

Free radicals capable of initiating the chain addition of mercaptan to an unsaturated compound may be formed by reactions (1), (2), and (3) or (3a).

Evidence that free radicals of the type  $\text{RCO}^\cdot$  are formed by the reaction of persulfate with sodium laurate has been presented in a previous paper.<sup>6</sup> That persulfate can attack a double bond to form a free radical of the type  $\text{RC}\cdot\text{COSO}_3^-$  (reaction 3a)

is evidenced from the data in Table V. Whether reactions (2) and (3) also involve an attack of the soap in the systems studied could not be established because of the very small amount of initiation reaction needed to cause the addition of relatively large amounts of mercaptan to the unsaturate. Previous work<sup>6</sup> has shown that the direct reaction of persulfate with mercaptan solubilized in sodium laurate solution does not occur to any measurable extent.

As shown by the data in Table I and Fig. 1,

persulfate reacts slowly with mercaptan solubilized in sodium laurate solution in the absence of an unsaturate, 2 moles of mercaptan being oxidized for every mole of persulfate consumed. Sulfate ion and disulfide are the products of the reaction. These reaction products and the observed stoichiometry in systems also containing an unsaturate are accounted for by the proposed mechanism. Both the reaction rate of mercaptan and the stoichiometry of the reaction are affected markedly by the addition of an unsaturate to the system. Mercaptan is consumed much more rapidly in the presence than in the absence of an unsaturated compound. Much more mercaptan than persulfate is consumed and only a small amount of disulfide is formed. The increase in weight with oleate as unsaturate was found to be equal to the amount of reacted mercaptan which did not form disulfide and is quantitatively accounted for by reactions (5) and (6).

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## The Differential Capacity of the Electrical Double Layer. The Role of the Anion

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RECEIVED JANUARY 30, 1952

The different capacity of the electrical double layer at a mercury-solution interface has been determined for twelve solutions of tenth-normal potassium salts. The results show that there is a strong correlation between the shape of the capacity curves and the solubility of the corresponding mercurous salts. Anion pairs which exhibit the same general solubility relationships (nitrate-perchlorate, carbonate-hydroxide) also exhibit similar capacity curves. The results are used to calculate the surface charge density of the electrical double layer.

A technique for the accurate measurement of the differential capacity of the electrical double layer at a mercury-solution interface has been described recently in a previous publication.<sup>1</sup> Certain results obtained by this method have already been presented.<sup>2</sup> It is the purpose of this paper to present the results of a systematic study of the influence of the anion upon the capacity of the double layer, all other factors being held constant.

The theoretical significance of these measurements has been discussed in some detail in a review paper<sup>3</sup> and also in numerous subsequent publications.<sup>4-6</sup> Briefly, the differential capacity is a quantity thermodynamically related to the interfacial tension (it is the second derivative of the electrocapillary curve) and as such its measurement provides experimental entree to all or nearly all of those properties generally grouped under the heading "electrocapillarity."

### Experimental Part

The technique previously described<sup>2</sup> has been used with minor modifications. It was neither convenient nor desirable to eliminate liquid junctions, since it was desired to establish the results relative to a given reference electrode.

A tenth-normal calomel electrode in potassium chloride has been used throughout (although results are reported relative to a normal calomel electrode as a matter of convenience) and corrections have been made for the liquid junction potential between the tenth-normal solutions, using the Lewis and Sargent or Henderson equations. This is a sufficiently satisfactory procedure for the following reasons: In those parts of the differential capacity curve where the measurements can be made with precision, the capacity varies only slowly with potential, so that the uncertainty introduced by this approximation is insignificant. In those parts of the curve where the capacity changes rapidly with potential, the experimental error is by chance also greater, so that uncertainties associated with liquid junction potentials are again unimportant. A study of the uses to which differential capacity curves may be put shows also that the liquid junction potential cancels out in any thermodynamic calculation, as one would expect, so that liquid junction potentials introduce no thermodynamic error at all except in so far as they are lacking in reproducibility. In work of this kind this is usually a very trifling source of error, except where hydrogen or hydroxide ions are involved.

