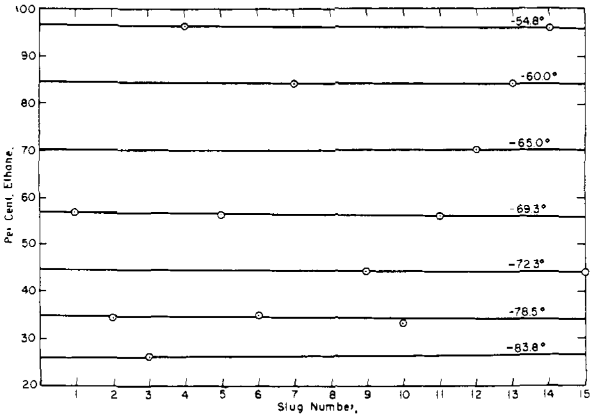

Fig. 2.—Testing data for catalyst IX.

conditions. In this case, a stream of synthesis gas would be passed over the catalyst and the doser would be used to collect measured volumes of the tail gas. This in turn would be carried through the chromatographic column as before, so that most of the advantages listed above would be applicable.

(6) In the present work, adsorption chromatography[3-6] was used because it was most convenient in dealing with the low molecular weight gases of interest. Vapor phase chromatography[5-11] would be preferable for studies involving molecules of higher molecular weight.

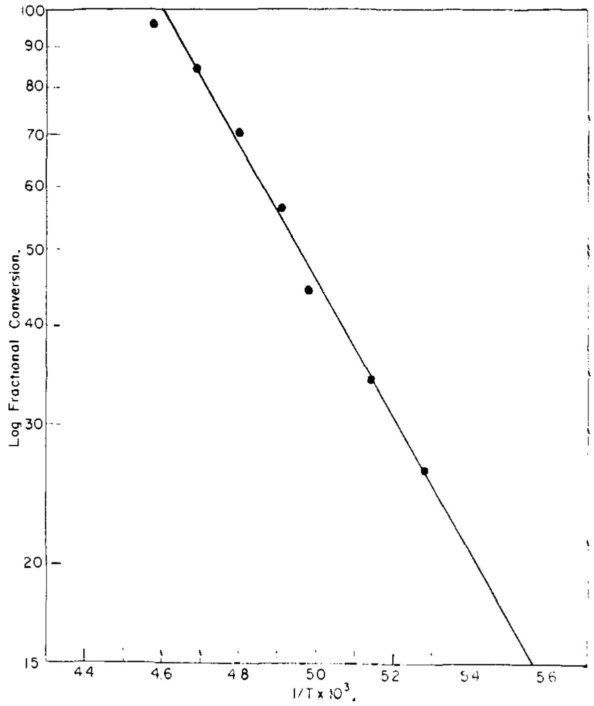

Fig. 3.—Activation energy data picked from Fig. 2 at the twelfth slug.

[3] H. W. Patton, J. S. Lewis and W. I. Kaye, *Anal. Chem.*, **27**, 170 (1945).

[4] J. Griffiths, D. H. James and C. S. G. Phillips, *Analyst*, **77**, 879 (1952).

[5] D. H. James and C. S. G. Phillips, *J. Chem. Soc.*, 1600 (1953).

[6] F. T. Eggertsen, H. S. Knight and S. Groennings, *Anal. Chem.*, **28**, 303 (1956).

[7] A. T. James and A. J. P. Martin, *Biochem. J.*, **50**, 679 (1952).

[8] N. H. Ray, *J. Appl. Chem.*, **4**, 21 (1954).

[9] E. M. Fredericks and F. R. Brooks, *Anal. Chem.*, **28**, 297 (1956).

[10] M. Dimbat, P. E. Porter and F. H. Stross, *ibid.*, **28**, 290 (1956).

[11] D. H. Lichtenfels, S. A. Fleck and F. H. Burow, *ibid.*, **27**, 1510 (1955).

PITTSBURGH, PENNA.

