TABLE I

HYDROLYSIS OF INDIUM TRICHLORIDE SOLUTIONS AT 25°

Moles of $InCl_3$ per liter	pH	Degree of hydrolysis x	Hydrolysis constant $K_h \times 10^5$
0.000500	3.75	0.3560	9.8
.005000	3.40	.0796	3.4
.01000	3.32	.0479	2.4
.02000	3.24	.0288	1.7
.03000	3.18	.0220	1.5
.04000	3.15	.0177	1.3
.05000	3.12	.0152	1.2
.06000	3.09	.0135	1.1
.07000	3.06	.0125	1.1
.1000	3.00	.0100	1.0
.1500	2.91	.0082	1.0
.2500	2.80	.0063	1.0
.3000	2.76	.0058	1.0
.3500	2.71	.0056	1.1
.4141	2.65	.0054	1.2

In this connection, it is interesting to note that a number of organic salts containing the $In(OH)^{++}$ group have been prepared.[8]

Calculations similar to those made by Hattox and de Vries[2] assuming the formation of InO^+ or $In(H_2O)_4(OH)_2^+$ ions yield hydrolysis constants of the order of 10^{-8} but of less constancy. That such ions be produced in the primary hydrolytic reaction seems unlikely, however, and it appears more probable that a constant so calculated would apply to a secondary reaction.[9]

The values for K_h are smaller than those obtained for indium sulfate solutions but more constant. Furthermore, indium sulfate solutions of a given concentration are more acid than indium trichloride solutions of the same concentration.

Summary

1. Variations of pH with concentration at 25° are given for pure indium trichloride solutions.

2. Hydrolysis constants are calculated for such solutions, assuming that the hydrolysis products are $In(H_2O)_5(OH)^{++}$ and H_3O^+.

URBANA, ILLINOIS RECEIVED JANUARY 2, 1941

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(8) Ekeley and Johnson, THIS JOURNAL, **57**, 773 (1935).

(9) Denham, *J. Chem. Soc.*, **93**, 41 (1908).

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

Properties of the Electrical Double Layer at a Mercury Surface. I. Methods of Measurement and Interpretation of Results

BY DAVID C. GRAHAME

Measurements of the electrical capacity of the system formed when a metal is immersed in a solution of some chemically indifferent electrolyte such as aqueous potassium chloride are of much interest because of their intimate relation to other surface properties such as the surface tension of the metal, the specific surface charge or the electrokinetic *zeta*-potential. Although many experimenters[1–10] have measured the capacity of a mercury surface in contact with solutions of various electrolytes, an intercomparison of the results obtained reveals many examples of serious disagreement. Proskurnin and Frumkin showed in 1935 that a considerable part of the disagreement existing in the literature at that time could be attributed to the effects of traces of surface-active impurities, since these latter were shown to have a very large effect upon the measured capacities. Yet even in cases where such an explanation could not reasonably be invoked, discrepancies continued to exist. It will be the primary purpose of this paper to show that by the use of suitable techniques and methods of calculation, values of the capacity of the electrical double layer can be obtained by three independent methods, and the results so obtained stand in good agreement with one another. From the new results several significant conclusions can be drawn regarding the structure and behavior of the electrical double layer.

A comprehensive theory of the electrical double layer has been presented by Stern,[11] who assumes the double layer to be composed of two parts, a compact "two dimensional" layer of ions at the surface and a diffuse, three dimensional layer of

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(1) Krüger, *Z. physik. Chem.*, **45**, 1 (1903).

(2) Bowden and Rideal, *Proc. Roy. Soc.* (London), **A120**, 59 (1928).

(3) Erdey-Grúz and Kromrey, *Z. physik. Chem.*, **157A**, 213 (1931).

(4) Philpot, *Phil. Mag.*, **13**, 775 (1932).

(5) Ilkovic, *Coll. Czech. Chem. Commun.*, **8**, 170 (1936).

(6) Thon, *Compt. rend.*, **200**, 54 (1935).

(7) Proskurnin and Frumkin, *Trans. Faraday Soc.*, **31**, 110 (1935).

(8) Borissova and Proskurnin, *Acta Physicochim. U. R. S. S.*, **4**, 1819 (1936).

(9) Vorsina and Frumkin, *Compt. rend. acad. sci. U. R. S. S.*, **24**, 918 (1939).

(10) Frumkin, *Trans. Faraday Soc.*, **36**, 117 (1940).

(11) Stern, *Z. Elektrochem.*, **30**, 508 (1924).

ions held to the surface by long range electrical forces in a manner analogous to that by which the earth's atmosphere is held near its surface. Stern considers the effect of an adsorption of ions to the metal surface by introducing so-called "specific adsorption potentials" which are by implication constant and which are supposed to govern the extent of the adsorption and to predict the manner in which this adsorption changes with a change in the applied potential. Although these specific adsorption potentials are not susceptible to direct measurement, it will be shown in this paper that other kinds of adsorption, not regularly included in Stern's specific adsorption potentials, must be included in order to explain the observed results.

