

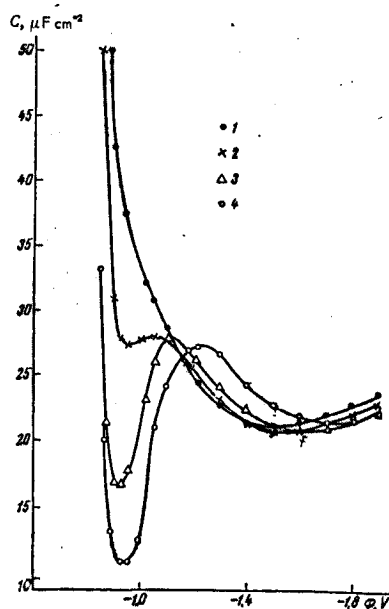


Fig. 2. Differential-capacity curves for 40% thallium amalgam in NaF solutions at 400 c/s: 1) 0.9; 2) 0.1; 3) 0.01; 4) 0.002 N.

The relay operates as follows. At the instant of separation of the drop a voltage impulse is observed in the measuring diagonal of the bridge, since the resistance of the system rises, while the capacity falls almost to zero. This signal passes from the plates of the cathode-ray tube of the null instrument via a cathode follower comprising the first 6Zh4 valve, is detected by a DGTs-24 diode, and triggers a second 6Zh4 valve, which is cut off in the absence of a signal. The relay I closes the contacts I'. In the absence of balance, the second half of the 6N8 valve is cut off, since a signal of negative polarity is supplied to its grid by the DGTs-7 diode. Relay II, connected in the anode circuit of this valve, does not operate, and since its contacts II' are normally closed, relay III closes contacts III' and switches on the electric clock. Since relay III has a locking device III'', the clock remains switched on until relay II is opened. This corresponds to the instant at which the bridge is in balance, when the potential difference in the measuring diagonal of the bridge is zero. At this moment the voltage blocking the second half of the 6N8 valve is a minimum, the valve is triggered off, and current flows through the winding of relay II. The contacts II' open, and interrupt the current in the winding of relay III, which thus switches off the clock.

The dropping electrode of thallium amalgam used in the present work differed from the usual polarographic electrodes in that the tip of the capillary was splayed out in order to eliminate the screening of the drop by the edges of the capillary and thus to achieve a more uniform polarization¹¹. The auxiliary electrode was a platinum sphere symmetrically surrounding the dropping electrode and having two openings, the upper one for admission of the capillary and the lower one for removal of the drops of amalgam which had broken off. The reference electrode

was a normal calomel electrode, and all values of potentials in this paper are given in volts relative to the potential of this electrode as zero. Measurements were carried out at frequencies of 50, 400, 2500, and 10000 c/s. It was difficult to employ frequencies above 400 c/s in solutions more dilute than 0.01 N because of the insensitivity of the bridge, due to the capacitive reactance in this case becoming far smaller than the resistance.

In work with amalgam electrodes there is a possibility of ready oxidation of the amalgam, as a result of which the capillary may become obstructed, and the rate of discharge of the amalgam may change, inevitably leading to errors in the determination of the surface of the drop [see Eqn. (1)]. To avoid this, hydrogen is usually passed for a long time through the system containing the amalgam. In the present work this difficulty was overcome by sealing the capillary directly to the vessel containing the thallium amalgam. The amalgam was covered with a layer of redistilled water, and subjected to strong cathodic polarisation. No oxidation of the amalgam occurred, and its rate of discharge from the capillary remained constant within the limits of experimental error.

The amalgam was prepared from metallic thallium of high purity and mercury which had first been purified in the usual way and then twice redistilled in a vacuum. The amalgam was analysed by Daniels' method¹⁵, a weighed amount being placed in an excess of standard sulphuric acid and air being sucked through a capillary immersed in the amalgam. After the amalgam had decomposed, the excess of acid was back-titrated. All salts were recrystallised twice from redistilled water and ignited. Redistilled water was used to make up the solutions. Before an experiment, a current of purified hydrogen was passed through the test solution for 1½ h to remove dissolved oxygen. All experiments were carried out at a room temperature of 18°–20°.