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

Capacity of the Electrical Double Layer between Mercury and Aqueous Sodium Fluoride. II. Effect of Temperature and Concentration

BY DAVID C. GRAHAME

RECEIVED NOVEMBER 12, 1956

The differential capacity of the electrical double layer between mercury and aqueous solutions of sodium fluoride has been measured at five different temperatures and four different concentrations. The results are in agreement with a theory previously proposed. The results also provide several clues to the anomalous behavior of the electrical double layer and suggest a new theory according to which the rise in the capacity on the *anodic* side of the potential of the electrocapillary maximum is attributed to electrostriction. The "hump" is attributed to the formation of a pseudo-crystalline semi-rigid layer through which anions pass only with difficulty, but without activation energy. The solvent next to the metal never achieves a state of free rotation comparable to that which it enjoys in the bulk of the liquid, which is offered as a partial explanation for the fact that the dielectric coefficient of the substance making up the inner layer is so much lower than that of pure water.

Introduction

The fluoride ion is unique among the univalent anions so far investigated in that it exhibits little or no specific adsorption on mercury even when the latter is positively charged.[1-3] This makes it particularly useful as a tool for studying the properties of the electrical double layer on mercury, since it eliminates the most complicating factor.

The choice of a positive ion is dictated largely by convenience, since monatomic cations are never observed to be chemisorbed on mercury. The sodium ion has several advantages for this investigation as follows: (1) its mobility in water is nearly the same as that of the fluoride ion,[4] which tends to reduce or eliminate liquid junction potentials between two concentrations of aqueous sodium fluoride, or between sodium fluoride and potassium chloride in solution. (2) Unlike KF and NH_4F, so-

[1] D. C. Grahame and B. A. Soderberg, *J. Chem. Phys.*, **22**, 449 (1954).

[2] D. C. Grahame, THIS JOURNAL, **76**, 4819 (1954).

[3] D. C. Grahame, *Z. Elektrochem.*, **59**, 740 (1955).

[4] H. Hartley and H. R. Raikes, *Trans. Faraday Soc.*, **23**, 393 (1927).

dium fluoride solutions in water do not attack Pyrex glass rapidly. (3) Sodium fluoride is much easier to purify than either KF or NH_4F. It can be handled in Pyrex vessels, as just indicated, and its solubility in water is about right for efficient recrystallization. Because it has nearly zero temperature coefficient of solubility, it has been necessary to evaporate the water solutions in a vacuum desiccator, an operation which usually produced large clear crystals which could then be dried and weighed prior to making up the desired solutions.

General Considerations.—It has been shown previously[2] that the capacity of mercury in contact with aqueous solutions of sodium fluoride at 25° can be adequately represented by a combination of the Gouy–Chapman theory and an assumption to the effect that the differential capacity of the inner region of the electrical double layer (the region between the metal and the plane of closest approach of the non-adsorbed ions, called by Overbeek the Gouy plane) is a function of the electronic charge on the metal but not of the concentration of the ions in the solution. The capacity of the inner region of the double layer will be denoted C^0. It is well known that the nature of the cation has only a small effect upon electrocapillary properties, so long as the cation is monatomic. The effect upon C^0 of a change of temperature is dealt with in the present paper. The effect of changing the solvent (from water to methanol) has been reported elsewhere.[3] It is found that in methanol the above-mentioned theory of the electrical double layer works very well, and that the capacity C^0 changes with potential in a manner which is qualitatively similar to that found for water solutions at elevated temperatures. In all cases C^0 goes through a pronounced minimum when plotted as a function of the potential or of the surface charge density q, and in methanol solutions there is no trace of the "hump" which is so characteristic a feature of differential capacity curves of mercury in contact with aqueous solutions at room temperature.

Experimental Details

The experimental procedure was the same as that described in part I.[2] For measurements at elevated temperatures, the solution was jacketed by a stirred water-bath of the desired temperature. For measurements at 0°, the jacket of the cell was packed in ice, covered with a minimum of water, and stirred gently with a stream of air bubbling up through the mixture.

The reference electrode was a normal calomel electrode held at 25°. This is better practice than changing the temperature of the reference electrode. The uncertainty in the absolute value of the potential is of no consequence, since no use is made of the *absolute* value of the recorded potential.

The mode of purification of the sodium fluoride has been mentioned above. Solutions were made up in conductivity water of specific conductance 1.0×10^{-6} or better. Special care was taken to prevent the contamination of the fluoride solutions by chloride ions from the calomel electrode. This is of particular importance in the present work because the chloride ion is chemisorbed on positively charged mercury.

The potential of the electrocapillary maximum (e.c. max.) was found by the drop weight method described earlier (method III of ref. 5) or from the potential of the capacity minimum in rather dilute ($\sim$0.01 N) solutions.[6] The latter method is somewhat more reliable in practice.

