ELECTROCAPILLARY PROPERTIES OF AMALGAMS

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Electrocapillary curves of dilute amalgams of different metals have been investigated by Rothmund,[1] Gouy,[2] and Christiansen.[3]

These investigators found that the maximum value of surface tension of these amalgams occurs at the same potential difference between solution and metal as is the case with pure mercury. On this basis it was often assumed that the position of the electrocapillary maximum is independent of the nature of the metallic phase. However, with a more concentrated amalgam of a Bi+Pb+Sn alloy, Gouy observed a marked shift of the maximum and a similar shift was found by Rothmund in the case of a thallium amalgam, but was ascribed to experimental errors caused by the action of the solution on the amalgam.

Frumkin and Gorodetzkaja[4] made an extensive study of the behavior of thallium amalgams in different solutions and found that the addition of the thallium causes a large shift of the maximum toward increased values of cathodic polarisation of the metallic surface. This shift may amount to as much as 0.45 volt for concentrated amalgams. Its value, although not quite independent of the nature of the solution, does not change very much with changes in the composition of the aqueous phase. The authors could show that it is possible to give a mathematical treatment of the curves observed on the basis of Gibbs' theory of surface equilibria. It follows from this theory that the electrocapillary curve of an amalgam must obey the same differential equation of Lippmann-Helmholtz which applies to a pure metal:

$$\frac{\partial\sigma}{\partial\phi} = E \qquad (1)$$

In equation (1) σ is the interfacial tension at the amalgam-solution interface, ϕ = the potential difference between solution and amalgam, and E is equal to the electric charge carried by the metallic ions which must be introduced in the solution (or removed from the solution if $E < 0$) in order to keep ϕ constant when the amalgam-solution interface increases by 1 sq. cm. The numerical values of ϕ given in this paper are referred to the normal calomel electrode.

In the case of pure mercury, equation (1) has been tested by various methods:[5]

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[1] Z. physik. Chem., **15**, 1 (1894).

[2] Ann. Phys., **9**, 129 (1917).

[3] Ann. Physik, (4), **16**, 382 (1905).

[4] Z. physik. Chem., **136**, 451 (1928).

[5] Frumkin: Z. physik. Chem., **103**, 55 (1922); Schofield: Phil. Mag., (6) **50**, 649 (1926).

As far as we know no such experiments have been carried out with amalgams. It appeared desirable to supply this deficiency, as the shape of electrocapillary curve of amalgams presents a considerable theoretical interest and no treatment of the question is possible without the assumption of the validity of equation (1). The method applied was based on the use of the so-called "null solutions." According to Palmaer[1] and to Smith and Moss[2] a "null solution" is a solution in which the quantity E is equal to zero.

This means there is no ionic exchange between the metal and the solution when a fresh surface of the metal is formed. Therefore, an increase of the amalgam surface in a null solution does not change the concentration of the ions of the metal of the amalgam, and the potential difference between a dropping amalgam electrode and still amalgam must be equal to zero. Measuring the E M F of the cell: normal calomel electrode | null solution | amalgam, it is easy to find the value of ϕ which corresponds to a zero value of E (point of zero charge). On the other hand, the value of ϕ max, which corresponds to the maximum of the electrocapillary curve, where $\partial\sigma/\partial\phi = 0$, can be determined from measurements of interfacial tension. If equation (1) holds, the values of ϕ as determined by these two methods must be identical. A comparison of the potential of pure mercury in various null solutions and of the corresponding positions of the electrocapillary maxima has been carried out by Smith and Moss. We have applied the null solution method also to the study of Cd amalgams for which there are no electrocapillary data available.

