duced by krypton, it may be wondered if some part of the magnetic effect previously reported[17] for such gases as ethane and benzene may not similarly be due to physical adsorption. But if the data are calculated in the same way, it will be seen that the magnetic change produced by benzene vapor is about 20 times greater than that produced by the same volume of krypton. The "physical" effect is, therefore, barely significant in comparison with the "chemical" effect. This does not mean that the effect produced by krypton would not be an interesting area for further investigation.

Another possible explanation for the effect of adsorbed nitrogen on the magnetization of nickel, and one which may not be mutually exclusive with the polarization idea, is based on the observations of Yates on the dimensional changes in unsintered Vycor glass caused by adsorbed gases. Yates[18,19] finds that non-polar gases, such as nitrogen and argon, cause a more or less linear expansion when adsorbed on unsintered Vycor. The nickel–silica catalyst samples bear some resemblance structurally to unsintered Vycor and, except for complications caused by the presence of the nickel, might be expected to behave in a somewhat similar manner. Any expansion of the silica network would increase the distance between adjacent nickel particles and this would be expected to lower the observed magnetization, insofar as it reduced any coöperative interaction between adjacent nickel particles. The failure of Broeder, *et al.*,[13] to observe the effects described in this paper is attributable to the fact that none of their measurements was made below room temperature.

Acknowledgments.—This work was sponsored by the Office of Ordnance Research, U. S. Army. The author is indebted to Mr. Robert Leak for some assistance with the measurements and to Mr. A. W. Ritchie for some helpful discussions.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, AMHERST COLLEGE]

Components of Charge and Potential in the Non-diffuse Region of the Electrical Double Layer: Potassium Iodide Solutions in Contact with Mercury at 25° [1]

BY DAVID C. GRAHAME

RECEIVED JANUARY 25, 1958

The differential capacity on mercury of aqueous potassium iodide solutions of 17 different concentrations has been measured and the components of charge and potential computed from the results. It is found that the differential capacity of the non-diffuse region of the electrical double layer, when measured at constant n^i (n^i = superficial density of adsorbed anions), is independent of n^i within the limits of accuracy of the measurements. The capacity does depend upon the electronic charge, however, in a manner resembling that found previously for unadsorbed electrolytes. It is also found that ψ^u, the potential generated across the non-diffuse region by specifically adsorbed anions, is proportional to n^i, the constant of proportionality being nearly independent of the surface charge density q. These results must be considered anomalous in relation to presently accepted concepts of the nature of the electrical double layer. A formal description of the electric fields within the non-diffuse region of the double layer requires the simultaneous use of two different values of the dielectric constant of that region, which is another expression of the same anomaly. The measurements permit a formal calculation of the relative distances from the interface of the inner and outer Helmholtz planes. The ratio varies with the surface charge density q in about the expected manner, though perhaps more rapidly. The measurements also permit the calculation of a specific adsorption potential, and this likewise varies with surface charge density in a reasonable manner.

Introduction

A theory of the non-diffuse part of the double layer (the inner region) has been presented elsewhere.[2] Methods of obtaining the components of charge in the diffuse and non-diffuse parts of the double layer from differential capacity measurements also have been described[3] and have been applied to a number of tenth-normal solutions of potassium and barium salts.[4] Measurements which might have been suitable for testing the theory outlined in ref. 2 have been reported by Esin and Markov,[5] by Devanathan and Peries[6] and by Anderson and Parsons,[7] but for one reason or another none of these investigations was entirely suitable for our objective. In particular it was desired to ascertain whether or not the theory described in ref. 2 is contradicted by experiment and, if not, whether an analysis along the lines indicated yields any new and significant information about the properties of the inner region of the double layer.

Experimental Details and Methods of Calculation

The experiment consisted in the measurement at 25° of the differential capacity of mercury in contact with aqueous solutions of potassium iodide of 17 different concentrations ranging from 0.015 to 1.2 *N*. The technique has been described in the literature many times[8,9] and was not modified in any essential detail. The solutions of potassium iodide were made up in conductivity water from twice recrystallized reagent grade salt. Measurements of potential were made relative to a normal calomel electrode, and no correction was or should have been made for liquid junction potentials. What was done, rather, was to compute the potential relative to a hypothetical electrode reversible to the iodide ion and kept always at the concentration of the salt

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[1] Reproduction in whole or in part permitted for any purpose of the U. S. Government.

[2] D. C. Grahame, *Z. Elektrochem.*, **62**, 264 (1958).

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TABLE I

COMPONENTS OF CHARGE AND POTENTIAL IN THE ELECTRICAL DOUBLE LAYER. 1.0 N KI

q, μcoul./cm.²	$-E$, v.	C, mfds./cm.²	Γ_+ ← μcoul./cm.²	Γ_-	n^i →	$-\psi^0$, v.	$-\psi^u$, v.	$\frac{\partial\psi^v}{\partial \log a_\pm}$	$\frac{\partial\psi^i}{\partial\psi^v}$	$\frac{\gamma}{\beta+\gamma}$	$-\psi^A$, v.
−20	1.5388	19.51	15.73	4.27	0.01	0.0669	0.9839				
−18	1.4290	18.15	13.92	4.08	.05	.0624	.8786				
−16	1.3201	18.08	12.41	3.59	.40	.0584	.7737				
−14	1.2132	19.84	11.36	2.64	1.23	.0553	.6698				
−12	1.1223	24.82	11.09	0.91	2.93	.0545	.5798				
−10	1.0514	32.14	11.49	− 1.50	5.39	.0557	.5077			0.261	0.1326
− 8	0.9953	39.31	12.25	− 4.25	8.21	.0579	.4494	0.156	0.151	.325	.1462
− 6	.9480	45.05	13.15	− 7.15	11.20	.0603	.3996	.159	.212	.382	.1527
− 4	.9057	49.59	14.01	−10.07	14.21	.0628	.3549	.156	.251	.432	.1533
− 2	.8667	52.90	14.99	−13.00	17.21	.0651	.3136	.151	.285	.476	.1493
0	.8299	55.63	15.84	−15.85	20.13	.0672	.2747	.147	.309	.520	.1429
2	.7947	58.14	16.61	−18.62	22.96	.0690	.2377	.147	.320	.579	.1376
4	.7611	61.02	17.29	−21.30	25.69	.0705	.2026	.144	.336	.630	.1276
6	.7292	64.54	17.89	−23.90	28.32	.0718	.1694	.137	.363	.672	.1139
8	.6992	69.15	18.41	−26.42	30.87	.0729	.1383	.132	.385	.706	.0977
10	.6714	74.89	18.86	−28.87	33.35	.0739	.1095	.129	.400	.736	.0806
12	.6458	81.73	19.25	−31.26	35.76	.0747	.0831	.125	.418	.768	.0638
14	.6224	89.11	19.57	−33.58	38.10	.0753	.0590	.127	.414	.792	.0467
16	.6009	97.25	19.84	−35.85	40.38	.0759	.0379	.127	.417	.811	.0300
18	.5812	105.9	20.06	−38.07	42.61	.0763	.0169				

in question. The only uncertainty in this procedure arises from the possibility that the liquid junctions actually present in the experimental set-up may not have been sufficiently reproducible. With salts like potassium chloride and potassium iodide, whose anions are so much alike in mobility, this is a wholly negligible difficulty.

