A. (1928) ibid. **136**, 451.
FRUMKIN, A., DAMASKIN, B. and NIKOLAJEVA, N. (1957) C.R. Acad. Sci. U.S.S.R. **115**, 751
FRUMKIN, A. and POLJANOVSKAJA, N. (1958) J. Phys. Chem. U.S.S.R. **32**, 157.
FRUMKIN, A. and TITIEVSKAJA, A. (1957) ibid. **31**, 485.
GRAHAME, D. C. (1952) Proc. Third Meeting C.I.T.C.E. p. 330.
GOUY, G. (1906) Ann. Chim. Phys. [8], **9**, 75.
LEWIS, G. N. and RANDALL, M. (1921) J. Amer. Chem. Soc. **43**, 233.
OBRUCHEVA, A. (1958) J. Phys. Chem. U.S.S.R. in the press.