Solutions were made up in conductivity water from recrystallized materials (except KOH). The effect of purification was hardly noticeable in the results, except for a slight onset of polarization resistance, noticeable at a potential around  $-0.25$  volt relative to a normal calomel electrode. The effect was absent from the purified materials. We attribute the effect to traces of ferric iron, but experiments designed to test this supposition proved inconclusive and were not pursued further.

Other precautions were as mentioned previously.<sup>1,2</sup> Instead of measuring the absolute values of capacity as before, however, it was more convenient and more accurate to make measurements alternately with solution of tenth-normal potassium chloride and of the salt under test. Knowing the capacity of the double layer in tenth-normal potassium chloride, it was then a simple matter to find it for the solu-

(1) D. C. Grahame, *THIS JOURNAL*, **71**, 2975 (1949).

(2) D. C. Grahame, *J. Electrochem. Soc.*, **98**, 343 (1951). See also ref. 1.

(3) D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

(4) D. C. Grahame, *J. Chem. Phys.*, **18**, 903 (1950).

(5) D. C. Grahame, *Rec. Chem. Prog.*, **11**, 93 (1950).

(6) See also ref. 13 and ref. 2.

tion in question. About forty suitably spaced points were taken on each curve and measurements were taken back and forth on the two solutions until the character of the agreement indicated that the results were of the desired accuracy. Oxygen was excluded from the system not only during the measurements but also during the operation of changing the solutions. These latter were, of course, deaerated before being admitted to the cell, and suitable precautions were taken to prevent the contamination of one solution by the other.

An absolute accuracy of about  $\pm 1\%$  is believed to have been attained at potentials such that the differential capacity did not exceed 30 mfd./cm.<sup>2</sup>. At other potentials the error varies approximately as the square of the capacity. The relative accuracy of closely spaced points on the curve is about ten times as great as the absolute accuracy, so that the plotted curves were always smooth.

Measurements were made at 1,000 cycles per second. There is a possibility that where the capacity is high there may be a sufficient activation energy for the anion adsorption process to make the results systematically low. There is ample evidence that this is not a large effect,<sup>7-10</sup> since no considerable frequency dependence is observed and since the results are in agreement with the electrocapillary measurements, in cases where a comparison has been possible. But it is now felt that evidence for the complete absence of an activation energy of adsorption is lacking and that some revision of these results may eventually become necessary when better methods of measurement become available. A detailed investigation of this point has been under way in this Laboratory for several years, but so far without definitive results. If any modification of the present results arises from this cause, it will have the effect of increasing the capacity values by an amount approximately proportional to the square of the capacity. It was with this possibility in mind that the limits of error mentioned in the preceding paragraph were assigned.

### Results and Discussion

Graphs of the results are presented in Figs. 1 and 2.<sup>11</sup> The results are in satisfactory agreement with earlier but less extensive and less precise data obtained by essentially the same method.<sup>10</sup> They bear out the conclusions reached earlier<sup>2,13</sup> which were, briefly, that simple anions like those here investigated move in closer to the mercury-solution interface than simple cations; that nitrate and perchlorate ions are adsorbed by a non-coulombic type of force which is probably of the London-van der Waals type; that ions whose mercurous salts are insoluble exhibit specific adsorption as a result of covalent bonding of the anions to the mercury; and that this covalent bonding becomes stronger as the mercury acquires a positive charge.

The new data make possible a more comprehensive study of the relationship between the differential capacity and the solubility of the corresponding mercurous salts. At the potential of the e.c. max. the correlation is not very evident except that the anions of those salts of mercury which are least soluble (iodide, bromide and thiocyanate<sup>12</sup>) exhibit the largest capacity at potentials for which the comparison is valid. A more useful and more generally valid method of comparison

(7) T. Borissowa and M. Proskurnin, *Acta Physicochim. U. R. S. S.*, **4**, 819 (1936).