Differential-Capacity Measurements

Capacity curves were determined for 40% thallium amalgam in 0.9, 0.1, 0.01, and 0.002 N NaF solutions at a frequency of 400 c/s. Fig. 2 shows that the minimum in the capacity curve is most clearly defined in 0.002 N NaF (10.8 $\mu\text{F cm}^{-2}$), and gradually disappears as the concentration increases, being 16.8 $\mu\text{F cm}^{-2}$ in 0.01 N and 27.4 $\mu\text{F cm}^{-2}$ in 0.1 N solution. In 0.9 N NaF solution the minimum in the differential-capacity curve has completely disappeared, which indicates that the minimum is related to the diffuseness of the double layer in the vicinity of the zero-charge point. In fact, the potential corresponding to the minimum in the capacity curve in 0.01 N NaF, which was measured most carefully, was -0.925 V, while the zero-charge point of a 41.5% thallium amalgam determined in 1 N Na_2SO_4 from electrocapillary curves is at -0.930 V.⁸ The minimum in the capacity curves near zero charge is known to be shifted towards negative potentials in the presence of surface-active anions¹⁶. Fig. 3 shows capacity curves for 40% thallium amalgam measured in 0.1 and 0.01 N KCl solutions at frequencies of 400 and 10000 c/s. In 0.01 N KCl minimum capacity occurs at a potential of -0.950 V, i.e. 25 mV more negative than with 0.01 N NaF, which exhibits no specific adsorption on a mercury surface¹⁷. The differential-capacity curve of 40% thallium amalgam in 0.1 N NaF has a minimum close to the zero-charge point (Fig. 2), whereas no minimum is present in the case of mercury. As calculations have shown,

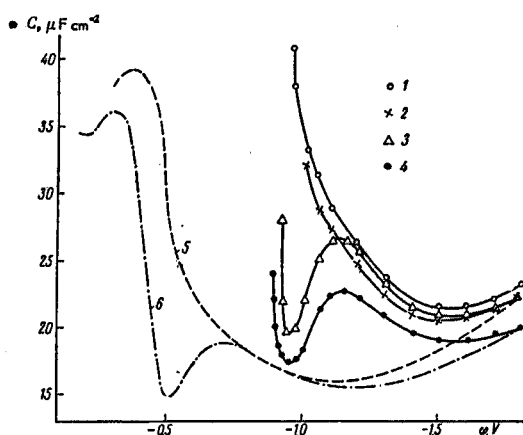


Fig. 3. Differential-capacity curves for 40% thallium amalgam and mercury in KCl solutions. Tl amalgam: 1) 0.1 N, 400 c/s; 2) 0.1 N, 10 000 c/s; 3) 0.01 N, 400 c/s; 4) 0.01 N, 10 000 c/s. Mercury: 5) 0.1 N; 6) 0.01 N.

this result is associated with the fact that the capacity of the dense layer is appreciably greater for 40% thallium amalgam than for mercury. On passing to 0.1 N KCl solution, however, the minimum in the capacity curve disappears also with 40% thallium amalgam (Fig. 3), which again is linked with the specific adsorption of the Cl^- anion diminishing the diffuseness of the double layer near the zero-charge point.

In order to study the dependence of the position of the zero-charge point on the concentration of the thallium amalgam, capacity curves were measured for more dilute amalgams right down to 0.01%, the results for 0.01 N NaF being illustrated in Fig. 4. With dilution of the amalgam the depth of the minimum can be seen to diminish, and the minimum itself is shifted towards more positive potentials. With a 0.1% thallium amalgam the minimum has completely disappeared. The sharp rise in the capacity curve to the left of the minimum is due to a pseudo-capacity. Actually, in the case of reversible electrode reactions, among which the ionisation of thallium can be included to a first approximation, an equilibrium concentration of metal ions is formed at the electrode surface. The equilibrium concentration of Tl^+ ions at the zero-charge point has been determined for different thallium amalgams by Frumkin and Cirves⁹, who showed that this concentration increases with dilution of the amalgam right down to 0.1%. On the other hand, the pseudo-capacity is greater the higher the equilibrium concentration of metal ions at the electrode surface¹⁸. Thus the more dilute the thallium amalgam, the greater the influence of the pseudo-capacity in determining the zero-charge point and the shallower the minimum in the capacity curve. It is reasonable to assume that the rise in the curve due to the pseudo-capacity may not only make the minimum less deep but also shift it to more negative potentials. In fact, on comparing the results obtained for the zero-charge point of thallium amalgams by Frumkin and Gorodetskaya⁸ as well as by Frumkin and Cirves⁹ with the potentials of the minimum capacity (Fig. 4), it is readily seen that with dilute amalgams the potentials of the minimum are 70–80 mV more negative than the zero-charge points obtained from electrocapillary

curves and by the method of zero-charge solutions. Determination of the zero-charge point from the position of the minimum in the capacity curves in dilute solutions thus leads to correct results only with a concentrated thallium amalgam, when the equilibrium concentration of Tl^+ ions at the electrode surface is sufficiently low.

