The Electrode Potential of Mercury against its Ions in Aqueous (1) Methyl Alcohol, (2) Acetone and (3) Pyridine.

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Numerous investigations have been carried out in aqueous solutions on electrocapillary phenomena since the Lippmann Helmholtz theory was developed; but they are rare in mixed solvents and excepting the researches of Krummreich (Z. F. Electrochem. *19*, 622, 1913) on aqueous ethyl alcohol, not very carefully done either. The importance of finding out how the absolute potential of metals against their ions changes with the nature of the solvent is obvious. The method which gives the most satisfactory results in this field, is the determination of the maximum position of the electrocapillary curve, and in order that the data obtained may be reliable, the conditions postulated in the Lippmann Helmholtz original equations must be fulfilled

$$dU = Edq + \gamma dS \qquad \ldots \quad (1)$$

$$dq = XdS + S\frac{\partial X}{\partial E}\,dE \qquad \ldots \quad (2)$$

$$X = CE$$

Where U = change in internal energy; γ = surface tension, X=density of electrification, S=area of capillary surface, E=potential difference at the boundary, dq=quantity of electricity and c=Capacity of Unit area of the double layer.

Then only a true parabola is obtained represented by the equation

$$\gamma=\gamma_{max}-\frac{1}{2}CE^2$$

the maximum of surface tension corresponding to zero value of electrode potential. The experimental conditions in this investigation, were always so determined by trial, that the curves approximated to an ideal parabola, indicating thereby, that the primary processes at the electrode surface contemplated by Lippmann and Helmholtz, have not been accompanied by uncertain disturbing factors.

EXPERIMENTAL PRECAUTIONS.

Clark (Trans. Roy. Soc. Canada, *14*, Ser. 3, Sect. 3, 73, 1921) maintains that the wet surface at the capillary is enormously greater than the cross-sectional area of the capillary due to the electrolyte creeping in between the glass walls of the capillary and the mercury column, and that the area of the wet surface never remains constant. Hence C′ the capacity of the double layer at the capillary surface does not remain constant in course of experiment, and a true parabolic curve is therefore out of the question.

In our experiments the capillary was made perfectly dry and clean, filled completely with mercury and then dipped into the electrolytic solutions. The glass wall beneath the capillary meniscus was therefore completely dry; the motion of the mercury column due to electric charge, and its re-adjustment to final level due to external pressure changes were too slow to leave behind a wet surface, enclosed between glass wall and mercury, which could be observed by the microscope. Only when the applied E. M. F. exceeded 1·6 volts, or the mercury column was, for some reason or other very sticky, a wet film between mercury and glass could be observed. For a capillary electrometer prepared with due precaution and used with care, it may be stated that the area of the capillary surface remains constant.

The nature of the electrocapillary curve depends a good deal on the ions, other than the mercurous ion, introduced into the solution, in order that the liquid may be sufficiently conducting. Thus Kruger and Krumreich (Z. F. Electro chem. *19*, 617, 1913) found that an ideal parabola is obtained very easily when an aqueous solution of normal potassium nitrate and O·IN $Hg_2 (NO_3)_2$ was used. It is unfortunate that potassium nitrate is not soluble in non-aqueous solvents, and this important property of potassium nitrate could not be taken advantage of in these investigations. Lithium nitrate, which is soluble in the solvents used by us, did not give a parabolic curve even in pure water, though the maximum obtained was quite sharp. The same difficulty was found in the case of potassium nitrate solutions. An aqueous solution of nitric acid (·0035N) and mercurous nitrate (·002N) gave a fairly good parabolic curve with the maximum at 1·05 volt. The expectation that mixed solvents having similar concentrations of nitric acid and mercurous nitrate would give approximate parabolas has been realised. It appears that the absorption of ions by mercury surface has considerable influence on electrocapillary processes.