The term "capacity" has been used by various authors in two different senses, and considerable confusion exists in the literature because of a failure of most authors to distinguish between the two kinds of capacity which have been measured or calculated. The two kinds of capacity will be designated as "static capacity" and as "differential capacity," in harmony with recent usage, the term "static capacity" being a contraction of the term "electrostatic capacity" used by Craxford.[12] Alternatively, static capacity could correctly be called integral capacity.

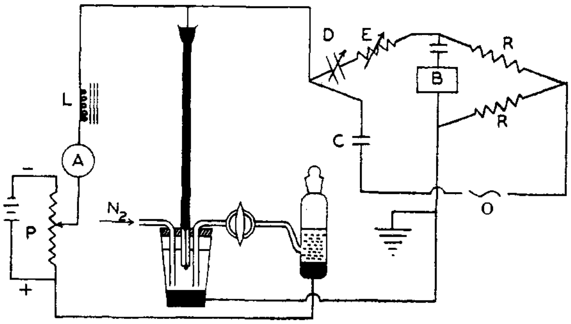

Fig. 1.—Apparatus for measuring the differential capacity of the electrical double layer.

The *specific static* (*or integral*) *capacity* will be here defined, as for an ordinary condenser, by the equation $C = q/E$ where q is the specific charge on the surface of the metal expressed in coulombs per sq. cm. and E is the potential difference between the metal and the solution reckoned as if this difference were zero at the potential of the maximum of the electrocapillary curve. It will be shown presently that this mode of calculating E is required by the definition of C here adopted, but carries no implication regarding the "true" potential difference between the phases. In the work which follows, all the measurements of capacity are reduced to unit area so that the quantities referred to will always be specific capacities.

The *differential capacity* will be exactly defined after the methods by which it may be measured have been discussed. For the present it may be regarded as the kind of capacity measured by any method which employs an alternating or pulsating potential. When no adjective is employed, the term "capacity" will refer to the differential capacity since this is the sense in which the word has been most used in the recent literature.

Experimental Methods

The apparatus used for all of the measurements described in this paper is shown in Fig. 1. The main feature of the apparatus is its use of a dropping mercury electrode to form the mercury surface upon which the measurements are made. Whereas previous investigators have experienced much difficulty in producing and maintaining a sufficiently clean mercury surface for capacity measurements of this sort, the use of a dropping mercury electrode eliminates this type of difficulty altogether. The disadvantage of making the measurements on an expanding surface is small compared with the difficulties encountered with a stationary surface. P in Fig. 1 represents a potentiometer of ordinary precision used as a source of potential for the polarization of the electrode to any desired value. A is a sensitive galvanometer used chiefly in an auxiliary experiment to be described later. L is a choke coil of high inductance (69 henries) which serves to block alternating currents from this part of the circuit. Its presence probably is not altogether necessary in view of the high resistance present in another part of the circuit. O is a 1000 cycle tuning fork oscillator. The resistors R are of high grade and have identical resistances of about 1000 ohms each. B is a two-stage high-gain audio amplifier which operates an ordinary pair of headphones. E is a non-inductive resistance box (0–10,000 ohms) and D is a capacitor decade whose capacity can be varied in steps of 0.01 mfd. from 0.01 to 3 mfd. A tuned filter in the output circuit serves to reduce hum to a negligible value. The measuring circuit is that of a symmetrical Wien impedance bridge; when the headphones are silent, the resistance and capacity of the cell under investigation are identical with the resistance and capacity of E and D, respectively. It was found that the resistance and capacity measured were unaffected by a change of frequency only when E and D were in series as shown. This is in agreement with the supposition that the resistance and capacity of the elements of the electrolytic cell are also in series.

The alternating current potential impressed upon the cell was never greater than one millivolt and was frequently much less. Too large a potential leads to erroneous results, although the measurements of Proskurnin and Frumkin indicate that potentials as great as fifteen milli-

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(12) Craxford, *Trans. Faraday Soc.*, **36**, 117 (1940).

volts may ordinarily be used without serious error. The necessity of using very small a. c. potentials exists only in those cases where the capacity changes very rapidly with the applied polarizing potential.

In order to avoid the uncertainties associated with the presence of liquid junction potentials the reference electrode shown in the figure ordinarily contained the same electrolyte as that present in the main body of the cell except for the addition of a small amount of the corresponding mercurous salt added in order to produce a reversible electrode. The stopcock shown in the figure was not greased, and the electrical conductivity past the stopcock when it was closed was sufficient to permit the very small "condenser current"[13] to pass without an appreciable *IR* drop. The alternating current, on the other hand, passed between the dropping electrode and the pool of mercury directly below, since a high resistance in this circuit would have rendered the bridge adjustment very insensitive to changes in the capacity of the circuit. The potential of the solution relative to that of the dropping electrode is fixed entirely by the circuit including the potentiometer and the reference electrode since there is no metallic connection between the pool of mercury at the bottom of the cell and the dropping electrode.