Two complete and independent sets of experiments and calculations have been performed. The second set (1957 data), which was performed under more closely controlled conditions, is the one here reported, except as otherwise stated, but it is of interest that the shapes of the curves and the general conclusions to be drawn are the same whichever data are used. The first set of data (1956) was not "smoothed," and the experiment was repeated when it was found that the original data could not be smoothed without undue arbitrariness.

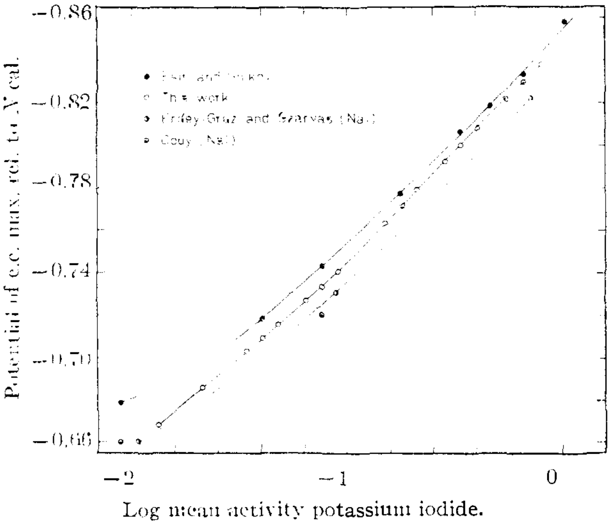

Fig. 1.—Potential of the electrocapillary maximum of mercury in potassium iodide as determined by four investigators.

The potential of the electrocapillary maximum (e.c.max.) was determined by back-integration of the capacity curves (ref. 10, method VII), using for the starting point (*i.e.*, the constant of integration) the value of the surface charge density of solutions of potassium chloride at −1.605 v. and at the same concentrations. Since the necessary data for potassium chloride were not at hand for all of the concentrations of potassium iodide studied, a smooth curve was drawn through the known values and the extra needed values read off. This procedure gave results lying between those of Esin and Shikov[11] and of Erdey-Gruz and Szarvas (for sodium iodide).[12] The results are shown in Fig. 1. To preserve internal consistency we have used our own values throughout, although it seems probable that the slight inflection in our curve is not real. The procedure used is extremely likely to introduce just such inflections. In addition to the results shown in Fig. 1, Erdey-Gruz and Szarvas, and also Esin and Shikov, have reported measurements at higher and lower concentrations and these have been considered in drawing the curves shown.

The differential capacity measurements were plotted on a very large scale and "smoothed" with respect to both chemical and electrical potential. The capacity was then integrated with respect to potential in the manner shown in detail in ref. 13. The starting values were chosen as indicated above, using data obtained with potassium chloride. The capacity values for a selected set of potentials and concentrations are reproduced in Tables I-III. Complete tables are contained in ref. 13.

The rate of change of capacity with chemical potential was computed, the operation being performed in two steps as indicated by the equation

$$(\partial C/\partial\mu)_{E^-} = (\partial C/\partial u)_E + (\partial C/\partial E)_\mu (\partial E/\partial\mu)_{E^-} \quad (1)$$

where μ is the chemical potential and the subscript E^- indicates that the potential is held constant with reference to an electrode reversible to the anion. The subscript E indicates that the potential was held constant with reference to a fixed electrode, no attention being paid to liquid junction potentials. The final coefficient in equation 1 is given by the familiar equation for concentration cells with transference

$$(\partial E/\partial\mu)_{E^-} = -t_+ F \quad (2)$$

where t_+ is the transference number of the cation in the solution and one electrode is considered fixed, as denoted by the subscript E^-.

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TABLE II

COMPONENTS OF CHARGE AND POTENTIAL IN THE ELECTRICAL DOUBLE LAYER. 0.1 N KI

q, μcoul./cm.^{2}	$-E$, v.	C, mfds./cm.^{2}	Γ_+ ←	Γ_- μcoul./cm.^{2}	n^i →	$-\psi^0$, v.	$-\psi^u$, v.	$\frac{\partial\psi^v}{\partial \log a_\pm}$	$\frac{\partial\psi^i}{\partial\psi^v}$	$\frac{\gamma}{\beta+\gamma}$	$-A$, v.
−20	1.5990	18.81	18.31	1.69							
−18	1.4894	17.71	16.33	1.67		0.1172	0.8842				
−16	1.3734	16.80	14.34	1.66		.1113	.7741				
−14	1.2522	16.27	12.36	1.64		.1046	.6596				
−12	1.1296	16.50	10.43	1.57		.0971	.5445				
−10	1.0136	18.58	8.77	1.23	0.20	.0892	.4364				
−8	0.9209	25.93	7.86	0.14	1.33	.0850	.3479	0.068			
−6	.8563	36.80	7.80	−1.80	3.40	.0855	.2828	.093		0.358	0.1012
−4	.8084	46.65	8.19	−4.19	5.83	.0873	.2331	.104	0.245	.420	.0979
−2	.7688	54.18	8.75	−6.75	8.46	.0906	.1902	.110	.319	.455	.0865
0	.7337	59.48	9.40	−9.40	11.14	.0936	.1521	.114	.351	.493	.0750
2	.7012	63.47	10.04	−12.04	13.87	.0967	.1165	.113	.387	.555	.0647
4	.6705	66.98	10.67	−14.67	16.56	.0993	.0832	.115	.400	.605	.0503
6	.6415	71.25	11.27	−17.27	19.27	.1018	.0517	.114	.418	.652	.0337
8	.6144	76.89	11.84	−19.84	22.00	.1040	.0224	.116	.422	.701	.0157
10	.5896	84.16	12.43	−22.43	24.62	.1063	−.0047	.115	.435	.728	−.0034
12	.5668	91.73	12.95	−24.95	27.15	.1085	−.0297	.114	.446	.756	−.0225
14	.5460	100.9	13.43	−27.43	29.65	.1098	−.0518	.112	.456	.784	−.0406
16	.5271	111.6	13.88	−29.88	32.16	.1120	−.0729	.112	.466	.799	−.0582
18	.5100	122.5	14.29	−32.29							

TABLE III

COMPONENTS OF CHARGE AND POTENTIAL IN THE ELECTRICAL DOUBLE LAYER. 0.025 N KI

q, μcoul./cm.^{2}	$-E$, v.	C, mfds./cm.^{2}	Γ_+ ←	Γ_- μcoul./cm.^{2}	n^i →	$-\psi^0$, v.	$-\psi^u$, v.	$\frac{\partial\psi^v}{\partial \log a_\pm}$	$\frac{\partial\psi^i}{\partial\psi^v}$	$\frac{\gamma}{\beta+\gamma}$	− /A, v.
−18	1.5250	17.81	17.11	0.89		0.1525	0.8845				
−16	1.3994	16.92	15.10	.90		.1458	.7656				
−14	1.2786	16.25	13.05	.95		.1388	.6518				
−12	1.1578	16.05	11.00	1.00		.1307	.5390				
−10	1.0411	16.57	8.98	1.02		.1217	.4315				
−8	0.9262	18.82	7.13	0.87		.1110	.3272	0.044			
−6	.8342	26.10	5.92	0.08	0.72	.1027	.2435	.075			
−4	.7705	37.74	5.57	−1.57	2.37	.1000	.1825	.089		0.397	0.0725
−2	.7240	48.47	5.72	−3.72	4.52	.1012	.1349	.101	0.163	.443	.0598
0	.6860	56.46	6.09	−6.09	6.90	.1040	.0941	.107	.280	.486	.0457
2	.6524	62.17	6.57	−8.57	9.38	.1074	.0570	.108	.345	.551	.0314
4	.6214	66.79	7.11	−11.11	11.94	.1109	.0224	.109	.383	.611	.0137
6	.5925	72.00	7.69	−13.69	14.52	.1145	−.0100	.111	.401	.628	−.0063
8	.5657	77.87	8.28	−16.28	17.12	.1179	−.0402	.109	.429	.692	−.0278
10	.5412	85.76	8.87	−18.87	19.71	.1211	−.0679	.109	.444	.722	−.0490
12	.5191	95.67	9.44	−21.44	22.29	.1240	−.0929	.108	.460	.746	−.0693
14	.4993	105.3	10.01	−24.01	24.89	.1267	−.1154	.108	.464	.765	−.0883
16	.4813	117.4	10.59	−26.59	27.44	.1292	−.1360	.107	.482	.784	−.1066
18	.4651	131.9	11.09	−39.09		.1316	−.1545				