Experimental Method

In the course of this work, two types of apparatus have been used. The curves given by Fig. 3–6 have been taken with the apparatus represented in Fig. 1. In the earlier part of the work a vessel with a rubber stopper was used which proved to be not sufficiently air-tight for experiments with the more dilute amalgams. In other respects this first apparatus did not differ very much from the one finally adopted. With the first type of apparatus, the curves given in Fig. 2 were obtained. Each single experiment was carried out in the following manner. Approximately 160 ccm of the solution to be used were introduced in A and the amalgam placed in B. Then hydrogen was bubbled for about half an hour through the solution so as to remove the air. Using the stopcocks *a* and *b* it was possible to force a part of the hydrogen current to flow through C, D and D′ and to displace the air from this part of the system The hydrogen was supplied from a tank. It was purified by passing it over platinized asbestos heated to 500° and through an efficient wash-bottle filled with an alkaline solution of lead oxide. All connections between the asbestos tube and A were of glass but for a few short rubber connections which were completely under mercury. The rubber tubes used were always first boiled with alkali. During the bubbling of hydrogen, special care was taken to fill the narrow tube E with air-free solution. This was

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[1] Z. physik. Chem., **59**, 129 (1907).

[2] Phil. Mag., (6) **15**, 478 (1908).

accomplished by opening the pinch-cock C from time to time, allowing the solution in A to flow through E. After the air had been removed in this fashion from the system, the amalgam was allowed to flow from B first to C and then into the tube DD^1. When it reached a definite level in D it started to run through the capillary tip d in the solution. Moving the vessel C, it was possible to bring the amalgam in D always to the same level. The velocity of the flow of the amalgam was equal to about 25 ccm per hour. It required but a few moments for the flowing amalgam to cover the surface of the platinum wire in the narrow tube E. As the time during which the platinum was in contact with both amalgam and solution was very short, the possibility of a decomposition of the amalgam in contact with platinum was minimized. The burette F was filled with a 0.1 normal Tl_2SO_4 solution in the case of Tl amalgams and with a normal solution of $CdSO_4$ in the case of Cd amalgams. After the dropping electrode had been running for a while so that a large meniscus of amalgam was formed in the lower part of the vessel A, increasing amounts of the solution from the burette F were introduced into the vessel A. After each addition, the current flowing from the dropping electrode to the amalgam at the bottom of A and the potential difference between the solution and amalgam were determined. The current

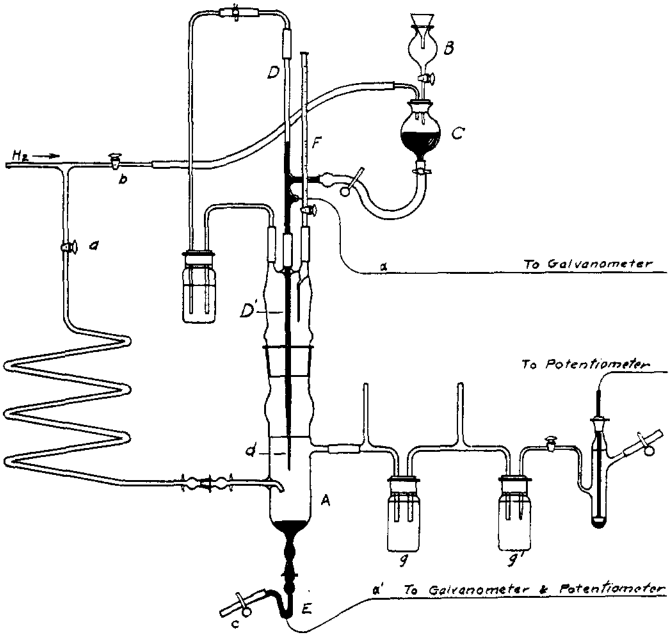

FIG. 1
Dropping Electrode Apparatus

was measured with a galvanometer which had its two poles connected with the wires α and α'. The current sensitivity of the galvanometer was equal to 9×10^{-8} amp. per division of the scale, and its internal resistance was 90 ohms. The current is said to be positive, if it flows in the outer circuit from α' to α ($E > 0$) and negative in the reverse case. The potential difference ϕ was determined by means of a potentiometer, whose poles were connected with α' and the normal calomel electrode. The calomel electrode was connected with the liquid in A by two syphons and two intermediate vessels. The syphons and the vessel g were filled with the same solution, which was introduced at the beginning of the experiment in A. The vessel g′ was filled with saturated KCl solution.