Although in most cases the removal of oxygen proved to have no detectable effect upon the results, the results reported here were all obtained in oxygen-free solutions. Oxygen was removed by bubbling through the solutions a stream of 85% nitrogen and 15% hydrogen which had been purified by passing it over hot catalytically-active metallic copper. The gas escaped from the cell through a mercury bubbler not shown in the figure. Rubber to glass connections were made gas-tight by the use of Apiezon-Q soft wax.

Both the capacity and resistance of the system depend upon the size of the mercury droplet, which is continuously changing. In order to overcome this difficulty, E and D (Fig. 1) were adjusted until an instant of silence occurred during the formation of each droplet. The time between the instant at which the preceding droplet fell from the capillary and the instant at which the bridge was balanced was measured with a $^1/_{100}$th second electric stop clock. Averaged results were reproducible to within about five-hundredths of a second; the time intervals measured were usually of the order of four seconds. Because the time interval occurs to the two-thirds power in the expression for the calculation of the capacity per square centimeter, the error arising from an error in timing should not exceed 1%, and this is about the magnitude of the discrepancies observed when measurements were repeated. The results obtained do not depend at all upon the accidental details of construction of the apparatus, such as the size of the capillary, the rate of dropping of the mercury, etc. No significant effect of temperature could be detected over a range of 10° in the neighborhood of room temperature.

In carrying out the calculations it was assumed that the droplet was spherical until the last half-second or so of its "life." Just before the droplet falls, it probably assumes a slightly distorted shape, and the area then becomes slightly greater than that of an equivalent sphere.

The position of the electrocapillary maximum was determined by a graphical method using data obtained by a modification of the drop-weight method. In this modification it was only necessary to determine (by interpolation) the potential at which the drop time was greatest, the values thus obtained agreeing satisfactorily with those obtained by other methods. It is unlikely that the errors in this determination exceeded ten millivolts in any determination, and an error of this magnitude would have almost no effect on the results because of a partial cancellation of errors. All of the potentials given in the graphs which follow refer to the potential relative to the potential of the electrocapillary maximum, since this potential proves to be of importance in the theory of the phenomena involved.

Results and Discussion

Results of measurements of this kind are shown in Figs. 2 and 3. About twenty points were taken for each curve, but in order to avoid confusion in the figures, these points are not indicated. Experimental points are given for one entirely typical case in a later figure. In certain cases a comparison is possible between the results shown in Figs. 2 and 3 and the results of measurements made by a somewhat similar method by Proskurnin and Frumkin,[7] by Borissova and Proskurnin[8] and by Vorsina and Frumkin.[9] The agreement is for the most part good, and this is especially true for the most recent work. In the opinion of the author, however, the technique described in this paper is simpler and a little more accurate than that used by previous authors. For use with very dilute solutions, the method of Proskurnin and Vorsina[14] is probably most suitable.

All of the curves shown in Figs. 2 and 3 possess the same general characteristics, namely, a steep rise at the left, a rather flat minimum at a value of about 16 microfarads per square centimeter, and a well-defined "hump" at or near the electrocapillary maximum ($E = 0$) in many of the curves. Curve 6 in Fig. 2 shows only a very slight hump which may not be real. Corresponding sodium and potassium salts, in so far as they have been investigated, give nearly identical curves. Such differences as are noted occur chiefly at potentials more positive than that of the electrocapillary maximum, an unexpected result. An example of this behavior is shown by curves 1 and 2 of Fig. 2.

In addition to the features just mentioned, all of the curves in Figs. 2 and 3, except those of the nitrates and of sulfuric acid, show at their right-hand extremities a very steep rise leading to values of several hundred microfarads per square centi-

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(13) Kolthoff and Lingane *Chem. Rev.*, **24**, 31 (1939).

(14) Proskurnin and Vorsina, *Compt. rend. acad. sci. U. R. S. S.*, **24**, 915 (1939).

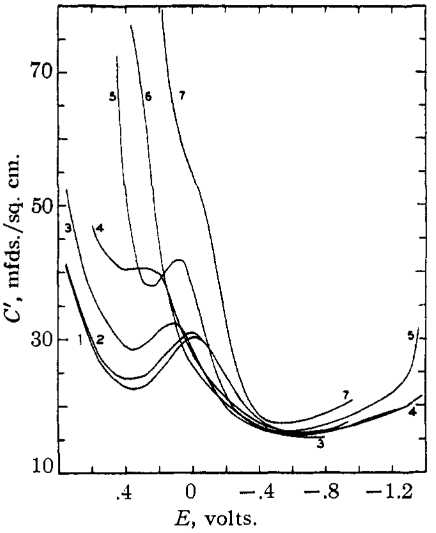

Fig. 2.—Differential capacity of the electrical double layer between mercury and the following solutions: (1) N $NaNO_3$; (2) N KNO_3; (3) N H_2SO_4; (4) N Na_2SO_4; (5) N NaCl; (6) N Na_2CO_3; (7) N NaI.