A study has also been made in the present work of the variation of the capacity of the double layer on thallium amalgam with the a.c. frequency. With dilute amalgams no frequency dispersion of the capacity occurs over the range 400–10 000 c/s, except at the most positive potentials, where the dispersion is due to pseudo-capacity (Fig. 5). With 40% thallium amalgam, however, dispersion of the capacity with frequency is observed at all potentials. Fig. 6 shows capacity curves for 40% thallium amalgam in 0.1 N NaF solution at frequencies of 50, 400, and 10 000 c/s. At potentials between -1.9 and -1.4 V the difference in the magnitude of capacities measured at frequencies of 50 and 10 000 c/s amounts to $2 \mu\text{F cm}^{-2}$, within the limits of experimental error. At more positive potentials a sharp increase in dispersion is observed, due to the effect of pseudo-capacity. A similar dependence of capacity on a.c. frequency was observed with 40% thallium amalgam in 0.9 and 0.01 N NaF solutions, as well as in 0.1 and 0.01 N KCl solutions (Fig. 3).

DISCUSSION

In order to confirm the conclusion that the minimum on the differential-capacity curves for 40% thallium amalgam in dilute solutions is associated with diffuseness of the

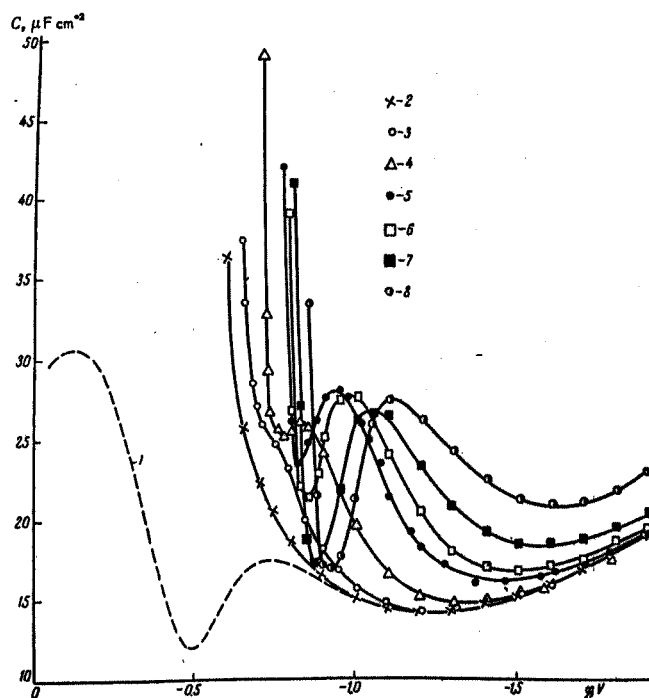


Fig. 4. Differential-capacity curves for mercury and for thallium amalgams of different concentrations in 0.01 N NaF at 400 c/s: 1) mercury; 2) 0.01% Tl; 3) 0.1% Tl; 4) 1.2% Tl; 5) 5.0% Tl; 6) 9.05% Tl; 7) 19.22% Tl; 8) 40.0% Tl.

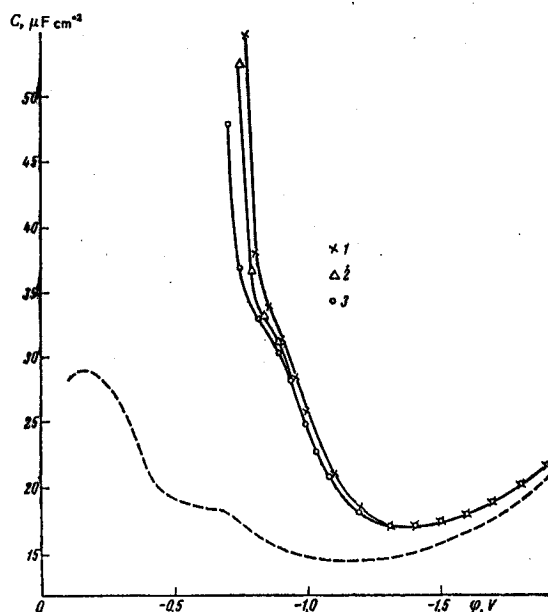


Fig. 5. Differential-capacity curves for mercury (broken curve) and 4.6% thallium amalgam in 0.1 N NaF at various frequencies: 1) 50; 2) 400; 3) 10 000 c/s.