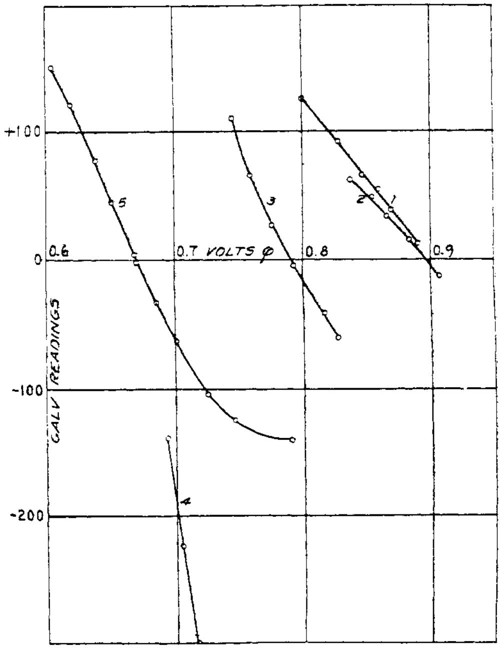

FIG. 2

Thallium Amalgams in Normal Na_2SO_4 Solution

Curve 1. 33% Tl amalgam in normal Na_2SO_4 + 0.1 H_2SO_4 + Tl_2SO_4.
Curve 2. 33% Tl amalgam in normal Na_2SO_4 + 0.1 normal NaOH + Tl_2SO_4.
Curve 3. 10% Tl amalgam in normal Na_2SO_4 + 0.1 normal NaOH + Tl_2SO_4.
Curve 4. 10% Tl amalgam in normal Na_2SO_4 saturated with iso amyl alcohol + Tl_2SO_4.
Curve 5. 1% Tl amalgam in normal Na_2SO_4 + 0.01 normal H_2SO_4 + Tl_2SO_4.

An example of a typical determination is given in Table I.

The measurements of ϕ present some difficulties at the beginning of a determination when the concentration of the ions, which determine the value of ϕ is very low, since the potential of the amalgam electrode fluctuates strongly in this region. Another disturbing influence observed under these conditions is that the pontential of the amalgam becomes more positive (higher values of ϕ) when the droplets from the dropping electrode coalesce on its surface. This is of course what we must expect, as the quantity E in these solutions is negative, and the coalescence of droplets then causes a decrease of the concentration of the ions of the metal dissolved in the mercury. This will affect the potential of the amalgam electrode if the concentration of these ions is very low. This effect is observed only if α and α' are disconnected. If a connection between them is established, the current flowing through the circuit cuts down the changes of the concentration caused by the steady increase of the amalgam surface in the neighborhood of the dropping electrode and by its decrease of the surface at the bottom of one vessel. Therefore, the measurements of ϕ had to be carried out without disconnecting α and α'. This precaution is no longer necessary after a few tenths of a ccm of the solution from F have been added. Apparently, at higher concentrations, the relative change of the concentration of the ions, caused by the coalescence of droplets on the surface of the amalgam, is too small to affect its potential.

TABLE I

0.1% Cd Amalgam, Initial Solution, Normal KBr.

ccm normal $CdSO_4$ added	ϕ	galvanometer readings	ccm normal $CdSO_4$ added	ϕ	galvanometer readings
0	0.807	−153	3.0	0.726	56
0.08	0.779	− 89	4.0	0.722	50
0.2	0.763	− 15	5.0	0.718	47
0.3	0.758	10	7.5	0.711	37
0.4	0.754	26	10.0	0.706	33
0.6	0.749	45	15.0	0.698	26
0.8	0.745	55	20.0	0.692	22
1.2	0.739	61	30.0	0.682	17
2.4	0.731	60			

With very dilute analgams it was observed that the precautions taken to exclude the oxygen from the system had not been quite sufficient. After an addition of larger amounts of the liquid from F (10 ccm. or more) values of the current were observed which could not be accounted for by the theory. It could be shown that these anomalies were caused by the oxidation of the amalgam by the oxygen dissolved in the solution in F which was not freed from air. This was evident from a comparison of the value of the current observed under the conditions described with the value which was observed when the same volume of the solution from F was introduced in A before the amalgam started to run and was then completely freed from air by bubbling hydrogen through it. In the latter case the anomalies mentioned above disappeared. Although the accuracy of the results which refer to the more dilute amalgams would be increased if the solution in F had been freed from air, we do not believe that the zero point values given in this paper are vitiated by this source of error.