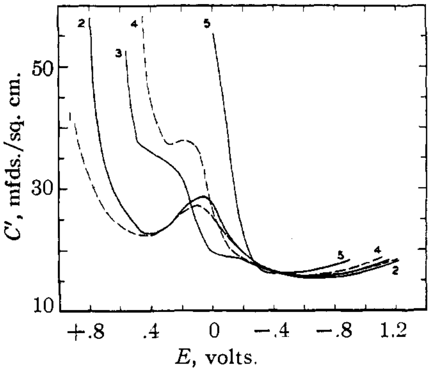

Fig. 3.—Differential capacity of the electrical double layer between mercury and the following solutions: (1) 0.1 N $KClO_4$; (2) 0.1 N $NaNO_3$; (3) 0.1 N Na_2SO_4; (4) 0.1 N NaCl; (5) 0.1 N NaI.

meter at potentials only one or two tenths of a volt more negative than the most negative potentials for which values are reported. Curve 5 of Fig. 2 shows an example of the beginning of this phenomenon; it has not been shown in the other curves because it is undoubtedly spurious in the sense that the capacity so measured does not correspond to the capacity of the electrical double layer in any ordinary sense. The abrupt rise of capacity at these potentials is always accompanied by a large increase in the direct current flowing through the cell, which signifies that electroreduction of sodium or potassium ions is taking place at the dropping electrode at these potentials.

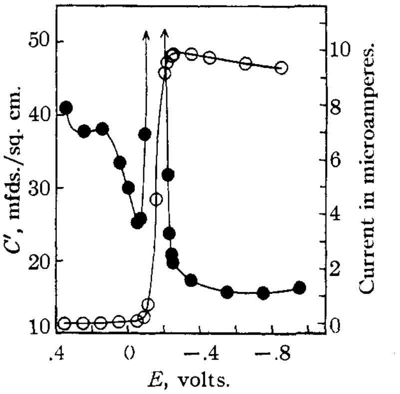

Fig. 4.—●, Differential capacity of the electrical double layer between mercury and 0.1 N NaCl + 0.002 N $CdCl_2$; ○, current passing through cell during capacity measurements (use right-hand scale of ordinates).

A better example of this phenomenon is obtained by studying the behavior of a solution containing large amounts of a "supporting" electrolyte and small amounts of some easily reducible metallic ion such as cadmium ion. Figure 4 shows the results of such an experiment. Along with the usual capacity measurements, current measurements were made in a manner similar to that used in polarographic analyses, and the results of these measurements are shown in the same figure. At potentials more positive than about −0.04 volt, practically none of the cadmium ions in the solution undergo reduction; at potentials more negative than about −0.24 volt, practically all of the cadmium ions which strike the surface of the mercury are reduced to metallic cadmium; at intermediate potentials, only a part of such ions are reduced, and it is in this range of potentials that the "capacity" of the system is anomalous. The large values of the capacity measured in this range are undoubtedly due to the electro-reduction and re-solution of cadmium ions at the surface of the mercury droplet in phase with the 1000 cycle alternating potential superimposed upon the steady potential supplied by the potentiometer. In such a system the largest current would flow when the potential was changing the most rapidly; in electrical parlance the current would lead the potential, and the system would behave like a condenser of large capacity. This is the effect observed. At potentials sufficiently negative to reduce every cadmium ion which strikes the electrode, the process would become inoperative because the deposited cadmium would not redissolve during the positive half of the alternating current cycle. This accounts for the return to normalcy in the values of the measured capacity when the potential becomes sufficiently negative. Since the excess capacity which arises from the reversible electro-reduction of an ion is not a characteristic of the electrical double layer, it will be termed a "pseudo-capacity" to distinguish it from the other kinds of capacity with which we are here chiefly concerned.

Irreversible processes such as the reduction of oxygen or of nitrate or hydrogen ions do not give rise to any noticeable pseudo-capacity. It is of interest to note that a solution of tetramethylammonium chloride does show the phenomenon, thus indicating the reversible formation of "metallic" tetramethylammonium, probably as an amalgam.

The very large values of the capacity shown by all of the curves in Figs. 2 and 3 at sufficiently large positive potentials (*i. e.*, on the left-hand branches of the curves) may be due, in a few cases, to a dissolution of mercury and a corresponding pseudo-capacity of the sort just described, but it will presently be shown that this phenomenon cannot be responsible for the beginning of the rise in these curves and that another and more important phenomenon is presumably of importance at potentials more positive than that of the electrocapillary maximum.