It takes a very long time for conditions of equilibrium to be established at the capillary junction in these mixed solvents. In aqueous solution of KNO_3 and $Hg_2(NO_3)_2$, it takes not more than 15 minutes for the mercury meniscus to become absolutely stationary ; but in these experiments, it was discovered, that for half an hour after starting the polarising current, the movement of the mercury meniscus was comparatively rapid, but after that interval there was an imperceptible change which continued for a very long time. The curves given below have been plotted, from readings taken after the polarising current has passed through the capillary electrometer for five to eight hours. An explanation of this long time necessary for the attainment of equilibrium can be attempted from the standpoint of "Reststrom Polarisation." The E. M. F. of a cell of the type—

$$Hg \left| \begin{array}{c} Hg_2(NO_3)_2 \\ KNO_3 \text{ or } HNO_3 \end{array} \right| Hg \text{ is Zero.}$$

If a very slight current is passed through the circuit mercury will dissolve at the anode as $Hg_2^{\cdot\cdot}$ ion and will be deposited at the cathode from the solution. For small values of applied voltage, the back E. M. F. of polarisation will be entirely due to changes in the concentration of the mercurous ion in the liquid layer immediately surrounding the electrodes. If however, the surface of the mercury anode is very large compared with that of the cathode, as in the capillary electrometer, we are justified, in considering that for small current, the anode film does not undergo any change in the concentration of the $Hg_2^{\cdot\cdot}$ ion. In fact, measurements of the anode potential of our capillary electrometers, showed that this was the case. Therefore, the back E. M. F. of polarisation

$$= RT \log \frac{C_o}{C_k}$$

where C_o is the concentration of $\ddot{Hg}_2$ ion in the bulk of the solution which is the same as that of the anode, and C_k is the concentration of $\dot{Hg}_2$ ion at cathode film. Obviously when C_k becomes so small, that the osmotic pressure of $\ddot{Hg}_2$ ion is equal to the electrolytic solution pressure of mercury, then we have an electrode at zero potential. In the stationary state, where to maintain a definite value of polarisation, a definite residual current is necessary, there must be coming as many $\ddot{Hg}_2$ ion from the bulk of the solution into the cathode layer by diffusion, as are being discharged. This number in gram equivalent—

$$N = \frac{1}{86,400} \cdot \frac{D.O.}{a} \cdot \frac{C_o - C_k}{\delta}$$

(Nernst & Merriam Z F Phys. Chem. *53*, 235, 1905.)

D = Velocity of diffusion ; O = area of the cathode surface ; a = electro-chemical equivalent and δ the thickness of the diffusion layer. For the enormous polarisation that we are dealing with in the case of the capillary electrometer, C_k will be infinitely small, and—

$$\frac{i}{96,540} = N = \frac{D.\ O.}{a.\ 86400.} \frac{C_o}{\delta}$$

In an actual experiment with the capillary electrometer, the residual current was found to be $4 \cdot 2 \times 10^{-8}$ amperes, for an area of capillary surface $= \cdot 0025$. Taking $D = \cdot 0023 \times M$ (M = molecular conductivity of the $\ddot{Hg}_2$ ion), δ comes out to be 10^{-3} cm. approximately.

This order of magnitude for δ is the same as that obtained by Nernst and Merriam and thus it is established beyond doubt that we are here dealing with the phenomena of Reststrom Polarisation.

A considerable time might elapse before the concentration gradient across the diffision layer $\frac{C_s - C_k}{\delta}$ attains equilibrium conditions and then again there exist the disturbing effects produced by the movement of the mercury meniscus in response to continuous charge in surface tension. This will specially be the case, when the mercury surface in the capillary, becomes negatively charged, for that condition will correspond to inconceivably low value of C_k.

It is satisfactory to note, that the electrocapillary curves obtained, when these precautions were taken, were approximate parabolas. See Figs. I and II.

EXPERIMENTAL PROCEDURE.