As has been shown previously (ref. 4, eq. 15)

$$F(\partial C/\partial\mu)_{E^-} = -(\partial C_+/\partial E)_\mu \qquad (3)$$

where C_+ is the capacity attributable to cations in the double layer. It follows that integration of $(\partial C/\partial\mu)_{E^-}$ with respect to potential gives C_+. The details are presented in ref. 13. The constant of integration is given by diffuse double layer theory (see, for example, ref. 3 and 4), it being assumed that at a potential of −1.585 v. relative to a normal calomel electrode specific anion adsorption could be considered absent.

A second integration gives Γ_+, the surface excess of cations in the double layer. The constant of integration was obtained from equation 23 of ref. 4.

The surface excess of anions, Γ_-, was obtained by integration of C_-. It could also have been obtained by difference between q and Γ_+, and this fact was used as a check on the numerical accuracy of the integrations.

The surface excess of *specifically adsorbed* anions n^i is found by subtracting from Γ_- the surface excess (actually a deficiency) of anions in the *diffuse* part of the double layer. The latter is found easily from Γ_+ using, for example, equations of 72 and 73 of ref. 3. The same equations give ψ°, the potential of the outer Helmholtz plane. These calculations require for their validity that cations be present solely in the diffuse part of the double layer. The calculations are not very sensitive to minor defects in the equations, such as arise from the neglect of dielectric saturation in the diffuse part of the double layer, because the surface deficiency of anions in the diffuse part of the double layer is a small quantity compared to Γ_-. Without much doubt experimental errors still exceed errors arising from defects in the equations used.

If from the observed potential difference one subtracts ψ° and also a constant (here taken as 0.488 v.) to correct for the potential difference observed at the e.c.max. of an unadsorbed electrolyte, one obtains ψ^u, the potential across the non-diffuse or inner region of the double layer. This is not an "absolute" potential difference, it is a "rational" potential difference in the sense discussed in ref. 3. ψ^u is composed of two parts, ψ^v and ψ^{02} (ref. 2). The former represents the potential arising as a result of the presence of adsorbed ions held at the inner Helmholtz plane, *i.e.*, in the inner region of the double layer. The latter represents the potential arising from the presence of electronic charge on the surface of the metal. There is, of course, a complementary charge in the diffuse part of the double layer, and the same could have been said of the adsorbed anions.

The evaluation of ψ^v and ψ^{02} can best be understood by reference to the actual observations and will therefore be discussed in the next section.

Results and Discussion

Tables I-III give values of ten properties of the double layer at even values of the surface charge density q. Figure 2 shows a plot of n^i, the surface concentration of specifically adsorbed anions, against q. Parsons[14] first pointed out the approximate linearity of such plots in the region where n^i is not too small. Now it is seen that the plots are not only approximately linear but also parallel to one another. It is somewhat remarkable that not only are the plots of n^i *vs.* q approximately linear and parallel for a given substance, but that even for other halides the results are much the same. This latter fact was pointed out by Parsons and is shown by Fig. 3, on which there are shown data for potassium iodide, bromide, chloride and nitrate. The last-named gives an approximately straight line of appreciably different slope from the halides. The data for potassium iodide shown on Fig. 3, although nearly identical with those of Fig. 2, represent results from the first (1956) set of experiments mentioned above. The method of calculation was also somewhat different.

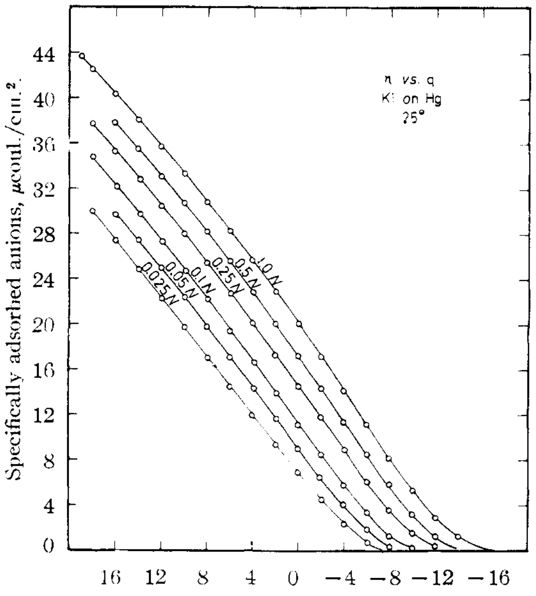

Fig. 2.—Amount of specifically adsorbed anion n^i as a function of surface charge density q.

It is of interest to plot n^i against $\log a_\pm$ to obtain an adsorption isotherm, as was suggested by Parsons,[14] but not done for lack of data. Figure 4 shows such a plot. Here we have used not the directly observed values of n^i but "improved" values based upon considerations presently to be discussed. Theoretical reasons for expecting these plots to be nearly linear were presented in ref. 2 and are discussed further below.

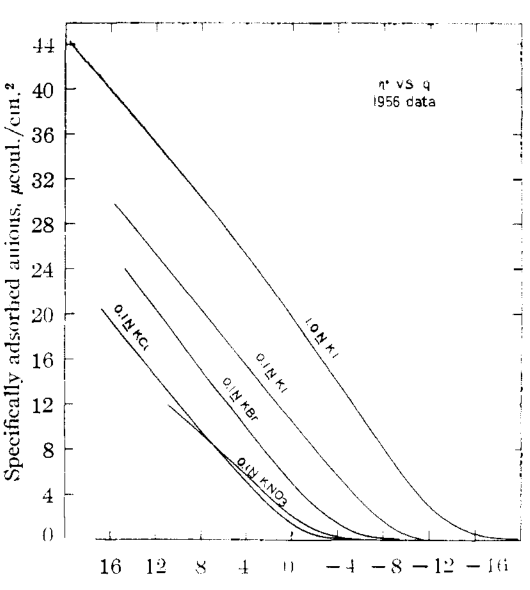

Fig. 3.—Amount of specifically adsorbed anion n^i as a function of surface charge density q.

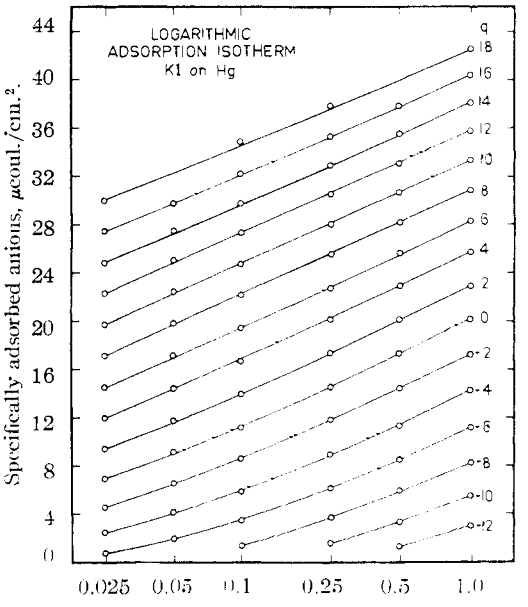

Fig. 4.—Amount of specifically adsorbed anion n^i as a function of log $a_\pm$. Numbers denote concentrations.