Results and Discussion

The differential capacity of the electrical double layer between mercury and aqueous solutions of sodium fluoride is shown as a function of potential, temperature and concentration in Figs. 1–5.[7] From differential capacity measurements made on 0.795 N NaF (data not shown), values of C^0 as a function of the surface charge density, q, have been computed. The method of computation is described in paper I.[2] In brief, q is found by integrating C (the observed differential capacity) against E (the observed potential), the constant of integration being fixed by noting that $q = 0$ at the potential of the e.c. max. The capacity of the diffuse part of the double layer C^d is known from Gouy–Chapman theory (see ref. 3 for the explicit equation most readily applicable), and the capacity of the inner region, C^0, is found by regarding the observed capacity C as the series capacitance of C^d and C^0. That is to say

$$1/C = 1/C^d + 1/C^0 \qquad (1)$$

This equation may be regarded as a definition of C^0. It is derived from more theoretical considerations in another place which in point of logic, therefore, give physical meaning to the C^0 defined by the equation.

The results of the computation are shown in Fig. 6. The first point to be noted in Fig. 6 is the convergence of the curves at the capacity minimum. This observation suggests and probably requires the assumption of complete dielectric saturation of the inner region at the point of convergence. To the right of the point of convergence (*i.e.*, on stronger cathodic polarization), the curves remain sensibly coincident in spite of the very considerable increase in the capacity. There is hardly room for doubt that this coincidence results from dielectric saturation of the inner region over this whole range of potentials in question.

To the left of the point of convergence the separation of the curves is also consistent with this interpretation. The capacity is lower at the higher temperature, as expected, and the ratios of the capacities at, say, $q = -4$ μcoul./cm.^{2} are about equal to the ratios of the dielectric constants of water at the various temperatures. No precise agreement is to be expected.

The folding over of the low temperature curves is manifestly related to the "hump" which forms so conspicuous a part of the differential capacity curves of most electrolytes in water. The results show that it is not a consequence of the specific adsorption of the anion, as was previously informally supposed, since the beginning of the hump is clearly observed at 25°, where specific adsorption of fluoride ions is surely absent.

Further evidence to the effect that specific adsorption is not responsible for the hump comes from the observation that the hump in solutions of

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(5) D. C. Grahame, R. P. Larsen and M. A. Poth, THIS JOURNAL, **71**, 2978 (1949).

(6) To be precise about this matter, it was not the capacity minimum which was used but the minimum in the capacity of the diffuse part of the double layer, C^d, as determined from an analysis of the capacity curves for 0.01 N solutions. C^d goes through a minimum when dC/dE is the same as dC^0/dE. The latter is known from measurements in more concentrated solutions, as described in the text.

(7) Tables of values corresponding to these figures, and also tables of values of q, the surface charge density, will be printed up separately and will then be available on request.

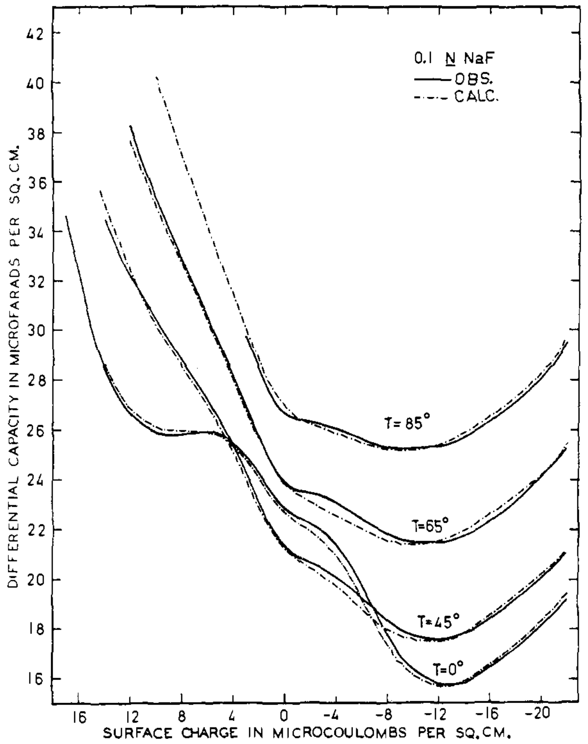

Fig. 1.—Observed and calculated values of the capacity of the electrical double layer between mercury and 0.1 *N* solutions of sodium fluoride at various temperatures. Calculated values depend upon measurements made with 0.8 *N* NaF solutions at same temperature.

