Summary

1. The results of experiments on the partition of mercuric chloride between aqueous potassium oxalate and benzene are presented.

2. The freezing point depressions of mercuric chloride and of potassium oxalate solutions and of mixtures of these have been determined.

3. It is shown that calculations from the distribution and freezing point experiments lead to the following scheme of complex formation in Eder's solution:

$$2HgCl_2 + 2C_2O_4^{=} \rightleftharpoons Hg_2Cl_2(C_2O_4)_2^{=} + 2Cl^-$$
$$HgCl_2 + Cl^- \rightleftharpoons HgCl_3^-$$
$$Hg_2Cl_4 + Cl^- \rightleftharpoons Hg_2Cl_5^-$$

4. This scheme is shown to be in harmony with reaction rate measurements on Eder solutions over a corresponding range of concentrations.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

A Study of Polarization Currents Due Solely to Changes in Electrode Area[1]

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Introduction

The purpose of this investigation was to study the adsorption of mercurous ions at a mercury surface by measuring the current flowing between two mercury electrodes immersed in a mercurous sulfate solution while one of the electrodes was undergoing a slow definite increase in area. Similar studies have been made in the past, but always under conditions that made the interpretations of results quite difficult.

Heyrovský and co-workers have used the dropping mercury electrode to investigate a variety of chemical problems. Semerano gives a discussion of the work of these investigators using the polarograph, an instrument for the automatic recording on photographic paper of the current–voltage curves obtained with the dropping mercury cathode.[3] Frumkin and Schofield[4] have used the dropping mercury electrode to verify the Lippmann equation. Frumkin measured the current caused by a stream of mercury drops falling through the various solutions used, while Schofield actually measured the amount of mercurous salt which was removed from a solution by an expanding mercury surface.

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[1] From a dissertation submitted by K. E. Glidden to the Board of University Studies of the Johns Hopkins University in partial fulfilment of the requirements for the Doctor of Philosophy Degree, June, 1932.

[2] Brown Company Fellow in Chemistry.

[3] Semerano, "Il Polarografo, sua Teoria e Applicazioni" (The Polarograph, Its Theory and Applications), Libreria Editrice A. Draghi, Padova, Italy, 1932.

[4] Frumkin, *Z. physik. Chem.*, **103**, 55 (1922); Schofield, *Phil. Mag.*, **I**, 641 (1926).

All the dropping electrode experiments, in regard to the adsorption at the expanding surface, are ambiguous due to the rapid formation of mercury drops in the solution with the subsequent changes of metal ion concentration at the electrode surface. Furthermore, the change of solute concentration thus produced causes a change of interfacial tension, which in turn causes a variation in the size of the drops. If we add to the above objections the possibility of a slow rate of surface orientation at the electrode surface, it is evident that most dropping electrode experiments are complicated phenomena that defy analysis.

The fundamental assumption in this paper is that the adsorption of mercurous ions is equivalent to the current measured. It is an experimental fact that a rain of mercury drops falling through a solution containing for example lead ions does not adsorb lead ions from solution, and hence it appears that we are dealing with specific adsorptive forces rather than purely electrostatic forces. At the present time there is no direct evidence that our fundamental assumption is correct. The fact that the adsorption of mercurous ions calculated from our polarization current measurements on the basis of the above assumption agrees fairly well with the adsorption obtained from an entirely different method, leads us to believe that our fundamental assumption is reasonable.

Apparatus

The currents were produced with the apparatus shown in Fig. 1. The slowly expanding surface consisted of a mercury drop on the tip of a ground and polished capillary tube *a*, 1.41 millimeters in diameter. The fixed surface electrode *b* was made by sealing a 1-cm. tube through the wall of the cell *c*. The cell was cylindrical in shape, approximately 8 by 50 cm. The area of the mercury drop in contact with the solution was increased by adding mercury to the main reservoir *d* from the auxiliary reservoir *e*. The cross sectional area of the main reservoir was approximately 800 times that of the capillary bore, and hence if dV_c is the volume increase of the mercury drop produced by a volume increase dV_r at the reservoir, dV_c is approximately equal to $dV_r/800$.

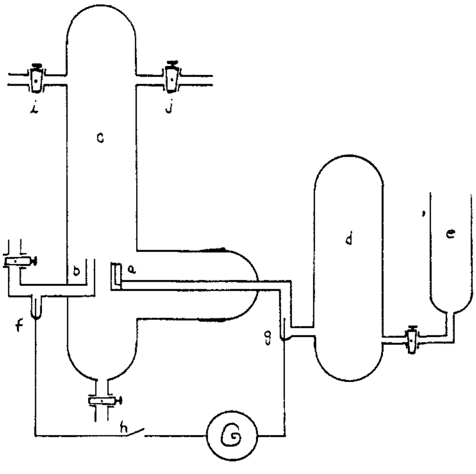

Fig. 1.—Diagram of apparatus (scale: 1 in. = 20 cm.).