The mercury, which was used in the preparation of amalgams, was purified in the usual way with mercury nitrate. The cadmium was a Kahlbaum product of high purity and the thallium was obtained from Eimer and Amend. The latter contained about 0.15% of lead. The more concentrated amalgams were prepared by dissolving a known amount of the solid metal in heated mercury; the others were obtained by subsequent dilutions. In the case of amalgams which contained less than 0.1% Tl or Cd the dilution was carried out in the interior of the vessel C, after it had been filled with hydrogen, as it was found that the concentration of the dilute amalgams is very strongly affected by contact with air. If an amalgam which came through the liquid in A is poured from E into another vessel and then returned to B for another determination, the curve obtained in this case will always show a certain shift with respect to the original. The direction of the shift indicates a decrease of the concentration of the metal of the amalgam which must be caused by oxidation during the transfer of the amalgam from E to B. This effect becomes very pronounced with dilute amalgams. Such discrepancies between different runs are not observed if the amalgams are taken from one single stock or prepared under identical conditions.

Results: Tl amalgams

A part of the curves obtained with the more concentrated thallium amalgams are presented in Fig. 2. The values of ϕ which correspond to a zero current are given in the second column of Table II. The values are averages from several determinations.

TABLE II

Tl amalgams in normal Na_2SO_4 + 0.01 normal H_2SO_4,
or normal Na_2SO_4 + 0.1 normal NaOH

% Tl.	Point of zero charge	ϕ max.
1.0	0.668	0.67
10.0	0.792	0.80 (10.3%)
33.0	0.898	0.92 (33.3%)

In the same table values of ϕ max. taken from the paper of Frumkin and Gorodetzkaya are given. As the uncertainty in the determination of ϕ max may amount to as much as 0.01 or even 0.02 volt, the agreement between the two sets of data is satisfactory. The measurements of Frumkin and Gorodetzkaja were carried out in the presence of small amounts of either H_2SO_4 or NaOH and therefore the same additions were used here. Both methods show that the pH of the solution does not exert a marked influence on the value of the surface charge of the amalgam. The concentration of Tl ions at the zero point is very different for different amalgams. With the 33% amalgam it is too low to be determined directly. The amount of the Tl present in the initial solution through oxidation of the thallium by traces of oxygen which could not be removed is of the same order of magnitude or even larger than the quantity which is necessary to bring the solution to the zero point. However, from the values of ϕ which are observed at higher concentrations and from the position of the zero point, we may conclude that if the initial solution really contained no Tl_2SO_4 at all, an addition of 0.04 ccm of 0.1 normal $Tl_2 SO_4$ would be sufficient to make a null solution. With a 10.0% amalgam this quantity as found now by experiment amounts to about 0.2 ccm and for a 1.0% amalgam to 1.5 ccm. The latter value agrees very well with the result of the calculations of Frumkin and Gorodetzkaja.[1]

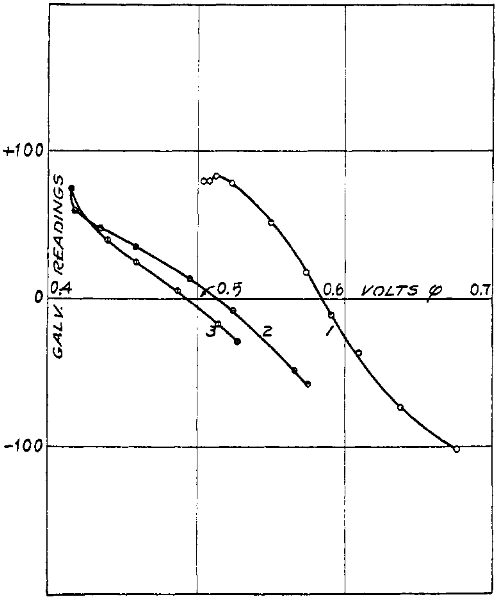

FIG. 3

Thallium Amalgams in Normal Na_2SO_4 Solution
Curve 1. 0.1% Tl amalgam in normal $Na_2SO_4 + Tl_2SO_4$.
Curve 2. 0.01% Tl amalgam in normal $Na_2SO_4 + Tl_2SO_4$.
Curve 3. 0.001% Tl amalgam in normal $Na_2SO_4 + Tl_2SO_4$.