By way of contrast, Fig. 5 shows a Henry's law isotherm using the same data. The departure from linearity is extreme and points up the danger of assuming the validity of Henry's law in these systems even as a first approximation. The reason for the failure of Henry's law is easily understood. It comes about as a result of the fact that the first entering ions build up a potential difference which later entering ions are called upon to surmount.

In ref. 2 the following equation is derived

$$\psi^v = -4\pi n^i \gamma / DD_0 \qquad (4)$$

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(14) R. Parsons, *Trans. Faraday Soc.*, **51**, 1518 (1955).

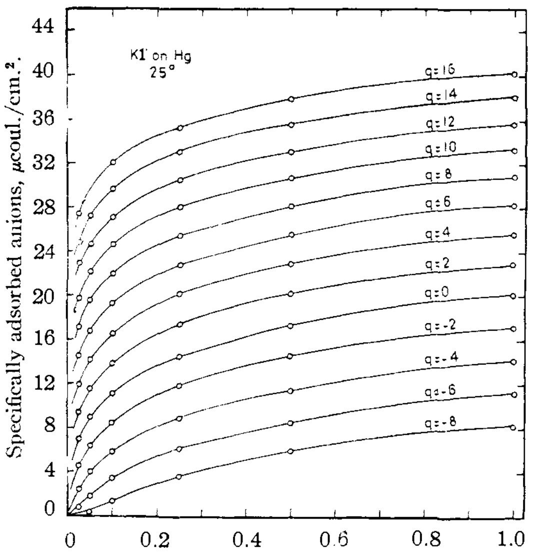

Fig. 5.—Amount of specifically adsorbed anion n^i as a function of concentration.

where D is an effective dielectric constant of the inner region, γ is the distance between the inner and outer Helmholtz planes (see Fig. 3 of ref. 2), and D_0 is a universal constant equal to 1.1128×10^{-12} coul.-volt^{-1} cm.$^{-1}$. As explained above, ψ^v is the potential developed across the inner region of the double layer as a result of the presence of specifically adsorbed anions and excluding that part of the potential developed across the inner region of the double layer as a result of the presence of any surface charge. In the present work n^i is considered to be a positive and ψ^v a negative quantity.

Let ψ^{02} be the potential across the inner region attributable to the electronic charge q on the metal. The total potential generated ψ^u is the sum of these two, as stated above

$$\psi^u = \psi^v + \psi^{02} \qquad (5)$$

A plot of ψ^u against n^i at constant surface charge density q is not expected to be linear (*cf.* equation 4) for two reasons: (1) there is no reason to expect γ/D to be independent of n^i and (2) there is no reason to expect ψ^{02} to be independent of n^i. Nevertheless Fig. 6 shows that the curves obtained by plotting ψ^u against n^i at constant q are not only linear but also that their slope is very nearly independent of q.

The linearity and parallelism of the curves is not perfect. Table IV shows values of $(\partial\psi^u/\partial n^i)_q$ as a function of q. This coefficient, equal to the slopes of the lines in Fig. 6, is the reciprocal of a differential capacity of a special kind. This capacity measures the ratio of the specifically adsorbed charge to the potential generated across the inner region by that charge. Although the total excursion from the minimum to the maximum value of $(\partial\psi^u/\partial n^i)_q$ is no more than 15% of the minimum (omitting the value at $q = -12$), the deviations from constancy are probably real and significant. The surprising fact is that they are so small. According to equation 4, and assuming for the moment that changes in ψ^u equal changes in ψ^v at constant q, $(\partial\psi^u/\partial n^i)_q$ is proportional to γ/D. The implied constancy of γ/D must be the result of accidental compensation, since γ, at least, surely varies by at least a factor of two over the range of values of q covered by Fig. 6.

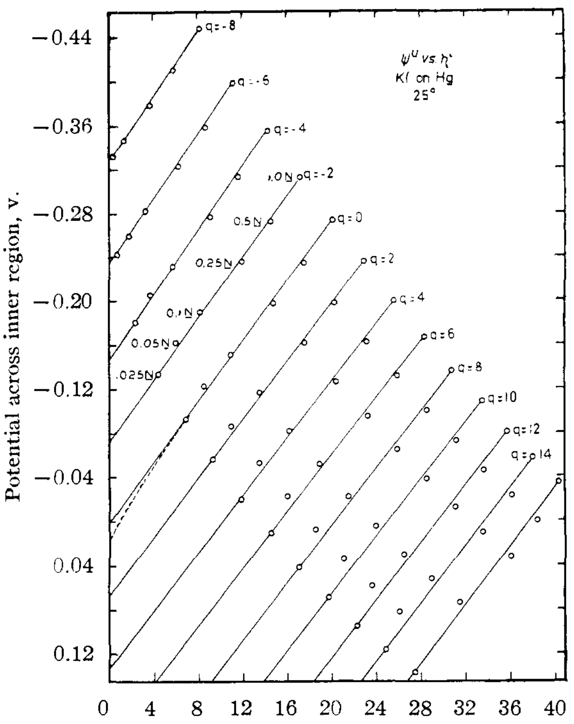

Fig. 6.—Potential across the inner region of the double layer, ψ^u, as a function of amount of specifically adsorbed anion, n^i.

TABLE IV

PROPERTIES OF THE INNER REGION OF THE DOUBLE LAYER NOT DEPENDING UPON CONCENTRATION

q, μcoul./cm.²	$(\partial\psi^u/\partial n^i)_q$, volt-cm.²/μcoul.	C^{02}, mfds./cm.²	$-\psi^{02}$, volt	log K'
−20			0.984	
−18		18.7	.878	
−16		18.0	.770	
−14		17.7	.656	
−12	0.0121	17.8	.544	
−10	.0140	18.4	.432	4.315
− 8	.0147	20.0	.329	4.537
− 6	.0149	22.1	.233	4.820
− 4	.0146	24.9	.148	4.977
− 2	.0141	27.1	.071	5.032
0	.0136	28.9	.000	5.027
2	.0133	29.9	− .068	5.025
4	.0131	30.6	− .134	4.930
6	.0130	31.1	− .199	4.752
8	.0130	31.8	− .262	4.545
10	.0131	32.9	− .324	4.306
12	.0132	33.4	− .384	4.066
14	.0134	33.9	− .444	3.815
16	.0136	34.0	− .502	3.567
18			− .562	

The vertical distance between consecutive lines on Fig. 6 leads to a direct evaluation of the differential coefficient $(\partial\psi^u/\partial q)_{n^i}$. The reciprocal of this coefficient is also a differential capacity related to the inner region of the double layer. It measures the capacity of that region under conditions such that the concentration of adsorbed anions within it remains constant. Thus it is identical with C^{02} and is wholly analogous to the capacity of the inner region, C^0, previously defined for non-adsorbed electrolytes.[3]

For the range of values of n^i accessible to experiment, and within the limits of the attained precision, C^{02} is practically independent of n^i. This unexpected result implies that the field generated by the adsorbed anions does not affect the dielectric properties of the inner region in the same way as does the field generated by the electrons on the metallic surface, since the latter affects C^{02} very markedly (Fig. 7). Some small changes in the distance between a chosen pair of adjacent lines in Fig. 6 can be detected, as can be seen from Table IV in the changes in the slopes of adjacent lines. When q is positive (anodic polarization), the coefficient $(\partial\psi^u/\partial n^i)_q$ is almost constant, however, indicating that under these circumstances the lines in Fig. 6 are indeed almost exactly parallel and C^{02} almost completely independent of n^i. When q is negative, slightly larger changes in $(\partial\psi^u/\partial n^i)_q$ are observed, showing the C^{02} here depends perceptibly upon n^i.