Tungsten wires were sealed in the electrodes at *f* and at *g* and connected to the poles of a Leeds and Northrup galvanometer as shown in the diagram. A switch *h* was employed to open and close the circuit. The entire apparatus was supported on hard rubber or bakelite to eliminate current leakage.

The drop was observed with a cathetometer telescope containing a calibrated screw micrometer eyepiece. A lens was placed between the telescope and object to increase the magnification.

Experimental

Introduction of Solution into Cell.—The entire cell was evacuated through the stopcock at *i* with a mercury diffusion pump backed by an oil pump. Carefully purified mercury was then added through the auxillary reservoir *e* until the level of the mercury in the capillary electrode was just at the tip. The level in *b* was likewise adjusted by adding mercury through a stopcock provided for that purpose.

A stock solution of mercurous sulfate was prepared by saturating distilled water with C. P. mercurous sulfate. A small amount of mercury was kept in contact with the solution to prevent the formation of mercuric salts. After standing in contact with solid mercurous sulfate for ten days or more, the solution was filtered and analyzed for mercury by electrolysis. The stock solution is of course acid due to hydrolysis, but the exact acidity was unknown.

A bulb of about 250 cc. capacity (not shown in the diagram) joined to stopcock *j* was then filled with a solution of mercurous sulfate, which was prepared by diluting the stock mercurous sulfate solution with boiled distilled water which had been cooled rapidly to prevent absorption of oxygen from the air. Stopcock *j* was then opened slightly to allow a trickle of solution to enter the polarization cell. During this process practically all of the dissolved gases are drawn out of the solution and removed from the system by the pumps. If the flow of solution from the bulb to the cell does not exceed 150 cc. per hour, the de-aerated solution will contain not more than 10^{-5} cc. of oxygen per 100 cc. of solution. The stopcock at *i* was opened for thirty seconds every five minutes to draw off air removed from the solution. Solution was added to the cell through the bulb until a total of 1000 cc. had been added. Since a great deal of water is lost through the pumps during the de-aeration process, boiled distilled water which had been cooled rapidly was added to the cell through the de-aerator until the total volume of solution was 1000 cc.

To change the concentration in the cell, a pear-shaped bulb was sealed on at *j*. This bulb was evacuated, sealed off from the pumps and cooled with a mixture of solid carbon dioxide and ether. Stopcock *j* was then opened and water from the cell allowed to distil over, approximately six to eight hours being required to distil over 100 cc. The initial concentration of mercurous sulfate solution in the cell was known and hence the successive concentrations could be estimated by weighing the amounts of water removed by distillation.

Current Measurements.—The procedure followed in the current measurement was as follows. The flow of mercury from the auxiliary to the main reservoir was adjusted to such a rate that the meniscus of the mercury drop on the capillary tip passed between two cross hairs in the telescope eyepiece in 120 ± 5 seconds. The switch *h* was thrown as the meniscus passed the first cross hair, and the galvanometer deflection read every ten seconds for the entire time interval. The above procedure was repeated several times for each particular concentration of mercurous sulfate solution in the cell.

Area Measurements.—The optical system for viewing the drop was not sufficiently sensitive to detect the area change over an interval of ten or fifteen seconds, and hence the average rate of change over the one hundred twenty second interval was measured.

The area of a segment of a sphere is $2\pi rh$ where r is the radius of the sphere and h the height of the segment. The radius of the drop on the capillary tip is not the same as the radius of the capillary and it varies with the height of the drop above the tip. Assuming that the drop is spherical, the average rate of change of mercury surface in contact with solution may be calculated as follows. Let h_0 be the height of the meniscus above the tip of the capillary at time 0; h_t the height after t seconds; r_0 and r_t the radii of curvature of the drop at the two positions; S_0 and S_t the areas of the segments; and a the radius of the capillary. Then $r_0^2 = a^2 + (r_0 - h_0)^2$ and $r_0 = (a^2 + h_0^2)/2h_0$. A similar expression for r_t in terms of h_t and a may also be written. Since $S_0 = 2\pi r_0 h_0$ and $S_t = 2\pi r_t h_t$ it follows that

$$\frac{\Delta S}{\Delta t} = \frac{S_t - S_0}{t - 0} = \frac{2\pi(r_t h_t - r_0 h_0)}{t - 0} = \frac{\pi(h_t^t - h_0^2)}{\Delta t}$$

This final expression gives the average rate of change of mercury surface in contact with solution during the time interval considered, and if the total area change is small, the average rate does not differ greatly from the instantaneous rate.