Curve 4 deserves special attention. It was shown by Gouy[2] that in the presence of amyl alcohol the maximum of mercury is strongly shifted toward smaller values of ϕ and according to Frumkin and Gorodetzkaja the same thing holds for Tl amalgams. This result is corroborated by this curve, which shows that in the presence of amyl alcohol the current is negative over the whole range of the ϕ values obtained. It is remarkable that the sign of

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[1] Z. physik. Chem., **136**, 459 (1928).

[2] Ann. Chim. Phys., (8) **8**, 291 (1908).

the surface charge can be reverted as shown by curves 3 and 4, by the addition of a non-electrolyte which does not affect the concentration of Tl ions. A similar effect was recorded by Frumkin in the case of pure mercury on addition of ether to an alkaline solution.[1]

The curves obtained with more dilute Tl amalgams are given by Fig. 3. Their slope cannot be directly compared with the slope of the curves of Fig. 2 as the capillary tips in the first and the second apparatus were somewhat different. The positions of the point of zero charge are recorded in Table III. The value for pure mercury is taken from measurements of the electrocapillary curve of mercury in normal Na_2SO_4 by Gouy[2] and by Frumkin and Gorodetzkaja.

TABLE III

Dilute Tl amalgams in normal Na_2SO_4

% Tl	Point of zero charge	% Tl	Point of zero charge
0	(0.48)	0.01	0.513
0.001	0.494	0.1	0.585

The approximate compositions of the null solutions were: for 0.1% amalgam, 160 ccm Na_2SO_4 + 2.5 ccm 0.1 normal Tl_2SO_4 and for 0.001% amalgam, 160 ccm Na_2SO_4 + 0.4 ccm 0.1 normal Tl_2SO_4. The approach of the position of the point of zero charge to the electrocapillary maximum of pure mercury as shown by Table III is very close to the 0.001% amalgam. Curve 1 of Fig. 3 shows a decrease of the intensity of the current when the concentration of Tl is increased beyond a certain limit (the smallest value of ϕ corresponds to an addition of 70 ccm of 0.1 normal Tl_2SO_4.) This is (as will be shown in the case of Cd amalgams) a general phenomenon, which was probably not observed with other Tl amalgams only because the experiments had not been extended to sufficiently high concentrations of Tl_2SO_4. With the more dilute amalgams (0.01% and 0.001%) an opposite change of the direction of the curve is observed in the same region. As was explained in the preceding paragraph this is caused by the oxidation of the metal of the amalgam and has no real significance.

Cd Amalgams

The behavior of a 4.8% Cd- amalgam was investigated in different solutions of inorganic electrolytes. The results are given in Fig. 4. The positions of the points of zero charge given by Table IV are compared with the values taken from Gouy of ϕ max for pure mercury in the same solutions. Table IV shows that an addition of cadmium to mercury shifts the point of zero charge in the same direction as an addition of Tl, the shift being the largest with the KCl solution and the smallest with KI solution. This is exactly what is observed with Tl amalgams if the values of ϕ maximum in different solu-

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[1] Z. physik. Chem., **103**, 55 (1922).

[2] Ann. Chim. Phys., (7) **29**, 145 (1903).

tions are determined. The zero point of the Cd amalgam in normal Na_2SO_4 solution could not be reached by the addition of normal $CdSO_4$ solution.