double layer and hence defines the zero-charge point, a calculation was made of the capacity curves for the 40% amalgam in 0.1, 0.01, and 0.002 N solutions from the experimental curve in 0.9 N NaF. The differential capacity of an electrode may be regarded as the result of connecting in series two condensers, equivalent to the dense and the diffuse parts of the double layer:

$$\frac{1}{C} = \frac{1}{C_{\text{den}}} + \frac{1}{C_{\text{diff}}}, \quad (2)$$

where C is the total measured capacity of the double layer, C_{den} is the capacity of the dense part of the double layer,

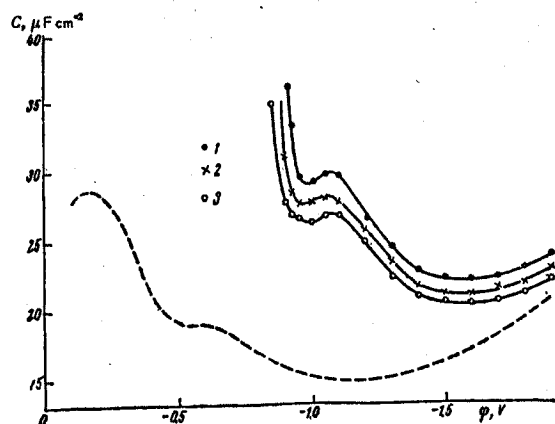


Fig. 6. Differential-capacity curves for mercury (broken curve) and 40.0% thallium amalgam in 0.1 N NaF at various frequencies: 1) 50; 2) 400; 3) 10 000 c/s.

which in the absence of specific adsorption is, on Grahame's hypothesis¹⁸, a function of the charge density q and is independent of the concentration of the solution; C_{diff} is the capacity of the diffuse layer, which for a uni-univalent electrolyte can be readily calculated from the equation²⁰

$$C_{\text{diff}} = 19.49(137c + q^2)^{1/2}, \quad (3)$$

where q is the surface charge in $\mu\text{C cm}^{-2}$ and c is the molar concentration of the solution. The calculation was carried out by first representing the capacity in 0.9 N NaF measured at 50 c/s as a function of the surface charge, the charge corresponding to a given potential being found by numerical integration of the equation

$$q = \int_0^{\varphi_a} C d\varphi, \quad (4)$$

where φ_a is the potential measured relative to the zero-charge point of 40% thallium amalgam. The capacity of the dense layer C_{den} was then determined as a function of the charge q on the electrode by means of Eqn. (2) from the experimental values of the capacity and the calculated values of C_{diff} [Eqn. (3)]. Using the values found for C_{den} and the calculated values of C_{diff} for 0.1, 0.01, and 0.002 N solutions, the total differential capacity for these solutions was calculated as a function of q from Eqn. (2). The values of the potentials corresponding to a given charge were obtained by numerical integration of the equation

$$\varphi_a = \int_0^q \frac{1}{C} dq. \quad (5)$$

The results of the calculation are illustrated in Fig. 7 (a-c), which includes for comparison experimental curves of the capacity of 40% thallium amalgam measured in the corresponding solutions of NaF at 400 c/s. The experimental and calculated curves are seen to be similar in shape and position, which indicates the applicability of the double-layer theory to 40% thallium amalgam electrodes. The agreement is not perfect, however, the difference exceeding the errors in the measurements. At positive potentials the discrepancy is caused by the pseudo-capacity. On the other hand, Grahame's method of calculation¹⁹ used here assumes that, at the same surface charge, the capacity of the dense layer is independent of electrolyte concentration, which is possible only in the absence of any specific adsorption of the ions comprising