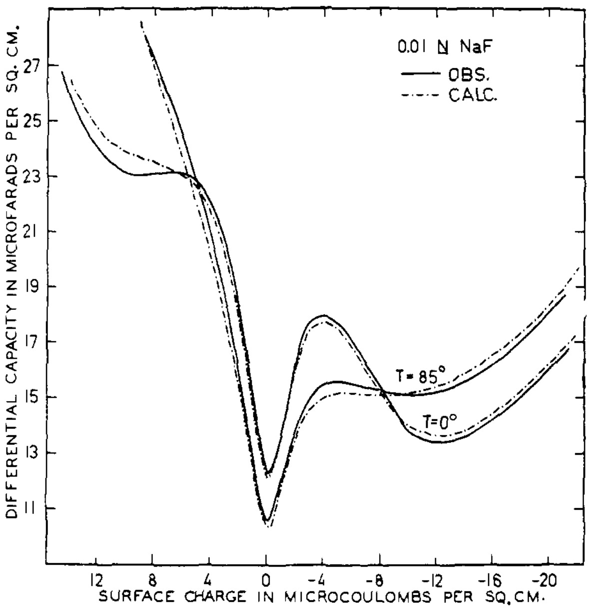

Fig. 2.—Observed and calculated values of the capacity of the electrical double layer between mercury and 0.01 *N* solutions of sodium fluoride at two temperatures.

chlorides vanishes above about 85°[8] although the specific adsorption of the ion is still strong, as evidenced by comparison of the capacity curves with those of fluorides.

A clue to the cause of the "hump" is furnished by the observation that at values of q more positive than about 6 μcoulombs/cm.^{2} the capacity of the inner region is larger at high temperatures than at low (Fig. 6). This means that comparatively weak forces (sufficient to be influenced by the *average* kinetic energies of the ions or molecules) are involved. In the absence of specific adsorption, the only two ways of increasing the capacity per unit area of the inner region are (1) increasing the dielectric coefficient of the region and (2) decreasing its thickness.

It is difficult to assess the dielectric coefficient of the inner region without knowing either its field strength or its thickness, but an increase with temperature of dielectric coefficient is seemingly unknown in any other context. Moreover, the comparatively normal variation with temperature of the dielectric coefficient to the right of the hump makes it unlikely that the dielectric coefficient behaves so very abnormally elsewhere.

A much more plausible explanation of the phenomena observed is found by exploring the second possibility, namely, that the thickness of the inner region may increase with decreasing temperature, a statement which immediately brings to mind the possibility that the surface may be covered with what the author has called[9] a "pseudo-crystalline ice-like" layer of solvent. The expression "ice-like" is not to be interpreted literally, since there is no assurance that the layer is hydrogen bonded. The significant property of the layer, and the only one for which we have any experimental evidence, is its ability to exclude anions, some more than others. With all these restrictions in mind, it is still convenient to speak of an ice-like layer and to refer to the theory as the ice-layer theory. A more accurate description would be to speak of the anion-excluding-layer theory.

The "ice-like" layer must have the property of "melting," not abruptly, like ice, but gradually, like tar. This property is indicated by the *gradual* disappearance of the hump as the temperature is raised (Fig. 6). The layer must also have the property of excluding certain anions, such as nitrate, more easily than it excludes others, such as fluoride. This is evident from the curves shown in Fig. 7, where even at 89° the "hump" has not completely disappeared.

It is natural to assume that the "ice-like" layer is composed of water molecules oriented with their oxygen atoms weakly chemisorbed to the positively charged mercury. This is a form of dielectric saturation, of course, and suggests that the rise of C^0 on strong anodic polarization may have the same cause as the rise of C^0 on strong cathodic polarization. The latter can be explained as the result of electrostriction compressing the solvent and making the inner region thinner.[10]

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(8) D. C. Grahame, unpublished results.

(9) D. C. Grahame, *J. Chem. Phys.*, **25**, 364 (1956).