Figure 5 shows values of the capacity of the electrical double layer in a solution of normal sulfuric acid. In this figure the filled circles are experimental values of the capacity, the open circles are values of $d^2\sigma/dE^2$ where σ is the surface tension of mercury in the solution at any potential E. The values of this coefficient are dimensionally the same as those of a capacity per square centimeter and may be converted into such units without the introduction of any arbitrary factors. Values of the above coefficient are taken from the work of Gouy,[15] whose extraordinarily precise measurements make possible an exact evaluation of this coefficient in certain cases. In view of the obvious difficulty of measuring any quantity with sufficient accuracy to give significance to the second derivative of the curves obtained, it may be stated that the agreement shown in Fig. 5 is complete, in confirmation of the findings of Proskurnin and Frumkin.[7] The second derivatives of the surface tension and the measured capacities are in equally good agreement for normal (*i. e.*, half molar) solutions of sodium carbonate and of sodium sulfate. Sufficiently accurate surface tension data are not available for an exact comparison with the other curves given in Figs. 2 and 3, though it may be stated that the figures given by Gouy for normal potassium chloride solution are in agreement with those of this research in so far as a comparison is possible. Gouy's data for 0.43 N sodium iodide fall in a reasonable position relative to the curves given for normal and tenth normal solutions of the same salt.

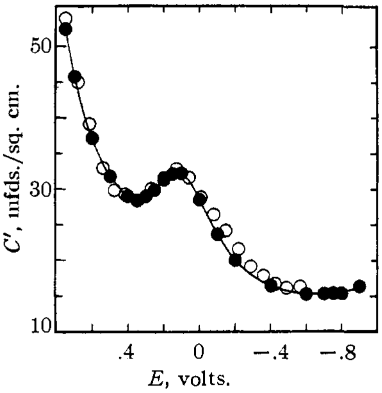

Fig. 5.—●, Differential capacity of the electrical double layer between mercury and 1 N H_2SO_4; ○, $d^2\sigma/dE^2$ according to Gouy.

Only in the case of normal potassium nitrate solutions is there any disagreement between the values of $d^2\sigma/dE^2$ given by Gouy and those of C' given in Fig. 2. The disagreement in this case is very evidently due to an arithmetical error in Gouy's figures, since in an earlier part of the same paper, Gouy gives values of σ *vs.* E from which values of $d^2\sigma/dE^2$ may be calculated; and the values so obtained do not agree with Gouy's later tabulation but do agree with the curve in Fig. 2.

Krüger and Krumreich[16] have also reported surface tension measurements for mercury in normal potassium nitrate solution. Although the electrocapillary curve obtained by them is very nearly parabolic, yet the values of $d^2\sigma/dE^2$ calculated from their data are not constant and follow in rough outline the contours of the curve in Fig. 2.

The thermodynamic relation between the electrocapillary curve and the capacity of the double layer has been derived in several ways by several authors. From one point of view it is possible to regard the accumulation or depletion of electrons

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[15] Gouy, *Ann. chim. phys.*, [7] **29**, 145 (1903).

[16] Krüger and Krumreich, *Z. Elektrochem.*, **19**, 620 (1913).

at the surface of the metal immersed in a liquid as an ideal case of surface "adsorption" in which the adsorbed particles are electrons. If one applies the familiar Gibbs adsorption equation to this situation, then by converting to electrical units one obtains

$$(\mathrm{d}\sigma/\mathrm{d}E)_s = q = CE \qquad (1)$$

where the subscript s implies a constancy of surface area and σ, E, C and q have the significance already explained. The condition of the constancy of s may be omitted since the surface tension is not a function of the extent of the surface under ordinary conditions. Since $\mathrm{d}\sigma/\mathrm{d}E$ is zero at the electrocapillary maximum, and since C can never be zero, it follows that E must be zero at the electrocapillary maximum. It may be well to repeat that this statement carries no implications regarding the real difference of potential between the phases.

Equation 1 has sometimes been differentiated on the assumption that C is a constant to give

$$\mathrm{d}^2\sigma/\mathrm{d}E^2 = C$$

Although at first sight this result might seem to be borne out by the results shown in Fig. 5, yet we see that it cannot be correct, since C is very evidently not a constant. We may write instead, as a statement of the experimental result

$$\mathrm{d}^2\sigma/\mathrm{d}E^2 = C' \qquad (2)$$

where C' is the differential capacity measured by any method similar to that previously described. Differentiating Equation 1, and substituting the result in Equation 2, we obtain

$$C' = \mathrm{d}(CE)/\mathrm{d}E = \mathrm{d}q/\mathrm{d}E \qquad (3)$$

This equation defines C' and shows clearly the distinction between the static and the differential capacity. Thus C is the total charge divided by the total potential difference whereas C' is the rate of change of the charge with respect to the potential. Since the condensers commonly dealt with in electrical work have a constant capacity, it has not been necessary to make this distinction in ordinary electrical theory.

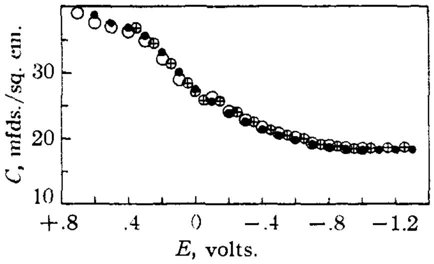

Fig. 6.—Static capacity of the electrical double layer between mercury and N $\mathrm{Na_2SO_4}$: ●, from measurements of differential capacity; ○, from surface tension measurements; ⊕, from direct current measurements.