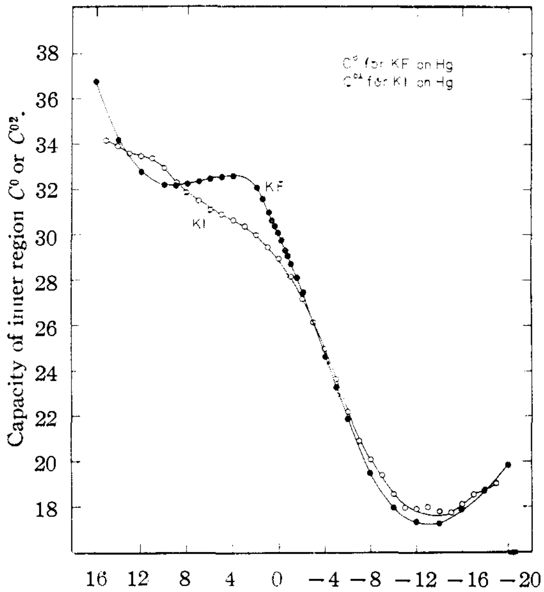

Fig. 7.—Differential capacity of the inner region of the double layer at constant n^i. Comparison of an adsorbed and non-adsorbed electrolyte.

If it is really true that C^{02} is independent of n^i, then it should be independent of the identity of the anion as well, since in the limit of $n^i = 0$, the identity of the anion can make no difference. In order to test this hypothesis we have plotted C^0 (the differential capacity of the inner region) for potassium fluoride[15] along with C^{02} of potassium iodide in Fig. 7. For negative values of q the curves are identical within the limits of error of the measurements. For positive values the agreement is less good but still almost within the limits of experimental error. The disagreement is nowhere greater than 6%, although at large positive values of q the values of C^{02} become so uncertain that the agreement shown in Fig. 7 ought not to be taken too seriously. Nevertheless the curves are surely quite close and tend to confirm the conclusion that the field generated by the adsorbed anions has little effect upon the differential capacity of the inner region.

This very remarkable conclusion, although not here explained, makes it possible to carry out essentially complete and reasonably exact calculations of the properties of the inner region of the double layer. In ref. 2 it was pointed out how these calculations could be made in principle, but it appeared that the amount of data needed would be very great. Now as a result of the simplification of the problem introduced by the constancy of C^{02}, these calculations can be carried out much more easily than was to be expected.

In the calculations which follow we shall assume that the lines in Fig. 6 are not only parallel (in the sense that the vertical distance between adjacent lines remains constant) but straight. This is much less fully supported by the data and calls for some justification.

As q becomes more and more positive, the points in Fig. 6 fall more and more away from a straight line; however, no definite curvature is indicated, unless it be sigmoidal. It is very clear that the method of calculation can produce just such systematic errors, because what is actually measured is in effect the distance between adjacent lines (at constant composition), and not the absolute values of the coördinates of the plotted points. Thus errors accumulate. In the first (1956) set of data there were similar departures from linearity, but they were not very similar to those observed in the second set. Although curves of a sigmoidal shape can be discounted as inherently unreasonable, it was to have been expected that the curves would bend either upward or downward to some extent. When q is negative, the curves are nevertheless found to be essentially straight. When q is zero, an estimate of the amount of curvature in the region not investigated experimentally (*i.e.*, at very low values of n^i) can be made by noting that in non-adsorbed electrolytes the potential of the electrocapillary maximum lies at 0.472 v. relative to a normal calomel electrode. Extrapolation to $n^i = 0$ of the straight line observed in a plot of $E - \psi^0$ *vs.* n^i at $q = 0$ gives a value of 0.488 v., or 16 mv. too cathodic. The dotted line at $q = 0$ shows the curvature which must therefore be present in the true curve of ψ^u *vs.* n^i.

For purposes of computation we have used the extrapolated straight line at $q = 0$ to fix the origin of the potential scale of Fig. 6. This is necessary unless one is willing to make arbitrary assumptions about the amount of curvature in each line.

When q is positive there is no certain way of estimating the curvature of the lines in the region not covered by experiment. The fact that C^{02} comes out almost as expected (Fig. 7) indicates that there is no serious lack of parallelism in the curves in the unexplored region, and the fact that $(\partial\psi^u/\partial n^i)_q$ is so

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[15] Calculated from data presented in ref. 4.

nearly constant when q is positive (Table IV) leads to the same conclusion. For purposes of computation it is in any case very convenient and leads to no error in the explored regions to assume linearity in the unexplored regions.

It will be necessary in what follows to evaluate ψ^{02} (the potential in the inner region produced by the electronic charge on the metal), defined formally through the equation[2]

$$\psi^{02} = \int (1/C^{02})\mathrm{d}q \qquad (6)$$

where the integration must proceed at constant n_i if C^{02} is a function of n^i. The constant of integration is fixed by noting that $\psi^{02} = 0$ when $q = 0$. On account of the independence (or near independence) of C^{02} upon n^i, the integration is very readily performed and leads to the results in Table IV. This table also includes values of C^{02} and two other quantities defined below.

ψ^{v} can be obtained from ψ^{02} and ψ^{u} through equation 5. It is needed in connection with the following equation, which is derived in ref. 2 and in the Appendix to ref. 13 and is in many respects identical with one given earlier by Ershler[16]

$$\frac{\mathrm{d}\psi^{\mathrm{v}}}{\mathrm{d}\ln a_{\pm}} = \frac{1}{\dfrac{RT}{F\psi^{\mathrm{v}}} - \dfrac{\mathrm{d}\psi^{\mathrm{i}}}{\mathrm{d}\psi^{\mathrm{v}}}}\frac{RT}{F}\left(1 + \frac{\mathrm{d}\ln(\gamma/D)}{\mathrm{d}\ln a_{\pm}}\right) \text{(constant } q\text{)} \qquad (7)$$

where ψ^{i} is the potential of the inner Helmholtz plane relative to the solution.

It has already been explained that γ/D is practically independent of n^i when q is constant. This makes the coefficient d $\ln(\gamma/D)/\mathrm{d}\ln a_{\pm}$ almost equal to zero. Numerical computation verifies that the small changes in γ/D which are actually found are wholly negligible in this coefficient. Thus the final factor in equation 7 has been set equal to unity.