Another interesting phenomenon observed with cadmium amalgams is the decrease of the positive current at higher concentrations of $CdSO_4$ (curves 3 and 4). Although this effect could be observed with Tl amalgams too, it was certainly much less pronounced than with Cd amalgams. For instance, with normal KI the decrease begins after the addition of only 0.5 ccm of normal $CdSO_4$ to the initial solution. It seems possible to account for this difference in the following manner. The decrease of the current at higher concentrations is caused by the diffusion of Cd ions. It is well known

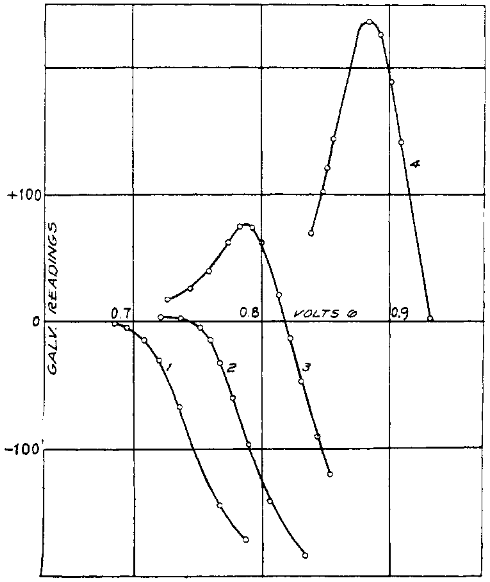

Fig. 4

4.8% Cd Amalgam in Different Solutions

Curve 1. 4.8% Cd amalgam in normal $Na_2SO_4 + CdSO_4$.
Curve 2. 4.8% Cd amalgam in normal $KCl + CdSO_4$.
Curve 3. 4.8% Cd amalgam in normal $KBr + CdSO_4$.
Curve 4. 4.8% Cd amalgam in normal $KI + CdSO_4$.

Table IV

4.8% Cd amalgam in different solutions

Solution	Point of zero charge	ϕ_{max} for pure Hg
Norm Na_2SO_4	?	0.48
" KCl	0.746	0.56
" KBr	0.818	0.65
" KI	0.933	0.82

that the same phenomenon is observed when mercury is flowing in a concentrated solution of $Hg_2(NO_3)_2$. Under these conditions there is no current between a dropping electrode and still mercury, although E has a high positive value. The influence of the diffusion can be explained in the following way. If a current has to flow between α and α' (Fig. 1) there must be a definite potential difference between the dropping electrode and the lower meniscus. The concentration of the ions of Cd (in the case of Cd amalgams) must therefore be somewhat different in the vicinity of the dropping electrode and in the bulk of the solution, although the dropping electrode and the large meniscus are closely connected. The diffusion process will tend to cut down this difference of concentration and to correspondingly decrease the current. The difference in concentrations for a given current, (i.e. for a given potential difference) is very much larger for a divalent ion than for a univalent one, and therefore the influence of diffusion must be more marked with Cd amalgams than with Tl amalgams.

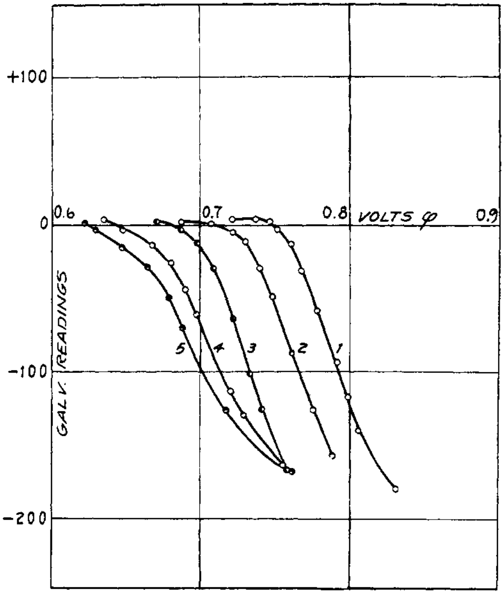

FIG. 5

Cadmium Amalgams in Normal KCl Solution

Curve 1. 4.8% Cd amalgam in normal KCl + $CdSO_4$.
Curve 2. 1.0% Cd amalgam in normal KCl + $CdSO_4$.
Curve 3. 0.1% Cd amalgam in normal KCl + $CdSO_4$.
Curve 4. 0.01% Cd amalgam in normal KCl + $CdSO_4$.
Curve 5. 0.004% Cd amalgam in normal KCl + $CdSO_4$.