(10) In ref. 3 the author attributed this effect to the increase in the dipole moment of the solvent molecules in the high field. This now seems to be a concurrent but less important effect than the simple compression of the dielectric by the field. The compressed dielectric allows the ions to move closer, thereby increasing the capacity of the inner layer. Macdonald (*J. Chem. Phys.*, **25**, 364 (1956)) takes the position that the ions themselves compress the solvent.

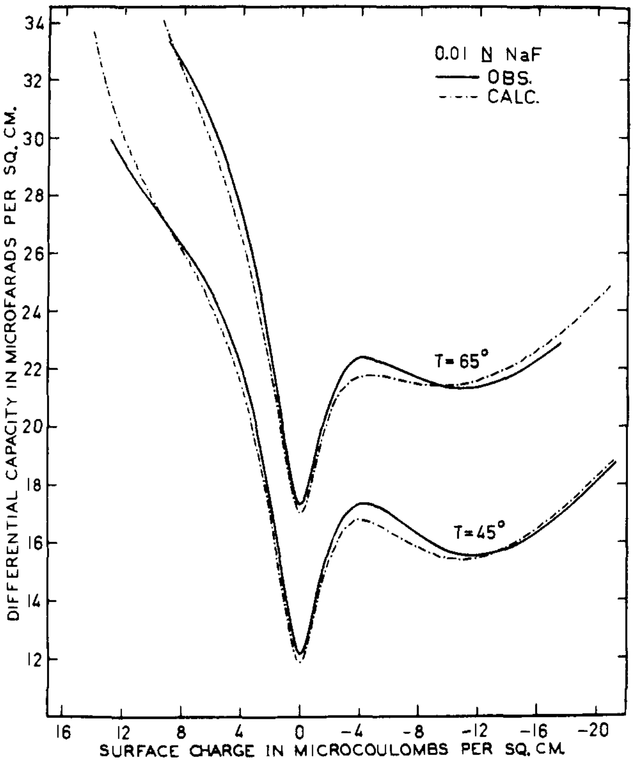

Fig. 3.—Observed and calculated values of the capacity of the electrical double layer between mercury and 0.01 *N* solutions of sodium fluoride at two temperatures.

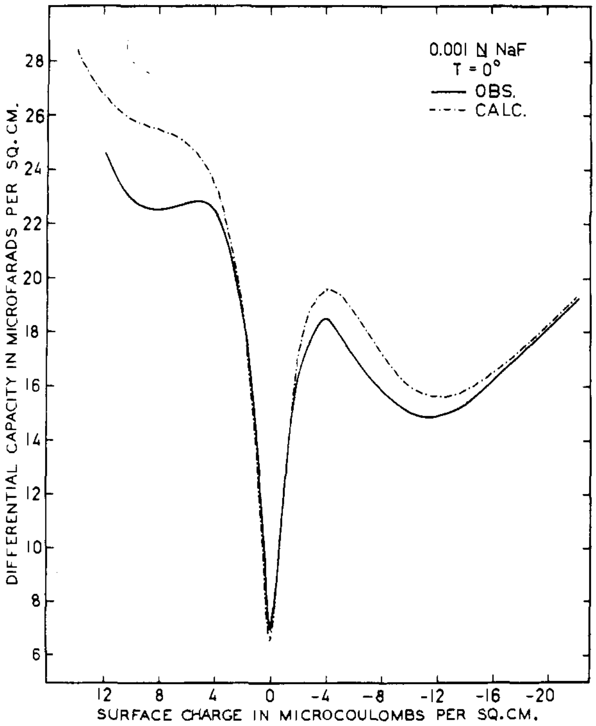

Fig. 4.—Observed and calculated values of the capacity of the electrical double layer between mercury and 0.001 *N* sodium fluoride at 0°.

Considerable support for the view that electrostriction is largely responsible for the capacity rise