All the needed data are now at hand for the evaluation of $\mathrm{d}\psi^{\mathrm{i}}/\mathrm{d}\psi^{\mathrm{v}}$ from equation 7. Some of the values found are presented in Tables I–III. Subtracting $(\partial\psi^0/\partial\psi^{\mathrm{v}})_q$ from these gives $(\partial\psi^{\mathrm{A}}/\partial\psi^{\mathrm{v}})_q$, where ψ^{A} is the potential of the inner Helmholtz plane relative to that of the outer. Values of $(\partial\psi^{\mathrm{A}}/\partial\psi^{\mathrm{v}})_q$ are plotted as a function of $n^i + 2q$ in Fig. 8. The choice of the function $n^i + 2q$ was based upon the observation that this would make all of the reliable points fall on a single curve, for which the equation is

$$(\partial\psi^{\mathrm{A}}/\partial\psi^{\mathrm{v}})_q = 0.467 + 0.00571y - 1.55 \times 10^{-5}y^2 \qquad (8)$$

where we have let $y = n^i + 2q$. Although the experimental points scatter some at low and negative values of y, the scatter is not systematic, which indicates that the fault is not in the choice of the function $n^i + 2q$. At more negative values of y, $(\partial\psi^{\mathrm{A}}/\partial\psi^{\mathrm{v}})_q$ must level off, since it cannot be less than zero. Hence one should not properly employ equation 8 for strongly negative values of y. Under these circumstances the specific adsorption goes to zero, however, so that errors in the equation will not actually introduce much error into any calculation which evaluates observable quantities.

The numerical coefficients in equation 8 are for y expressed in microcoulombs per sq. cm.

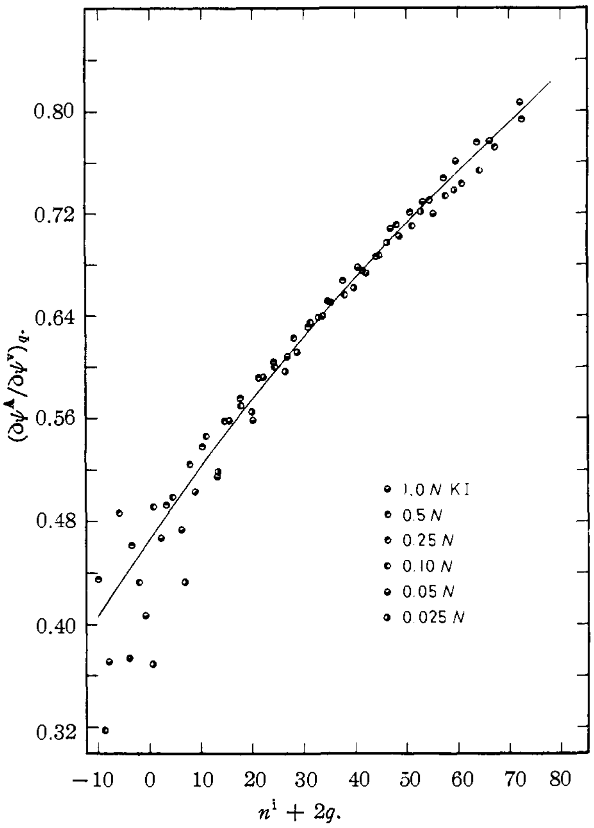

Fig. 8.—$(\partial\psi^{\mathrm{A}}/\partial\psi^{\mathrm{v}})_q$ as a function of $n^i + 2q$.

Referring back to equation 4, and recalling that γ/D is also almost independent of q, the straight lines in Fig. 6 lead to the equation

$$(\partial\psi^{\mathrm{v}}/\partial n^i)_q = -4\pi\gamma/DD_0 = -\lambda = -0.0136 \text{ v./}\mu\text{coul./cm.}^2 \qquad (9)$$

The numerical constant is the average of the values in Table IV. This makes $\gamma/D = 0.12$ Å., which is entirely reasonable.

Combining equations 8 and 9 gives

$$-(\partial\psi^{\mathrm{A}}/\partial n^i)_q = 0.467\lambda + 0.00571\lambda y - 1.55 \times 10^{-5}\lambda y^2 \qquad (10)$$

which integrates to

$$-\psi^{\mathrm{A}} = 0.467\lambda y + 0.00286\lambda y^2 - 5.2 \times 10^{-6}\lambda y^3 + B \qquad (11a)$$

$$= 0.00635y + 3.89 \times 10^{-5}y^2 - 7.0 \times 10^{-8}y^3 + B \quad (\lambda = 0.0136) \qquad (11b)$$

where the constant of integration B can be evaluated by noting that $\psi^{\mathrm{A}} = 0$ when $\psi^{\mathrm{u}} = 0$. Values of ψ^{A} given in Tables I–III have been computed from equation 11b when $q \geqq 0$.

For negative values of q the evaluation of the constant of integration by this method requires an extrapolation of the straight lines in Fig. 6 into regions of negative n^i. An alternative and possibly more convincing procedure has been used in preparing the tables. As is shown in ref. 2, and as is obvious from inspection when it is recognized that the potential is a linear function of the distance in the inner region of the double layer[2]

$$\psi^{\mathrm{A}}/\psi^{\mathrm{u}} = (\psi^{\mathrm{i}} - \psi^0)/\psi^{\mathrm{u}} = \gamma/(\beta + \gamma) \qquad (12)$$

where β is the distance between the metallic sur-

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(16) B. V. Ershler, *J. Phys. Chem. U.S.S.R.*, **20**, 679 (1946).

face and the inner Helmholtz plane. Then

$$\left(\frac{\partial \psi^{\mathrm{A}}}{\partial \psi^{\mathrm{v}}}\right)_q = \frac{\gamma}{\beta + \gamma} + \psi^{\mathrm{u}} \left(\frac{\partial \gamma/(\beta + \gamma)}{\partial \psi^{\mathrm{v}}}\right)_q \qquad (13)$$

where we have set $(\partial\psi^{\mathrm{u}}/\partial\psi^{\mathrm{v}})_q = 1$ because ψ^{02} is considered to be a function only of q (recall equations 5 and 6).

Equation 13 is solved readily for $\gamma/(\beta + \gamma)$ by a method of successive approximations. Then equation 12 permits the calculation of ψ^{A} for any desired value of q, and so permits the evaluation of the constant of integration. When the constant of integration B is plotted against q, a curve is obtained which can be represented by the equation

$$B = -0.0287q - 0.00057q^2 \qquad (14a)$$

or when $q \geqq 0$ by the slightly more accurate relation

$$B = -0.0316q - 0.00039q^2 \quad q \geqq 0 \qquad (14b)$$

and when one of these is inserted in equation 11b, a complete equation for ψ^{A} as a function of n^{i} and q results. Then ψ^{i} can be obtained by adding ψ^0. The latter is given by diffuse double layer theory as[3]

$$\psi^0 = -2(RT/F)\sinh^{-1}[(n^{\mathrm{i}} - q)/2A] \qquad (15)$$

where $A^2 = RTDD_0c/2\pi$ and c is the concentration in moles/cm.^{3}.

Values of $\gamma/(\beta + \gamma)$ are given in Tables I–III and are plotted against q in Fig. 9. It will be seen that $\gamma/(\beta + \gamma)$ varies between 0.3 and 0.8 over the range of conditions covered. To a fairly good approximation $\gamma/(\beta + \gamma)$ is seen to be a single-valued function of q. This means that the distance γ is not much altered by the introduction of ions into the inner Helmholtz plane. This is consistent with the observation that γ/D is constant under the same conditions and lends weight to the statement made above that the field of the anions does not alter the dielectric properties of the inner region very much. This is a surprising observation which should be studied on other systems and at other temperatures. $\gamma/(\beta + \gamma)$ shows a slight tendency to increase with increasing n^{i}, and this is a direct consequence of the fact that $(\partial\psi^{\mathrm{A}}/\partial\psi^{\mathrm{v}})_q$ depends upon n^{i}. Experimentally the effect seems real, but we can offer no reasonable explanation for it.