A series of more dilute amalgams have been investigated both in normal KCl and normal KBr. The data obtained are recorded in Figs. 5 and 6 and in Table V. The determination of the zero point in KCl solutions with Cd amalgams is rather inexact on account of the low slope of the curve in this region.

The composition of the null solutions in the case of Cd amalgams does not change with change in the concentration of the amalgam in the same way as was observed with Tl amalgams. In order to reach the zero point with KBr it was necessary to add about 0.2 ccm normal $CdSO_4$ to the initial solu-

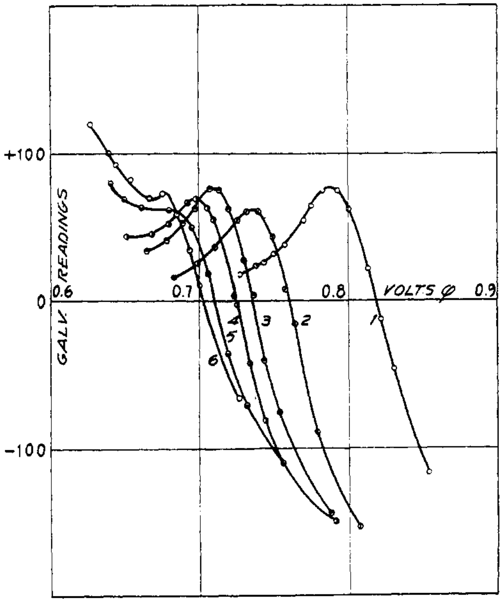

FIG. 6

Cd Amalgams in Normal KBr Solution

Curve 1. 4.8% Cd amalgam in normal KBr + $CdSO_4$.
Curve 2. 0.1% Cd amalgam in normal KBr + $CdSO_4$.
Curve 3. 0.01% Cd amalgam in normal KBr + $CdSO_4$.
Curve 4. 0.004% Cd amalgam in normal KBr + $CdSO_4$.
Curve 5. 0.001% Cd amalgam in normal KBr + $CdSO_4$.
Curve 6. 0.0003% Cd amalgam in normal KBr + $CdSO_4$.

TABLE V

Cd amalgams in normal KCl and normal KBr

% Cd	Point of zero charge KCl	Point of zero charge KBr	% Cd	Point of zero charge KCl	Point of zero charge KBr
0	(0.56)	(0.65)	0.01	0.640	0.736
0.0003	——	0.703	0.1	0.680	0.760
0.001	——	0.711	1.0	0.714	——
0.004	0.625	0.724	4.8	0.746	0.818

tion for all amalgams from 4.8 to 0.001%. With KCl the necessary amount of normal $CdSO_4$ fluctuated between 5 and 10 ccm for the more concentrated amalgams and 15 or 20 ccm for the more dilute ones.

The shift of the maximum persists with Cd amalgams at extremely high dilutions. We prefer to postpone the discussion of this interesting point until the results obtained here have been checked by determinations of ϕ_{max}.

We have also made some determinations with Zn amalgams. The current was always negative, and on addition of $ZnSO_4$ a zero point could not be reached irrespective of the composition of the solution. The addition of $ZnSO_4$ caused a strong decrease in the intensity of the current, but this was probably connected only with the increase of the influence of the diffusion and not with the approach toward a zero point as practically the same curve was observed with different electrolytes and with amalgams which contained Zn in varying concentrations. It appears that there is no adsorption of Zn at the interface mercury/solution, therefore the presence of zinc does not influence the value of E. This conclusion must also be tested by electrocapillary measurements.

Summary

It was shown with the help of the "null solutions" method that an addition of Tl and Cd to Hg causes a shift of the point of zero charge toward higher values of the potential difference between solution and metal. The data obtained with Tl-amalgams check with the results of the determinations of electrocapillary maxima which confirms the validity of the Lippmann-Helmholtz equation in the case of amalgams.

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