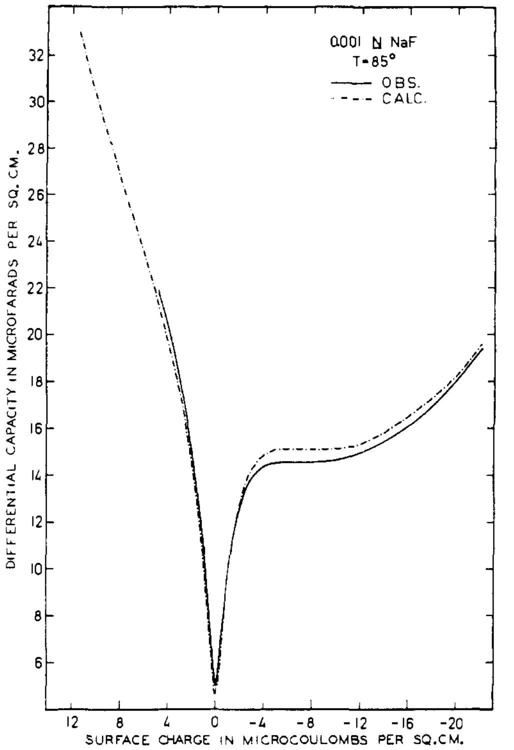

Fig. 5.—Observed and calculated values of the capacity of the electrical double layer between mercury and 0.001 *N* sodium fluoride at 85°.

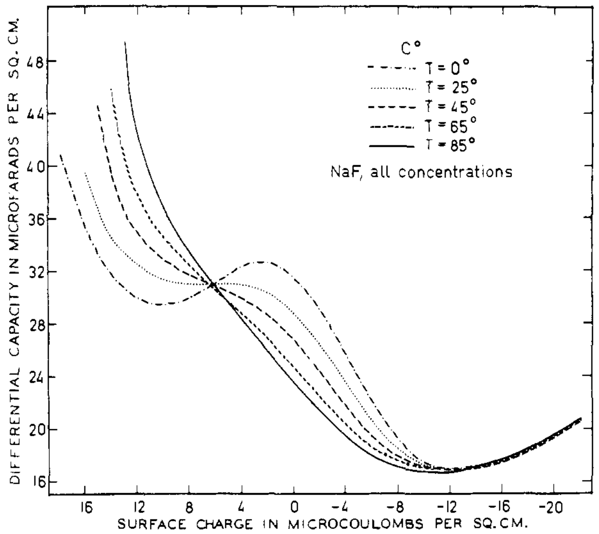

Fig. 6.—Calculated values of C^0, the differential capacity of the inner part of the electrical double layer, between mercury and aqueous solutions of sodium fluoride at several temperatures. Calculations made from data obtained with 0.8 *N* solutions.

on *both* branches of the curve (and in the absence of specific adsorption, which overwhelms the effect in question on the anodic branch) is found in data already presented on the capacity of the double layer in methanol.[3] Here the "ice-layer" is absent and the compressibility of the solvent is large (a point already made by Macdonald[11]), with the re-

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[11] J. R. Macdonald *J. Chem. Phys.*, **25**, 364 (1956).

sult that the curves are nearly symmetrical and rise very steeply from their minimum values. It is almost self-evident in this case that the rise in the capacity on the two sides of the minimum stems from the same fundamental cause, and it seems to be generally accepted that on the cathodic side this is some form of electrostriction or compression of the solvent.

It now appears likely that dielectric saturation of the inner region prevails over all but a very limited range of potentials (roughly those between the electrocapillary maximum and the capacity minimum) and that even in the absence of large externally imposed electric fields the dielectric coefficient never rises much above its saturation value because of the orienting influence of "chemical" forces as distinct from the orienting influence of the externally imposed fields. Thus there is probably no state of polarization where the solvent molecules are free to turn over as freely as in the bulk liquid.

It is of interest that C^0 shows no discontinuity or abrupt change of slope at $q = 0$ (Fig. 6). This again fits a picture of the double layer in which the potential of zero surface charge does not correspond to a condition of no orienting forces.

The concept of the double layer presented here differs from that published a year ago[3] in that the "natural" field of the metal is no longer called upon to account for the lack of a maximum in the plot of C^0 *vs.* q. The role of the "natural" field is now left unspecified; it may well turn out to be of no particular importance. The change in the potential of the electrocapillary maximum when the solvent is changed may now be attributed, as formerly,[12] to changes in the amount of dielectric orientation and to changes in the dipole moment of the solvent molecules.

What emerges from the above considerations is a qualitative but reasonably self-consistent picture of the electrical double layer. The "ice-layer" turns out to be a layer of oriented solvent molecules (not hydrogen bonded to one another) which excludes large anions at room temperature and even small anions (F^-) at lower temperatures. The "hump" in the capacity curves marks the formation of the layer, and its disappearance at elevated temperatures marks the "melting" of the layer. Electrostriction is responsible for the rise in the capacity both on the anodic and cathodic ends of the curve, although relaxation of dielectric saturation also makes a contribution to this rise over a limited range of potentials, as mentioned above.