Experimental Results

The data obtained for seven concentrations of mercurous sulfate solution in which the electrodes were immersed are summarized in Table I. The first column lists the concentration of mercurous sulfate solution in millimoles per liter; the second gives the average rate of change of mercury surface in contact with solution, expressed in square centimeters per second; the third column gives the actual current in amperes flowing between the electrodes, these values computed from the observed galvanometer deflections and the galvanometer sensitivity; the fourth column lists the adsorption per unit time, these values calculated from the current measurements and the factor 2.07×10^{-3} g. of mercurous ion per coulomb, and expressed in grams of mercurous ion per second; the final column gives the adsorption per unit surface, expressed in grams of mercurous ion per square centimeter of mercury surface. These values were calculated by dividing the adsorption per unit time by the change of mercury surface per unit time. All the values in Table I represent the mean of twenty or more individual measurements. The total area change in all cases was 0.00391 square centimeter.

TABLE I

Concn.	$\Delta S/\Delta t$	Current	Adsorp./sec.	Adsorp./sq. cm.
0.091	3.30×10^{-5}	2.22×10^{-9}	46.0×10^{-13}	0.14×10^{-6}
.093	3.22	2.80	58.0	.18
.100	3.35	3.72	77.0	.23
.131	3.20	5.27	109.0	.34
.157	3.21	5.50	113.0	.35
.203	3.31	5.36	111.0	.33
.302	3.20	5.38	111.5	.34

A plot of the values of adsorption of mercurous ion per square centimeter against concentration of mercurous sulfate solution is shown in Fig. 2.

Discussion of Results

These experiments were undertaken with a view to ascertaining whether or not these small currents could throw any light on the extent of ion orientation at the electrode surface. Experiments performed by Seidel in which he employed the micro-balance to measure the extent of mercurous ion adsorption at mercury surfaces, indicated that a unimolecular layer was formed at a concentration of 0.13 millimole of mercurous sulfate per liter.[5] Above this concentration no further increase in adsorption was detectable notwithstanding the fact that the interfacial tension between mercury and solution continued to diminish. The adsorption calculated from the polarization currents reported in this paper substantiates the results obtained by Seidel, especially in regard to the constancy of adsorption above a certain critical value of mercurous sulfate solution concentration. The actual value for the adsorption of mercurous ion per unit surface is of the same order of magnitude from both methods, that from the polarization current measurements being one-third that obtained from the micro-balance measurements.

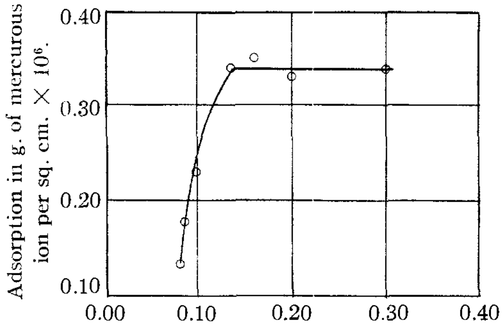

Fig. 2.—Adsorption curve for mercurous ions at a mercury surface.

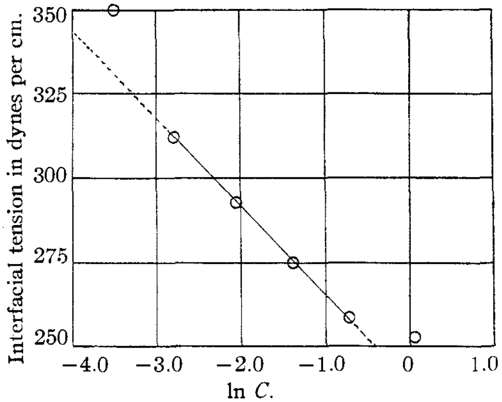

Fig. 3.—Surface tension–ln *C* curve for $Hg–Hg_2SO_4$.

The Gibbs adsorption equation for an ideal solute may be stated as follows:

$$u = -1/RT\ \partial\sigma/\partial \ln c \quad (1)$$

u being the number of moles of solute adsorbed per unit surface, σ the interfacial tension, c the bulk concentration, R and T having the usual significance.