If it is assumed that the electrical double layer remains in complete equilibrium with the applied potential throughout every phase of the thousand cycle variation of potential, then it is understandable that the apparatus here employed measures $\mathrm{d}q/\mathrm{d}E$ rather than some other poorly defined or non-reproducible quantity. Although it has not been customary in the past to consider the electrical double layer as coming to equilibrium with an applied potential in a time short compared to one-thousandth of a second, yet the above results appear to render such a conclusion necessary.

Integration of Equation 2 and substitution of the result in Equation 1 leads to the result

$$C = \frac{1}{E}\int_0^E C'\mathrm{d}E \qquad (4)$$

This equation gives a means of calculating the static capacity from the differential capacity; for comparison we may calculate the static capacity also from the electrocapillary curve using Equation 1.

Results of such a comparison are shown in Fig. 6. Filled circles are the results obtained by use of Equation 4; the open circles are calculated from Gouy's data for the surface tension of mercury in the same solution. The agreement is obviously very satisfactory. Shown in the same figure are values of C obtained by still a third method. If the solution is absolutely free from all traces of reducible matter, the current measured by the galvanometer A in Fig. 1 gives a measure of the average rate of flow of electrons to or from the surface of the expanding mercury droplet. In a given time, the total number of coulombs of electricity passing through the galvanometer divided by the number of mercury droplets falling from the tip of the capillary in the same time gives the total charge carried by each droplet as it falls. This quantity, divided by the surface area of each droplet (assumed spherical) gives the specific surface charge, q, defined above. By definition of the static capacity, $C = q/E$, we can then calculate C from these data, and the results so obtained are shown by the crossed circles in Fig. 6.

Philpot[4] has used this method also, and Ilkovic[5] has used a modification of it. The data obtained in this investigation are in qualitative agreement with those of the above workers, although quantitatively the differences are quite marked. In work of this kind, even the smallest trace of electroreducible matter produces large errors.

The agreement of the static capacity, as obtained by three wholly independent methods, leaves little room for doubt that the present interpretation is essentially correct, and that one can now state very definitely the relations existing among the surface tension, the surface charge, the static capacity and the differential capacity. For the measurement of the last three, the apparatus shown in Fig. 1 is the most suitable. Except for an integration constant, one can also calculate values of the surface tension from the differential capacity of the double layer, and such a calculation would lead to results of considerable precision.

Values of the static capacity of the double layer in a few typical solutions are given in Fig. 7. The general characteristics are the same in all—namely, a steep rise at the left, a broad minimum at the right, and a rise near the potential of the electrocapillary maximum. Some of the curves show maxima, as illustrated by curves 1 and 4.

The rise in all of the curves which occurs at sufficiently large positive potentials is associated, of course, with the similar rise in the curves in Figs. 2 and 3. At first sight it would appear that this rise might be due to the pseudo-capacity associated with a dissolution of mercury which occurs at sufficiently large positive potentials, but the potential at which that process occurs is marked by a very abrupt break in the current–voltage curve (*cf.* Fig. 4) and such a break always occurs at potentials considerably more positive than those at which the capacity begins to rise in Figs. 2 and 3. Moreover, there is no reason to believe that the second derivative of the surface tension with respect to the potential equals the pseudo-capacity of any system, which indicates that the observed differential capacity is not a pseudo-capacity for potentials at which agreement like that shown in Fig. 5 is obtained.

A specific adsorption of negative ions to the mercury in the sense of the Stern theory cannot account for the observed high values of the capacity at positive potentials since no possible constant values of the specific adsorption potentials give, when substituted in the Stern equation, results even approximately like those observed in actual experiments. An indication of the relative amounts of the specific adsorption of various anions at the potential of the electrocapillary maximum is given below, and it is there found that the order in which the ions fall in such a series bears no relation to the order in which the ions fall with respect to the extent of their effects at positive potentials.

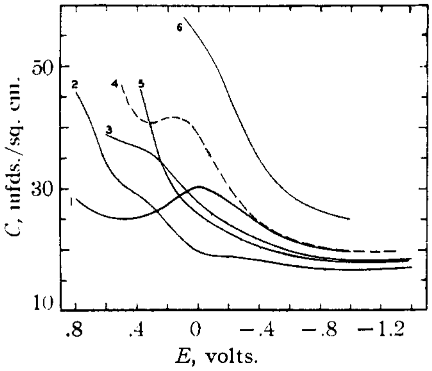

Fig. 7.—Static capacity of the electrical double layer between mercury and the following solutions: (1) N $NaNO_3$; (2) 0.1 N Na_2SO_4; (3) N Na_2SO_4; (4) N NaCl; (5) N Na_2CO_3; (6) N NaI.