The Effect of Concentration.—It has already been stated that at 25° C^0 was found to be a function of the surface charge density, q, and not of the concentration. It was of interest to see to what extent this result holds at higher and lower temperatures and also how the potential of the electrocapillary maximum varies with temperature.

The most satisfactory method of testing the constancy of C^0 is to calculate the capacity of the whole double layer, using eq. 1 and diffuse double layer theory in the classical manner, and then to compare the calculated and observed results.

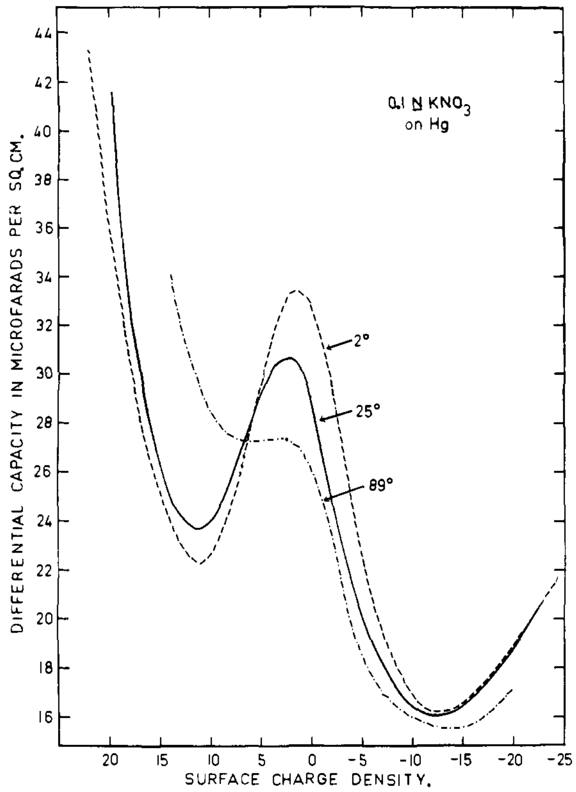

Fig. 7.—Observed values of the differential capacity of the electrical double layer between mercury and aqueous 0.1 *N* solutions of potassium nitrate at three temperatures.

This procedure has the advantage that it does not magnify errors in the observations or errors in the theory of the diffuse double layer in such a way as to produce uninterpretable results. The results of the calculations are shown in Figs. 1–5. The agreement is as good as one could expect, bearing in mind that the accuracy of the measurements falls off as one goes away from room temperature. Where the disagreement is systematic, this is attributable to small errors in the measurement at the highest concentration, which affects all the other results at that temperature.

The relatively good agreement between theory and experiment at 0° provides the first evidence that the fluoride ion is not adsorbed (strongly) on positively charged mercury at that temperature. It was self-evident that the adsorption at temperatures above 25° would not exceed that at 25°, a fact which these observations tend to confirm.

There is always some disagreement between theory and experiment on the anodic end of the curves. This disagreement is no worse at low temperatures than at high temperatures, a result which indicates that specific adsorption of the fluoride ion is not responsible for the disagreement.[13]

The potential of the e.c. max. varied from −0.48 v. at 0° to −0.44 v. at 85°.[14] Since there are two

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(12) A. Frumkin, *Colloid Symp. Ann.*, **7**, 89 (1930).

(13) If fluoride ion were specifically adsorbed on positively charged mercury, the adsorption would certainly be expected to diminish at elevated temperatures.

(14) This result is independent of concentration within the limits of error of the measurements. At 45° the value is −0.46 v. and at 65° it is −0.455 v.

thermal junctions in the circuit, one in the metal and one in the solution, the result has relatively little meaning except as it establishes the order of magnitude of the effects to be expected in other cases. For comparison it may be mentioned that the potential of the e.c. max. in 1.0 *N* KCl varies from −0.574 v. at 0° to −0.522 v. at 85°. All of these figures are stated relative to a normal calomel electrode at 25°.

Anyone who wishes to perform experiments like those discussed in this paper will have use for data on the absolute value of the minimum capacity at the various temperatures employed. Table I gives such data at five temperatures. It should be mentioned that absolute values of capacity are always a little uncertain and may require revision by several tenths of a per cent. as better methods are worked out.