From equation (1), it is evident that the condition for a constant value of positive adsorption is that the interfacial tension decrease linearly with the logarithm of the concentration. Patrick's data on the interfacial tension between mercury and mercurous sulfate solution show that the relationship is linear

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[5] Seidel, Dissertation, the Johns Hopkins University, June, 1931.

from a concentration of 0.13 to 0.50 millimole of mercurous sulfate per liter, and that deviations occur in dilute or concentrated solutions. These data are shown in Fig. 3.[6]

A thermodynamic interpretation of equation (1) may be obtained by the following considerations. Assume an interface of area ω, interfacial tension σ, in contact with a solution of osmotic pressure p and volume v. A small change of area $d\omega$ results in the following change of internal energy

$$dU = TdS + \sigma d\omega - pdv \qquad (2)$$

σ is by definition the work required per unit increase of surface, and hence the term $\sigma d\omega$ represents the increase in the free energy of the system. TdS and pdv are, respectively, the heat absorbed and the volume work performed when the area of the interface is increased by $d\omega$.

The free energy (F) is defined as

$$F = H - TS = U + pv - TS \qquad (3)$$

This expression is differentiated and combined with equation (2), and at constant temperature the following expression is obtained

$$dF = \sigma d\omega + vdp \qquad (4)$$

By applying the criterion for equilibrium, *i. e.*, $dF = 0$, we obtain

$$\sigma d\omega = -vdp \qquad (5)$$

This equation shows that with an increase $d\omega$ of the interface, the change in free surface energy is exactly equal to the osmotic work performed in the process.

By differentiating equation (5) and neglecting all differentials of higher order than the first, we obtain

$$d\sigma d\omega = -dv\, dp \qquad (6)$$

This equation may be written as

$$\left(\frac{\partial\sigma}{\partial v}\right)_\omega = -\left(\frac{\partial p}{\partial\omega}\right)_v \qquad (7a) \qquad \text{or} \qquad \frac{\partial\sigma}{\partial c}\frac{\partial c}{\partial v} = -\frac{\partial p}{\partial c}\frac{\partial c}{\partial\omega} \qquad (7b)$$

All of the coefficients in (7b) with the exception of $\partial\sigma/\partial c$ may be evaluated from the osmotic pressure law for an ideal solute, and the Gibbs definition of concentration.

$$p = cRT \qquad (8) \qquad\qquad c = (n - u\omega)/v \qquad (9)$$

In equation (9), c gives the bulk concentration, n the total number of moles of solute, v the total volume, ω the total surface and u the adsorption coefficient of the constituent in the surface layer. If an increase of surface decreases the concentration of one constituent in the body of the solution, that constituent is said to be adsorbed at the surface. Hence u represents the excess of the adsorbed constituent in the surface layer above that required to give the surface layer the same composition as the body of the solution.

(6) Patrick, *Z. physik. Chem.*, **86**, 545 (1914).

An evaluation of the coefficients in equation (7b) results in the Gibbs adsorption equation for an ideal case. We have seen that the sole condition for a constant value of adsorption is that the intensity factor of the surface energy, the interfacial tension, decrease linearly with the logarithm of the solute concentration. In spite of the fact that Patrick's data on the interfacial tension between mercury and mercurous sulfate solution show that this condition is fulfilled (within a certain range of concentration), the authors believe it worth while to present a modification of the Gibbs theory.[6]

If one accepts the fact that above a certain critical concentration no further increase in adsorption occurs, it is necessary to account for the continued lowering of the free surface energy. Our contention is that this lowering is due entirely to the orientation of electrically charged particles at the surface. In other words, the free surface energy lowering only occurs through the mechanism of orientation, and this oriented surface layer is the seat of a definite amount of electrical energy which is governed primarily by the geometry of the surface particles.

We now define concentration in terms of an oriented unimolecular layer of adsorbed particles as follows

$$c = (n - q/NF)/v \tag{10}$$

q being the total charge at the surface, NF the number of coulombs associated with a mole of surface particles, n the total number of moles and v the total volume. The ratio q/NF hence gives the number of moles of solute particles absorbed at the surface.

With an interface of area ω, interfacial tension σ, surface charge q, surface potential ϵ, in contact with a solution of osmotic pressure p and volume v, a change of area $d\omega$ results in the following change of internal energy

$$dU = TdS + \epsilon dq - pdv \tag{11}$$

This equation is identical with the fundamental equation in the derivation of the Gibbs equation with the exception that an electrical energy term (ϵdq) replaces the term ($\sigma d\omega$) for the lowering of the free surface energy. ϵ is the intensity factor in the electrical energy term which is comparable to the intensity factor σ in the surface energy term of equation (2).