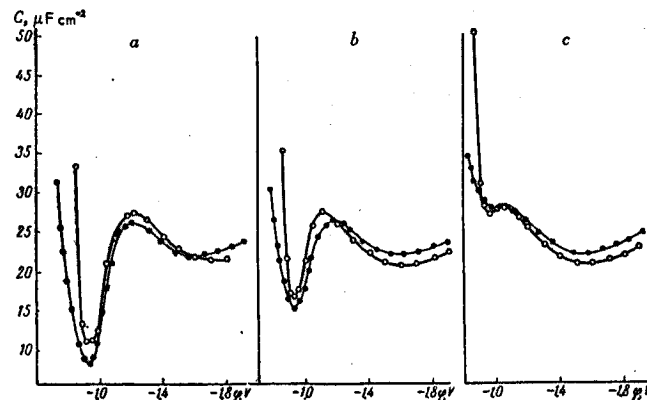


Fig. 7. Calculated and experimental differential-capacity curves for 40% thallium amalgam in NaF solutions: a) 0.002 N; b) 0.01 N; c) 0.1 N; solid points - calculated; open circles - experimental.

the electrolyte and forming part of the double layer. This assumption evidently does not apply so well to thallium amalgam as to mercury. In order to explain such a difference there is no need to assume any specific adsorption of F^- or Na^+ ions on the surface of the thallium amalgam. It is sufficient that the conditions for the adsorption of ions, determined by their effective radii, should be somewhat different for the two metallic systems. Change in the concentration of thallium atoms, with the charge remaining constant, should then have an effect on the structure of the double layer. Since the composition of the surface of the thallium amalgam changes with potential⁸, variation in the electrolyte concentration should affect the adsorption of thallium atoms [in the surface layer? (Ed. of Translation)] and hence the capacity of the dense layer at constant surface charge.

Another noteworthy result with 40% thallium amalgam is the presence of a constant dispersion of the capacity of the double layer at negative potentials. This dispersion cannot be explained by ionisation of thallium at such negative potentials, nor by the discharge of Tl^+ ions which may be present in solution as a result of decomposition of the amalgam which accumulates at the bottom of the cell. Indeed, we have shown that the capacity curves are of the same form whether or not Tl^+ ions are added to the solution. Besides, with more dilute amalgams, dispersion of the capacity with frequency is absent at these potentials (Fig.5).

If it is assumed that the heat of adsorption of water is greater on the surface of 40% thallium amalgam than on a mercury surface, the dispersion of capacity with frequency at negative potentials can then be explained, according to Bockris and Conway¹³, by the slow relaxation of H_2O molecules in the double layer. On the other hand, negative adsorption of thallium atoms occurs at the negatively charged surface of the amalgam, as Frumkin and Gorodetskaya⁸ have shown; a second cause of dispersion of the capacity in this potential range may therefore be slow establishment of the adsorption equilibrium.

Further investigation is required to ascertain the causes of the relatively potential-independent dispersion of capacity on 40% thallium amalgam. Nevertheless, it was of interest to determine at what frequencies the results of the measurements would correspond with the true values of the capacity of the double layer. For this purpose a comparison was made of the difference in charges on 40% thallium amalgam and on mercury at a potential of -1.85 V determined from electrocapillary curves in 1 N Na_2SO_4 ⁸ and by integration of capacity curves in 0.9 N NaF measured at different frequencies.

The calculations showed that the charge differences determined by the two methods agree only at low a.c. frequencies. In fact, the difference in charges found from electrocapillary curves is $1.20 \mu C \text{ cm}^{-2}$, and that from the capacity curve at 50 c/s is $1.0 \mu C \text{ cm}^{-2}$. Thus the true values of the capacity of the double layer on 40% thallium amalgam at negative potentials correspond to the results of measurements made at low a.c. frequencies.

We express our thanks to Academician A. N. Frumkin for suggesting the subject and for his interest, and also to B. S. Sekovanov for valuable advice in designing the relay.

SUMMARY

1. A method has been worked out for obtaining differential-capacity curves at a dropping amalgam electrode.

2. Capacity curves have been measured for thallium amalgams (between 0.01 and 40%) in NaF and KCl solutions of different concentrations at a.c. frequencies between 50 and 10 000 c/s. The minimum in the differential-capacity curve in dilute solutions coincides with the zero-charge point in the case of 40% thallium amalgam but is more negative than the latter with more dilute amalgams.
3. Capacity curves were calculated for 0.1, 0.01, and 0.002 N solutions from values of the differential capacity of 40% thallium amalgam in 0.9 N NaF at 50 c/s. Experimental and calculated curves proved to be similar in shape and position, which indicates the applicability of the double-layer theory to 40% thallium amalgam electrodes.
4. In the case of 40% thallium amalgam, a frequency-dependent dispersion, differing little with potential, is observed in the differential-capacity curves at negative polarisations; true values of the capacity of the double layer are determined at low frequencies of the alternating current.

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