A Wolff Dial Potentiometer standardised by the Reichsantalt was connected to a 4-volt battery, and any required E. M. F. was applied through a galvanometer, the exact value of the E. M. F. being obtained by reference to a standard Weston element. The sensitiveness of the galvanometer in the circuit being known, the strength of the residual current corresponding to a definite polarising voltage can be ascertained. The capillary tube was cleaned before each experiment by washing with strong nitric acid and keeping under chromic acid overnight. It was washed finally with conductivity water, dried in a current of dust-free air, and filled with redistilled mercury. It was then immersed in the electrolytic solution. The U-tube capillary electrometer was found to have an advantage over the vertical tube ending in a capillary, in that, it was more stable. The position of the mercury meniscus was read off as usual with a reading microscope and the difference between the levels of the mercury column in the manometer and in the capillary was measured by means of a travelling microscope capable of reading height to $\frac{1}{1000}$ cm. For capillaries of large bore, an adjustable mercury reservoir was not necessary, the difference in the levels of the mercury columns in the instrument itself was measured directly, the variation in the diameter of the capillary tubing along its length being too small in this case, to be taken into account. A large number of capillary electrometers were prepared, and only those were selected, which gave easily an ideal curve with an aqueous KNO_3, $Hg_2(NO_3)_2$ solution.

The back E. M. F. of the polarised capillary surface is always less than the applied voltage by an amount equal to i × R where R is the resistance of the circuit and i the strength of the residual current. The resistance of the circuit is primarily due to the galvanometer and to the electrolytic solution in the capillary lying above the mercury meniscus. It is impossible to measure directly the magnitude of this resistance, but it is easily calculated from the following data: (1) galvanometer resistance, (2) bore of the capillary and length of the column of electrolyte, and (3) specific resistance of the solution. It was found that in no case, the correction in back E. M. F. due to this factor exceeded 1 millivolt.

Pyridine, acetone and methyl alcohol used in this investigation were obtained from Kahlbaum and distilled in the laboratory until constant boiling points were obtained.

EXPERIMENTAL RESULTS AND DISCUSSION.

The experimental results are given in Figs. I and II and in Tables 2, 3 and 4.

The electrocapillary curve for aqueous solution ought to have been almost identical with that obtained by Kruger and Krumreich (*loc. cit.*). They obtained a maximum at ·8 volt approximately while our experiments give a maximum at 1·005 volt. Ley and Heimbücker (Z. F. Electrochem. *10*, 301, 1904) found that the cell

$$\mathrm{Hg—\underset{\cdot 05}{Hg_2}\,(NO_3')_2\;KNO_3—\underset{\frac{N}{10}}{KCl}.\;HgCl/Hg}$$

had an E. M. F. of ·391 volt. Decinormal calomel element has a value of ·612 volt as obtained from innumerable electrocapillary data. The maximum therefore should lie at (·612+·391) or 1·03 volt in agreement with our results. If Kruger and Krumreich's value were true, decinormal calomel element would have an electrode potential of ·412 volt, which is a move in the direction suggested by Billitzer's data, obtained from the observation of the movement of metal wires dipped in salt solution (Ann. der. Phys. *11*, 902, 1903). Unfortunately their results could not be confirmed.

Tables 2, 3 and 4 give the electromotive forces corresponding to maximum of surface tension in mixed solvents of water-methyl alcohol, water-acetone and water-pyridine, containing mercurous nitrate and nitric acid as electrolytes. The influence of the concentration of the $Hg_2^{\cdot\cdot}$ ion on the magnitude of the electrode potential is comparatively small. For the same concentration of mercurous nitrate in the various solvents, it can be shown on the basis of Walden's empirical generalisation,—for the same value of $D\sqrt{v}$, the degree of dissociation is the same,—that the relative concentration of $Hg_2^{\cdot\cdot}$ ion in these solvents does not vary beyond the ratio 2 : 1.

The above values may therefore be accepted as the electrode potential of mercury against $\frac{N}{100}$ mercurous ion in the respective solvents. Table 1 reproduces the date of Krumreich (*loc. cit.*) in aqueous ethyl alcohol solution of potassium nitrate and mercurous nitrate The results are, as has been noted before systematically about ·2 volts less than the generally accepted values.