The free energy expression (3) is then differentiated and combined with (11)

$$dF = \epsilon dq + vdp \quad \text{(at constant temperature)} \tag{12}$$

By applying the criterion for equilibrium, $dF = 0$, differentiating and neglecting all differentials of higher order than the first, we obtain

$$d\epsilon\, dq = -dv\, dp \tag{13}$$

This equation may be written as

$$\left(\frac{\partial \epsilon}{\partial p}\right)_q = -\left(\frac{\partial v}{\partial q}\right)_p \quad \text{(14a)} \qquad \text{or} \qquad \frac{\partial \epsilon}{\partial c}\frac{\partial c}{\partial p} = -\frac{\partial v}{\partial c}\frac{\partial c}{\partial q} \quad \text{(14b)}$$

The coefficients appearing on the right-hand side of (14b) may be evaluated from the definition of concentration previously stated, equation (10); $\partial c/\partial p$ may be found from the osmotic pressure law for an ideal solute. If one regards the adsorbed layer as a double electric layer, the question immediately arises as to how the potential of such a combination varies with the solute concentration. We postulate that the potential of the surface layer will vary with the solute concentration according to the usual thermodynamic relationship

$$\epsilon = (RT/NF) \ln c \tag{15}$$

An evaluation of the coefficients in (14b) leads to the identity

$$\frac{RT}{NF}\frac{1}{c}\frac{1}{RT} = \frac{v}{c}\frac{1}{NFv} \text{ or } 1 = 1 \tag{16}$$

This final step shows that the argument presented above is thermodynamically correct.

It now remains to show that the decrease of free surface energy between mercury and mercurous sulfate solution with increasing solute concentration is of an order of magnitude to be accounted for by the formation of an oriented unimolecular layer of solute particles. The problem may best be attacked by considering the adsorbed layer as a parallel plate condenser.

The capacity of a single parallel plate condenser may be calculated from its geometry, *i. e.*, the area of the plates and the distance of separation; capacity is also related to the charge and potential of the plates. These relationships are shown in the expression

$$C = K\omega/4\pi d = q/e \tag{17}$$

In order to simplify the calculation, we will assume that the radius of the cation and anion are the same, and hence in the above expression, $d = 2r$. If ω is the area occupied by one charged particle of radius r, the capacity then becomes

$$C = K\pi r^2/8\pi r = Kr/8 \tag{18}$$

Since the mercurous ion bears two unit charges, the potential of the double layer becomes

$$\epsilon = 16/Kr \tag{19}$$

The charge per square centimeter may be obtained by multiplying the number of surface particles per square centimeter by the charge of each surface particle, hence

$$q/cm^2 = 1/\pi r^2 \quad 2 \times 9650/N \quad \text{e. m. u.} \tag{20}$$

Since electrical energy is the product of charge and potential, the energy associated with one square centimeter of surface is given by the expression

$$\epsilon \cdot q = 16/Kr \quad 2 \times 9650/N\pi r^2 = 16.2 \times 10^4/Kr^3 \tag{21}$$

This final expression for the energy is given in ergs per square centimeter if r is expressed in Ångström units, and shows that the energy associated with the surface layer depends primarily on the geometry of the surface particles.

In order to make the calculation for the electrical energy per unit surface, the dielectric constant K and r must be known. The value of r may be calculated from the experimental value of the adsorption of mercurous ion, 0.34×10^{-6} g. of mercurous ion per square centimeter of mercury surface, and is found to be 2.5 Å. The dielectric constant of the oriented layer is unknown but will very probably be close to that of water.

Using the values $K = 81$ and $r = 2.5$ Å., the energy per square centimeter of an oriented unimolecular layer of mercurous sulfate particles is found to be approximately 120 ergs.

Since we have postulated that the lowering of the free surface energy is due entirely to the formation of an oriented unimolecular layer of solute particles, it is evident that the lowering of the interfacial tension between mercury and mercurous sulfate solution must be of the same order of magnitude as the energy required to form this surface layer. Patrick's data for the interfacial tension between mercury and mercurous sulfate solution show that the lowering from 0.13 to 1.03 millimole of mercurous sulfate per liter (the approximate region in which we postulate a unimolecular layer of solute particles) is 42 ergs per square centimeter. Since our calculation for the electrical energy associated with one square centimeter of surface involves many questionable assumptions, the agreement between the two values is all that can be expected.

Summary

1. The current flowing between a fixed and expanding mercury surface, both surfaces in contact with a mercurous sulfate solution, has been measured. On the assumption that the current measured is equivalent to adsorption of mercurous ions, the adsorption of mercurous ions is constant above a certain critical solute concentration.

2. The lowering of the interfacial tension between mercury and mercurous sulfate solution can be accounted for by the formation of an oriented unimolecular layer of mercurous sulfate particles at the mercury surface.

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