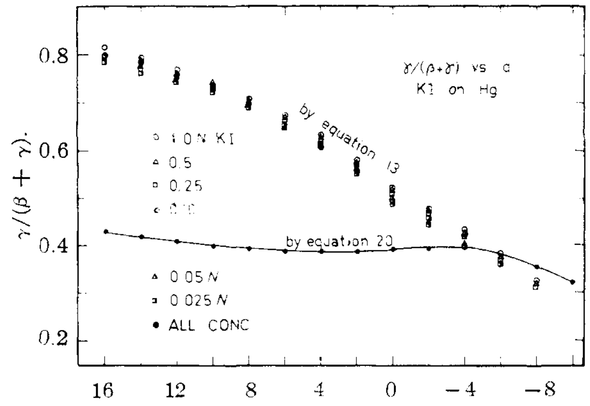

Fig. 9.—$\gamma/(\beta + \gamma)$ as a function of surface charge density, q, as computed correctly by equation 13 or incorrectly by equation 20.

A more detailed study of this effect shows that $\gamma/(\beta + \gamma)$ is almost a single-valued function of $q + (n^{\mathrm{i}}/7)$. That is to say, the addition of seven anions has the same effect on $\gamma/(\beta + \gamma)$ as the removal of one electron from the metal, and both have the effect of moving the anions closer to the interface. If $\gamma/(\beta + \gamma)$ is regarded as a measure of the strength of the bond between the anion and the metal, it follows that the bond becomes stronger as more anions are added to the inner Helmholtz plane. This is a conclusion for which there is no independent evidence and no apparent reasonable cause.

If $\gamma/(\beta + \gamma)$ is in reality independent of n^{i}, that fact could be used to discover and correct errors in the experimental data. We have not so used it because we have not considered the fact itself well enough grounded.

The strong increase of $\gamma/(\beta + \gamma)$ with q is just what one has to expect from electrostatic considerations. The anions are pulled toward the metal as the latter acquires a positive charge. In another terminology the anions are polarized so that their centers of charge move toward the metal. This point of view has been current in the literature for some time,[17] but this is believed to be the first clear-cut demonstration of its correctness.

It is of interest that to say that the anion is polarized is equivalent to saying that the anion is chemically bound to the metal. The formation of a chemical bond is, in the last analysis, the result of a shift of charge to a region intermediate between the bound atoms. This fact becomes of major importance in understanding the inner region of the double layer, as will become more evident below.

When $q = 0$, $\gamma/(\beta + \gamma) \approx 1/2$. That is why the potential of the e.c.max. shifts at about half the rate expected on the basis of the Stern theory or of any theory which neglects discreteness-of-charge effects, as was first pointed out by Esin and Markov.[5] It is of interest that the anomaly, if it can be called that, practically disappears under conditions of strong anodic polarization. This is clearly understandable as the result of the simple electrostatic considerations mentioned above. It is also of interest that the Esin and Markov effect is observed at an air–solution interface, as has been known for some time[18] and as has been convincingly demonstrated recently by Gurenkov,[19] and that the rate of change with chemical potential of the electrical potential measured across the interface is virtually the same as at a metal–solution interface at the potential of the e.c.max. This probably means that $\gamma/(\beta + \gamma)$ is about the same as at the potential of the e.c.max., where the ordinary electrostatic influence of the metal is small.

It has been assumed in the discussion above that $\beta + \gamma$ is independent of n^{i}. This seems very probable. If it is also independent of q, which is debatable, then changes in $\gamma/(\beta + \gamma)$ are attributable strictly to changes in γ, and the constancy of γ/D means that D also varies with q in the manner shown in Fig. 9. This is not unreasonable or un-

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[17] A. Frumkin, *Trans. Faraday Soc.*, **36**, 117 (1940).

[18] M. Gerovich and Giliman, Dissertation, Karpov Institute, cited by Ershler, ref. 16.

[19] B. S. Gurenkov, *J. Phys. Chem. U.S.S.R.*, **30**, 1830 (1956).

expected. The variation of C^{02} with q shown in Fig. 7 also leads one to expect that D varies with q in about this manner. These facts suggest that $\beta + \gamma$ may be independent of q, but there is at present no known way of proving or disproving this suggestion.

It is shown in ref. 2 that for a charged or uncharged interface

$$n^{\mathrm{i}} = Ka_{\pm} \exp(\varphi F/RT) \exp(\psi^{\mathrm{i}} F/RT) = K'a_{\pm} \exp(\psi^{\mathrm{i}} F/RT) \quad (16)$$

where φ is an adsorption potential (in the sense of Stern)[20] related to the chemical or geometrical influences impelling (*i.e.*, "outsqueezing") the ions to the interface, but not including "chemical" effects which may alternatively be regarded as electrostatic attraction of the metal for the anion. Here K is a constant, independent of q. The factors K and $\exp(\varphi F/RT)$ have been combined to form a new constant K', which depends upon q because of the dependence of φ upon q. The simplicity of the second form of equation 16 is noteworthy. This equation is the same as one obtains by disregarding the concomitant motion of cations during the adsorption of anions. Physically this results from the fact that the addition of a cation to the double layer requires much less energy than the addition of an anion, when the specific adsorption is moderately strong, so that the limiting factor in the adsorption is related to the concentration of the *anions* and to ψ^{i}, the potential of the region into which they must move.

Taking natural logarithms in equation 16 gives, after introducing equations 11a and 15

$$\ln n^{\mathrm{i}} = \ln a_{\pm} - [0.467\lambda y + 0.00286\lambda y^2 - 5.2 \times 10^{-6} \lambda y^3 + B]F/RT - 2 \sinh^{-1} (n^{\mathrm{i}} - q)/2A + \ln K' \quad (17a)$$

or for $\lambda = 0.0136$

$$\ln n^{\mathrm{i}} = \ln a_{\pm} - [0.00635y + 3.89 \times 10^{-5}y^2 - 7.0 \times 10^{-8}y^3 + B]F/RT - 2 \sinh^{-1} (n^{\mathrm{i}} - q)/2A + \ln K' \quad (17b)$$

Equation 17b could have been used by successive approximations to arrive at "improved" or "smoothed" values of n^{i}, since n^{i} itself does not enter into the determination of the coefficients of that equation in a serious way. (The constants B and K' are determined by reference to a single concentration.) This has been done for a few values of q. It turns out, however, that almost exactly the same results can be obtained much more simply and at least as accurately by reading from the graph in Fig. 6 values of n^{i} corresponding to the observed values of ψ^{u} at any given concentration. This is what was done to obtain the values of n^{i} quoted in the tables and plotted in Fig. 4.

Equation 17b permits the calculation of $\log K'$, and Fig. 10 shows $2.3(RT/F) \log K'$ plotted as a function of q. Except for an additive constant, this is the adsorption potential, φ. As expected, φ varies with q, but the variation is not monotonic, as was reported earlier for sodium chloride on mercury (ref. 3, Fig. 15). The difference arises from differences in the method of computation of φ. In ref. 3 the position of the inner Helmholtz plane was assumed fixed and differences in the binding energy showed up in φ. In the present work the distance γ increases and β diminishes as the binding becomes stronger; hence the binding energy of the anion to the mercury is not revealed in φ, and what one probably sees instead is the effect of removing the anion from the solvent, which requires energy and appears as a diminishing effect upon φ.