TABLE 1.

Water-Ethyl Alcohol.

Electrode Potential	Composition by weight in per cent	Dielectric constant D	$\frac{E}{D}$
773	0%	81	95
628	10%	75	84
604	30%	60	1 0
479	50%	48 5	97
451	70%	38 1	1 12

TABLE 2.

Water-Methyl Alcohol.

	Composition by vol in per cent		
1 04 (Kruger's value 773)	0%	81	1 20 (95)
719	10%	77	93
611	20%	72	95
636	30%	68	92
581	40%	63 5	92
	50%	58 0	94

TABLE 3.

Water-acetone.

Electrode Potential.	Composition by vol. in per cent.	Dielectric constant	$\frac{E}{D}$
1·05	0%	81	1 2
906	10%	77	1 18
620	20%	72 5	[illegible]
855	30%	67 5	1 25
775	40%	62·0	1 25
751	50%	55·0	1·36
732	60%	48·0	1 51

TABLE 4.

Water-pyridine.

Electrode Potential.	Composition by vol in per cent.	Dielectric constant.	$\frac{E}{D}$
1·05	0%	81	1 25
·560	10%	74	75
·498	20%	68·3	·73
·450	0%	60	·75
·412	40%	53	·77
·383	50%	44	·90

The values of dielectric constants in Tables 1, 2, and 3 are calculated from data given in Landolt's Tabellen. The dielectric constants in aqueous pyridine given above are not very accurate and are taken from the work of Ghosh (J. C. S., *117*, 1390, 1920). The fourth columns in the tables give the ratio of the electrode potential as determined from the maximum of the capillary curve, to the dielectric constant of the solvents. It will be noticed that in aqueous ethyl alcohol solution the electrode potential of mercury is proportional to the dielectric constant of the solvent up to 50% of alcohol. Thereafter the ratio of $\frac{E}{D}$ increases.

In aqueous methyl alcohol, the same constancy in the value of $\frac{E}{D}$ is observed. This ratio varies about the mean value, ·93, and if we accept Kruger's data for pure water as solvent, $\frac{E}{D}$ for water also has approximately the same value, *viz.*, ·95.

In aqueous acetone, results obtained with 20% acetone are very peculiar in that abnormally low value of electrode potentials is obtained. With this exception, the ratio $\frac{E}{D}$ remains constant up to 40% acetone and thereafter increases as in the case of aqueous ethyl alcohol.

There is a very large drop in the value of the electrode potential as pyridine is added to water. Further addition of pyridine beyond 10% by volume, produces a slow gradual change in the value of electrode potential and we find that the ratio $\frac{E}{D}$ remains practically constant within the range 10-40% pyridine. Thereafter $\frac{E}{D}$ increases as in the case of the other mixed solvents.

The electromotive force at the boundary between a metal and its ions in solution is a measure of the free energy A of the process:

$$\text{Metal atom} \rightleftarrows \text{Metal ion in solution.}$$

for $E \cdot \times F = A$.

On the reasonable assumption that the free energy of the atom of an element in the metallic state remains constant at constant temperature, this investigation points to the conclusion, that at 30°, *the free energy of mercurous ion in the above mixed solvents is within a certain range directly proportional to the dielectric constant of the solvent.*