TABLE I

MINIMUM VALUES OF THE DIFFERENTIAL CAPACITY[a]

Temp., °C.	1 *N* KCl	0.8 *N* NaF	0.1 *N* NaF	0.01 *N* NaF
	Microfarads per square centimeter			
0	16.58	16.00	15.76	15.65
25	16.50	15.97	15.74[b]	15.62[b]
45	16.43	15.90	15.66	15.52
65	16.27	15.77	15.52	15.37
85	16.08	15.56	15.31	15.13

[a] In those cases where there are two minima, the table refers to the one on the cathodic branch of the curve. [b] This is a redetermination of a value published previously in the author's Technical Report No. 14 to the Office of Naval Research, dated February 18, 1954.

It is a great convenience in this work to have values of the surface charge density, *q*, at some sufficiently cathodic potential that the effect of the anion is virtually eliminated. For this purpose Table II gives values of *q* at a potential of −1.205 v. This potential is sufficiently cathodic for all but the most strongly adsorbed anions (I^-, SCN^-, $S^=$) and is convenient for the integration of capacity data by the trapezoidal rule using potential intervals of 0.01 v. These data, like those in Table I, are a little uncertain in absolute value but give correct results for the potential of the e.c. max. when used together.

TABLE II

SURFACE CHARGE DENSITY, *q*, AT POTENTIAL AT −1.205 VOLTS[a]

Temp., °C.	1 *N* KCl	0.8 *N* NaF	0.1 *N* NaF	0.01 *N* NaF
	Microcoulombs per square centimeter			
0	14.60	14.20	13.58	12.73
25	14.22	13.73	13.03	12.14
45	13.86	13.49	12.79	11.83
65	13.51	13.14	12.40	11.47
85	13.28	12.86	12.10	11.14

[a] All potentials measured relative to a normal calomel electrode at 25°.

Conclusion

The investigation of the capacity of the electrical double layer in aqueous solutions of sodium fluoride in contact with mercury at several temperatures has provided a clue to the behavior and structure of the double layer. This has permitted the formulation of a theory which is at least qualitatively understandable and for which the next step will be to provide a quantitative expression. The author wishes to make it clear that he is merely *proposing* a theory and is not yet prepared to underwrite it.

Acknowledgments.—The author is grateful to Professor Earle S. Scott for stimulating discussions leading to the formulation of the theory proposed in this paper. He is indebted to Miss Vera Brewus for making many of the measurements and to the Office of Naval Research for the support of the project of which this work forms a part.

AMHERST, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Primary Quantum Yield for the Dissociation of Iodine Molecules in Carbon Tetrachloride Solution and the Rate Constant for the Recombination Reaction[1]

BY R. L. STRONG AND J. E. WILLARD

RECEIVED NOVEMBER 24, 1956

The quantum yield for the dissociation of iodine molecules in carbon tetrachloride solution at room temperature by a continuous spectrum of visible light has been found to be 0.13 ± 0.04. The determination has been made by the flash photolysis technique with a d.c. analog computer used to aid in correcting for the fact that the duration of the flash is appreciable relative to the time of recombination of I atoms. The recombination rate constant obtained is $k = 5.7 \pm 0.5 \times 10^9$ liters mole^{-1} sec.$^{-1}$ where $d[I_2]/dt = k[I]^2$. The relative extinction coefficients of iodine in the gas phase and in carbon tetrachloride solution and the visible spectrum of the xenon flash lamp have been determined.

Introduction

When a gaseous iodine molecule in the presence of a foreign gas absorbs a quantum of visible light, it always dissociates.[2] If, however, it is surrounded by a "cage" of solvent molecules, the atoms may lose their energy to the cage walls and immediately recombine[3] or they may recombine by diffusion after having escaped only a molecular diameter or so from each other.[4]

Knowledge of the quantum yield for the escape of such atoms from each other is relevant in interpretations of the over-all quantum yields of photochemical reactions, in reasoning about caging ef-

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[1] R. L. Strong and J. E. Willard, Abstracts of the New York Meeting of the American Chemical Society, Sept., 1954, p. 26-R.

[2] W. A. Noyes and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941.

[3] J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[4] R. M. Noyes, *J. Chem. Phys.*, **18**, 999 (1950).