The presence of large concentrations of ions held at the double layer by forces which are neither purely electrical nor related to specific adsorption potentials of the sort postulated by Stern leads to the supposition that the forces which hold the ions to the mercury when the latter is made sufficiently positive are chemical in nature and that the phenomenon might be described as an incipient precipitation of the corresponding mercurous salt. Anions at the surface of the mercury evidently attach themselves by chemical forces identical with those which cause precipitation of the corresponding mercurous salt. As long as the mercury atoms remain in the surface of the metal, no continuous current flows through the system and the phenomenon has the aspects of a simple but powerful adsorption. When the metal becomes sufficiently positive to expel the atoms into the solution as mercurous ions, then fresh metallic surface is exposed and a continuous current flows through the system. Under these latter conditions, only, will a pseudo-capacity be observed. In confirmation of these conclusions it will be observed from Figs. 2 and 3 that nitrates and perchlorates require the largest positive potential for the exhibition of the phenomenon, iodides the least, and that the other anions are arranged approximately in the order of the solubilities of their respective mercurous salts. Mercurous sulfate is considerably more soluble in sulfuric acid than in sodium sulfate solution, which accounts for the marked difference in the properties of the double layer in the two solutions. Perchlorates give curves very similar to those of the nitrates, a fact in harmony with the ready solubility of mercurous perchlorate and of mercurous nitrate.

This phenomenon of incipient precipitation differs from the Stern concept of specific adsorption chiefly in that it increases rapidly as the potential becomes more positive, unlike the behavior predicted by the Stern equation. To explain the failure of the Stern equation at positive potentials, it is probably necessary to postulate a change in the character of the metallic surface, according to which the adsorption of the anions on the surface would depend, as it were, on the amount of ionic character possessed by the positively charged surface. A more detailed treatment of this process will be presented at a later date.

The "humps" in the curves of Figs. 2 and 3 are associated with the rise near the electrocapillary maximum in the static capacity curves shown in Fig. 7. Further work will be necessary before a satisfactory explanation of these "humps" can be given. The negative branches of the curves in Fig. 7 may be more significantly represented in the form of q *vs.* E curves as shown in Fig. 8. Except for a lateral shift, the curves are virtually identical at potentials more negative than -0.6 volt when solutions containing the same cation at the same concentration are compared. This shows that the capacity and condition of the double layer at these potentials is determined almost entirely by the nature and concentration of the positive ions and practically not at all by the nature of the anions. The lateral shift of the curves arises from the manner of plotting. If the curves had been plotted against the potential measured relative to any standard reference electrode, they would be almost superimposed at potentials more negative than that corresponding to -0.6 volt on the scale shown. The separation of the curves in Fig. 8 gives a measure of the relative differences of potential between the metal and the solution at the electrocapillary maximum in the various solutions, and this in turn depends upon the amount of adsorption of the anions at the electrocapillary maximum. Thus it is found that in the solutions studied, the carbonate ion is adsorbed the least, the iodide ion the most, and the other ions to an intermediate extent. It is important to note that this is not the order of the solubilities of the corresponding mercurous salts, and that the adsorption at the electrocapillary maximum does not depend solely upon these solubilities, unlike the so-called incipient precipitation. It is probable, however, that the large adsorption displayed by the iodide ion is due to an incipient precipitation even at the potential of the electrocapillary maximum caused by the extreme insolubility of mercurous iodide.

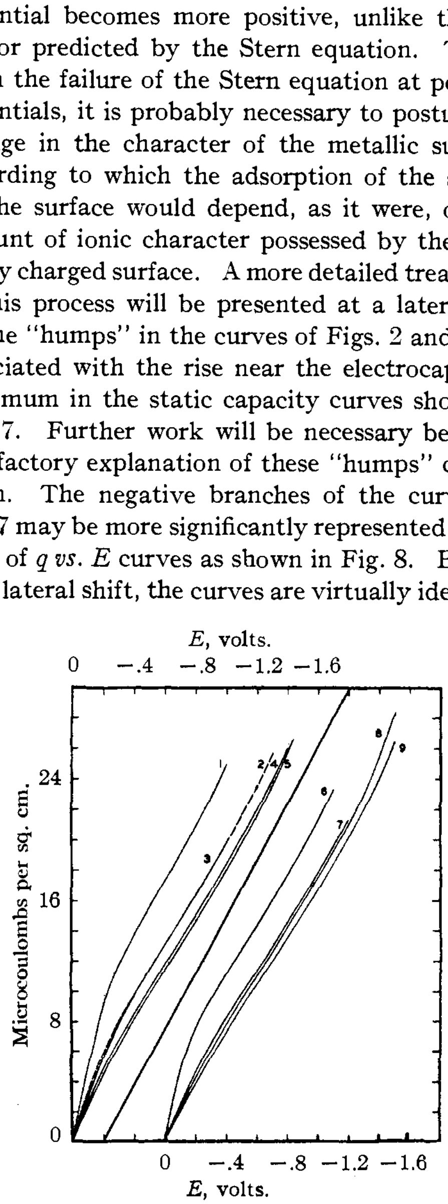

Fig. 8.—Charge in the electrical double layer between mercury and the following solutions: (1) N NaI; (2) N NaCl; (3) N $NaNO_3$; (4) N Na_2SO_4; (5) N Na_2CO_3; (6) 0.1 N NaI; (7) 0.1 N $NaNO_3$; (8) 0.1 N NaCl; (9) 0.1 N Na_2SO_4.