It will be noted that φ reaches a maximum slightly to the cathodic side of the potential of zero charge. The falling off of φ at cathodic potentials can be understood by considering that a negatively charged surface pushes anions back into the solvent from which they would emerge if there were air in place of metal, and that to the extent that this is an energy-consuming process, φ is smaller than it would be otherwise. It seems extremely probable, judging from the low values found for $\gamma/(\beta + \gamma)$ and comparing our results with those of Gurenkov, that $\gamma/(\beta + \gamma)$ is smaller at a negatively charged metal–solution interface than at an air–solution interface. Thus the explanation we suggest for the falling off of φ under these conditions is not without experimental foundation.

A polynomial has been fitted to the curve for potassium iodide in Fig. 10, and this equation, when substituted in equation 17b, gives $\log a_{\pm}$ as a function of n^{i} and q. Differentiation at constant composition gives $(\partial n^{\mathrm{i}}/\partial q)_{\mu}$, which is the slope of the curves in Fig. 2. There is nothing in the equation which explains the constancy or near constancy of the slope of the curves in that figure. It should be noted, however, that considerable deviations from constancy can and do take place without making much difference in the appearance of the curves in Fig. 2.

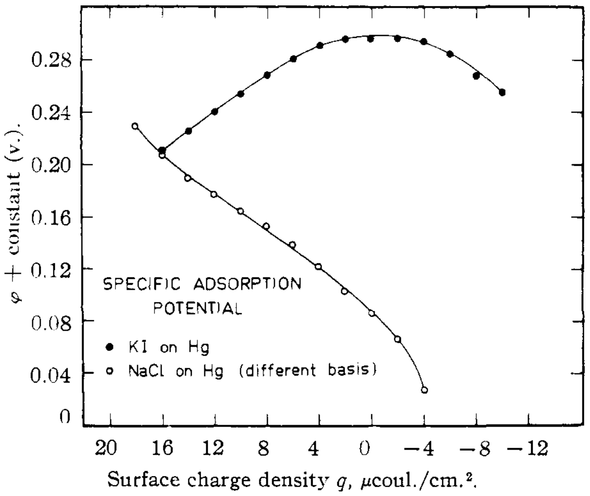

Fig. 10.—Specific adsorption potential as a function of q.

The observation that γ/D does not vary much with q appears to be the result of the fact that γ and D both tend to increase with increase in q. That they do so at almost the same rate may be no more than a coincidence. It will be interesting to see whether this is generally true with other anions.

It should be mentioned that γ/D is smaller for bromide than for iodide ions. This is not what one expects from simple geometrical considerations and points up the danger of taking too geometrical a view of the significance of β and γ. Presumably the smaller value of γ/D for bromide ions results

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(20) O. Stern, *Z. Elektrochem.*, **30**, 508 (1924).

from the lesser tendency of the latter to form a covalent bond with the metal, which is to say, it is less distorted by the presence of the metal. These observations refer to the potential of zero charge, which shows that even an uncharged surface exerts an "electrostatic" influence on a polarizable anion. The electrostatic influence arises from the attraction between the electrons in the iodide ion and the mercury ions in the surface. The electrons associated with the latter are able to move away sufficiently to make the net result a decrease in free energy, whereupon the process continues until the change of free energy resulting from additional motion of the center of charge of the anion becomes zero.

In the discussion of chemical binding it is usually convenient to distinguish between electrostatic and covalent forces, even while recognizing that the latter are in the last analysis electrostatic. As the preceding discussion indicates, however, this distinction breaks down rather badly and may have to be abandoned altogether in order to get a valid picture of the factors influencing the behavior of the electrical double layer.

There is a further equation relating to the inner region of the double layer which has not been used in this work. It is

$$\psi^{02} = -4\pi q(\beta + \gamma)/DD_0 \qquad (18)$$

which is the ordinary equation for a two-plate condenser applied to the inner region under conditions of constant n^i. From equation 4 we have

$$(\partial\psi^v/\partial n^i)_q = -4\pi\gamma/DD_0 = -\lambda \qquad (19)$$

where λ is not necessarily to be regarded as independent of q. From equations 18 and 19 it follows that

$$\lambda q/\psi^{02} = \gamma/(\beta + \gamma) \qquad (20)$$

Values of $\gamma/(\beta + \gamma)$ computed in this manner are shown in Fig. 9. The disagreement with the values computed through equations 12 and 13 is marked. What this means is that D in equation 4 is not identical with D in equation 18. This possibility was considered in ref. 2 where a prime was put on the D of what is here called equation 18. The ratio of $\gamma/(\beta + \gamma)$ found in the two ways equals the ratio of the two kinds of D.

Conclusion

The method of calculation adopted in this work makes great demands upon the precision of the experimental data. An alternative and possibly less demanding method of calculation would be to assume the linearity of the curves in Fig. 6 and to calculate from these the differential capacity. By comparison with the observed values of the latter, one could in principle select the best values of the parameters controlling the curves shown in Fig. 6. This procedure is mathematically possible but would represent a very formidable task even by modern methods of computation. Another disadvantage of this procedure is that one would be obliged to make certain auxiliary assumptions which ought to be tested further by the direct method of computation used here.

The computations employed in this work are based upon a combination of thermodynamics and Gouy–Chapman theory, as modified by Stern and as further modified by the author with respect to the nature of the inner region of the double layer. These latter modification, at least, are by no means universally accepted, and it may be that later work will indicate a need for their revision. The most that can be said is that the present picture of the electrical double layer serves as a convenient frame of reference which fits the facts well enough to serve as a basis for detailed calculations.

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AMHERST, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

Reactions of the High Voltage Discharge Products of Water Vapor

BY P. J. FRIEL* AND K. A. KRIEGER

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The recombination of the high voltage discharge products of water vapor has been investigated on the surface of silica gel. The recombination reaction was accompanied by a temperature increase and a green luminescence on the surface on the gel. The principal products of the reaction were H_2 and O_2. Both the H atom and OH radical were removed as a result of the surface reaction but the silica gel surface did not catalyze the recombination of H atoms. It was concluded that the surface reaction is: S + OH = S-OH, S-OH + H = S-O + H_2, 2S-O = 2S + O_2 where S is the surface. A study of the intensity of the luminescence on the surface of the gel as a function of time and the temperature to which the gel was preheated showed that the activity of the gel was initially high and then decreased to an equilibrium value after 30 minutes. The water content of the gel controlled its activity in these recombination reactions. The addition of sodium ions to the gel resulted in a change in the color of the luminescence from green to yellow indicating that the luminescence is a result of an excitation of the surface caused by the exothermic reactions occurring thereon. The reactions of the water vapor discharge products in a liquid air trap were also studied. H_2O_2, H_2O, H_2 and O_2 were formed and the molar ratios of product to water vapor admitted to the system were 26.8, 38.0, 35.2 and 4.2%, respectively. On the basis of two simple assumptions, it was possible to show that the reactions in the trap leading to O_2 are H + OH = H_2 + O, 2O = O_2; and to account approximately for the observed product distribution.

Introduction

The recombination of the high voltage discharge products of water vapor on solid surfaces such as KCl, K_2CO_3, Al_2O_3 and KOH has been studied by several authors.[1-4] Taylor and Lavin[1] observed a

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* Missile and Ordnance Systems Department, General Electric Company, Philadelphia, Pa.

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(3) W. V. Smith, *ibid.*, **11**, 110 (1943).

(4) D. R. Warren, *Trans. Faraday Soc.*, **53**, 206 (1957).