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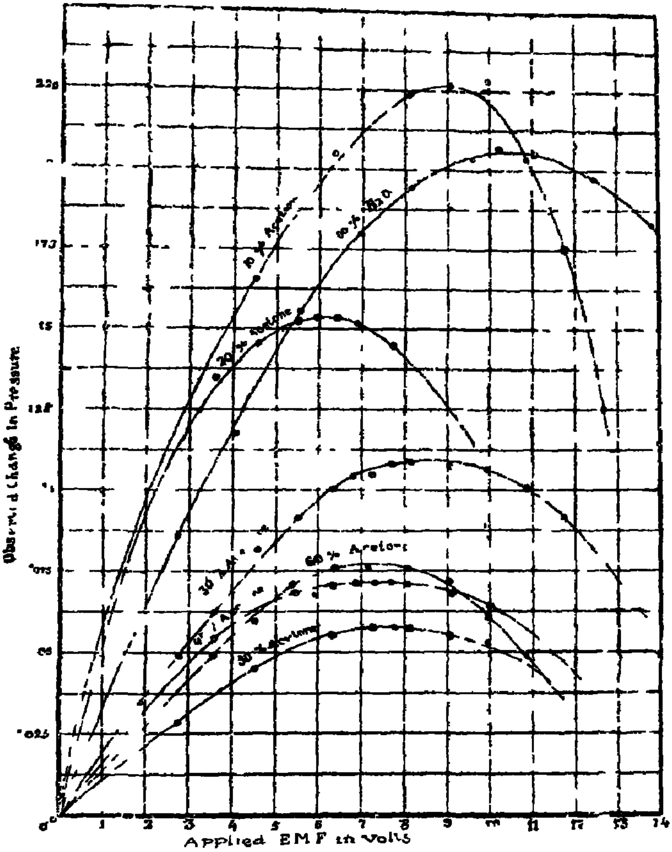
[*Received Oct. 25, 1924.*]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10
11
12
13
14
Observed Change in Pressure
Applied EMF in Volts
10 % Acetone
80 % H2O
20 % Acetone
30 % Acetone
60 % Acetone
30 % Acetone

Fig. I.

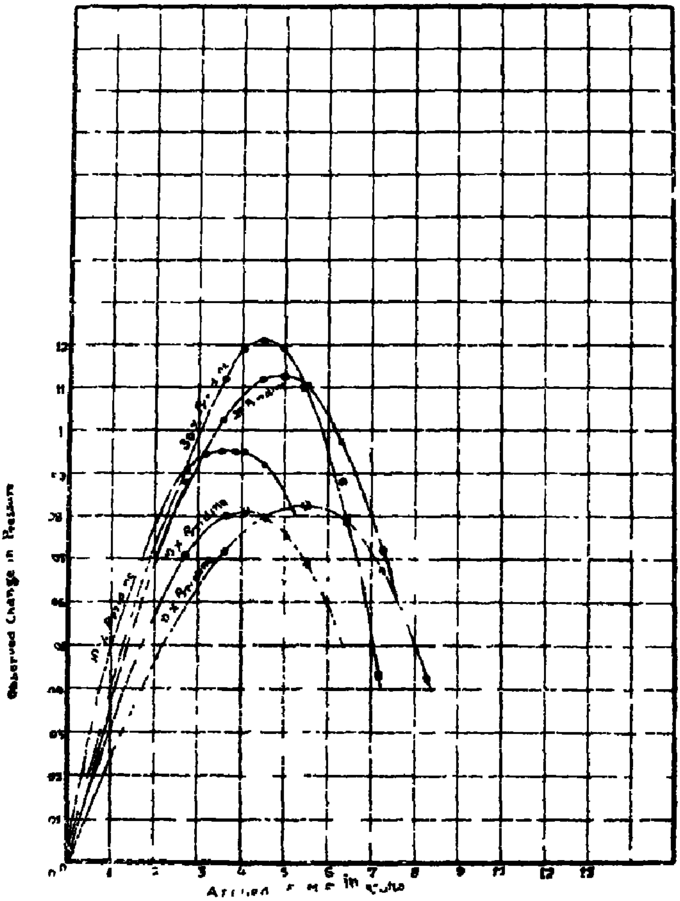
Observed Change in Pressure
12
11
1
·09
·08
·07
·06
·05
·04
·03
·02
·01
0
1
2
3
4
5
6
7
8
9
11
12
13
Applied E.M.F. in volts

Fig. II.