Summary

1. It has been shown that a clear distinction must be made between the several kinds of capacity which may be encountered in a study of the properties of the electrical double layer.
2. A technique is described whereby accurate values of the differential capacity of the double layer may be measured.
3. Equations are given whereby the static capacity and the surface charge may be calculated from several independent kinds of data.
4. Results of such measurements are given for a number of solutions.
5. It is shown that an incipient precipitation of certain anions gives rise to large values of the capacity of the double layer under appropriate conditions.
6. It is shown that the reversible electro-

reduction of an ion gives rise to phenomena which simulate the behavior of a condenser of very large capacity.

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Molecular Size Distributions and Depolymerization Reactions in Polydisperse Systems

BY ELLIOTT MONTROLL*

When experimenting with long chain polymers it is desirable to use molecules which are all composed of the same number of monomeric elements. Since such a homogeneous system is difficult to prepare, one must often be satisfied with more or less heterogeneous mixtures. An indication of the molecular size distribution of this type of system can be obtained by applying statistical methods to the various molecular weights that can be determined experimentally.

If a long chain molecule in a system of N similar polymers consists of p monomeric elements or fundamental units (for example, the monomeric elements in cellulose are glucose units), it will be a p-mer and its molecular weight will be denoted by M_p. Letting n_p be the fraction of p-mers in the system and m the molecular weight of a monomeric element, Nn_p is the total number of p-mers and $M_p = mp$. Now any experimental method (such as chemical analysis, vapor or osmotic pressure measurements) which in effect involves the counting of molecules, measures the "number average" molecular weight

$$\mathbf{M}_1 = \sum_p M_p n_p / \sum_p n_p \qquad (1)$$

The average value resulting from a procedure depending on weights of the molecules (*e. g.*, Staudinger's viscosity method) is given by the "weight average" molecular weight:

$$\mathbf{M}_2 = \sum_p M_p^2 n_p / \sum_p M_p p_p \qquad (2)$$

Sedimentation equilibrium measurements in an ultracentrifuge make available the "*z*-average" molecular weight[1]

$$\mathbf{M}_3 = \sum_p M_p^3 n_p / \sum_p M_p^2 n_p \qquad (3)$$

It is now apparent from (1), (2) and (3) that the moments of the distribution function, n_p, the i-th of which is

$$\mu_i = \sum_p p^i n_p \qquad (4)$$

can be expressed in terms of the $\mathbf{M}_i$'s

$$\mathbf{M}_i = \frac{\sum_p M_p^i n_p}{\sum_p M_p^{i-1} n_p} = m \frac{\sum_p p^i n_p}{\sum_p p^{i-1} n_p} = m \frac{\mu_i}{\mu_{i-1}} \qquad (5)$$

or, since

$$\sum n_p = 1$$

$$\mu_i = \mathbf{M}_1 \mathbf{M}_2 \ldots \mathbf{M}_i / m^i \qquad (6)$$

In a polydisperse system in which the molecular size distribution has a single maximum, this distribution might be almost normal. As has been discussed by Lansing and Kraemer,[1] a logarithmically normal distribution function is applicable when there is reason to believe that a strong deviation toward the high molecular weight components exists. Since only two moments are required to calculate normal and logarithmically normal distribution functions, they do not make use of all the possible experimental information. We will now proceed to derive a distribution function which involves all the measurable moments, and then we will develop a theory of depolymerization of polydisperse systems with arbitrary initial distributions.

Almost Normal Molecular Size Distributions.—The fraction of p-mers in a system with a normal distribution[2] of molecular sizes is

$$n_0(p) = e^{-(\mu_1 - p)^2/2\sigma^2}/\sigma\sqrt{2\pi} \qquad (7)$$

where μ_1 is the average degree of polymerization or first moment of the distribution and σ^2 is the mean deviation, $\mu_2 - \mu_1^2$. Since any continuous function, $f(p)$, such that $\int_{-\infty}^{\infty} |f(p)|^2 \mathrm{d}p < \infty$, can be expanded as a product of a Gaussian error function (7) and a linear combination of Hermite polynomials, an almost normal distribution function can be written

$$n_p = \sum_{n=0}^{\infty} c_n n_0(p) H_n\left(\frac{\mu_1 - p}{\sigma}\right) \qquad (8)$$

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(1) See Kraemer's article on polydisperse systems in "The Ultracentrifuge," edited by Svedberg and Pedersen, Oxford Press (1940); or Lansing and Kraemer, THIS JOURNAL, **57**, 1369 (1935).

(2) The treatment for logarithmically normal distributions similar to those of Lansing and Kraemer[1] but involving three observable moments proceeds in a similar manner. See, for example, A. Fisher, "The Mathematical Theory of Probabilities," New York, N. Y., 1926, p. 235.