(8) D. C. Grahame, *THIS JOURNAL*, **68**, 301 (1946).

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

(10) D. C. Grahame, *THIS JOURNAL*, **63**, 1207 (1941).

(11) A detailed table of values is included in the authors' Report No. 7 to the Office of Naval Research, dated Dec. 18, 1951, and available at the Library of Congress. Copies of these tables may be had on request from the first-named author (D. C. G.) or from the Secretary, Department of Chemistry, Amherst College.

(12) Capacity curves for the cyanide and sulfide have never been obtained.

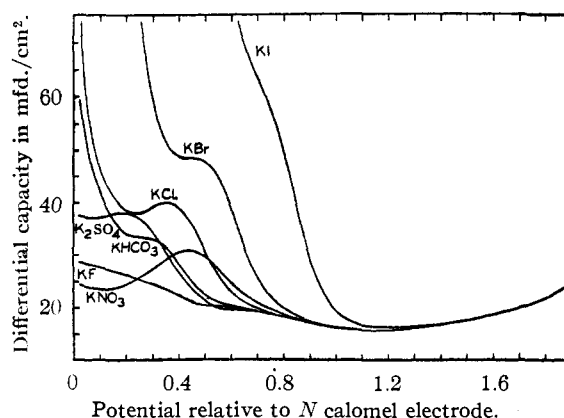


Fig. 1.—Differential capacity of the mercury-solution interface in tenth normal solutions at 25°.

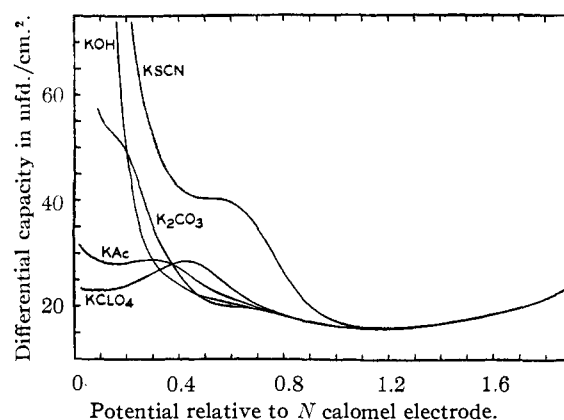


Fig. 2.—Differential capacity of the mercury-solution interface in tenth normal solutions at 25°.

is to compare the capacity values at the most anodic potentials at which the measurements have been made. This is close to the limit of anodic polarization, the potential at which spontaneous dissolution of mercury occurs. Since this is not the same potential for all, and since it would be misleading to compare values which were not close to the limit of anodic polarization, the ions have first of all been arranged in order of their increasing capacities as follows:  $\text{ClO}_4^- < \text{NO}_3^- < \text{F}^- < \text{SO}_4^- < \text{Ac}^- < \text{HCO}_3^- < \text{Cl}^- < \text{CO}_3^- < \text{OH}^- < \text{CNS}^- < \text{Br}^- < \text{I}^-$ . Then adjacent pairs in this list have been directly compared at the most anodic potential for which *both* members of the pair have been measured. Since adjacent pairs of ions behave rather similarly at these potentials, this gives a reasonably fair basis of comparison. The results are presented in Table I and show a 190-fold spread in the relative values of capacity.

TABLE I

MERCURY-SOLUTION INTERFACE NEAR THE LIMIT OF ANODIC POLARIZATION IN TENTH NORMAL SOLUTIONS

Anion	Relative capacity	$\rho\text{Hg}$	Anion	Relative capacity	$\rho\text{Hg}$
$\text{ClO}_4^-$	0.073	$\sim 1$	$\text{Cl}^-$	1.00	15.7
$\text{NO}_3^-$	.093	$\sim 1$	$\text{CO}_3^-$	1.21	14.2
$\text{F}^-$	.096	$\sim 1$	$\text{OH}^-$	2.5	20.6
$\text{SO}_4^-$	.115	4.3	$\text{CNS}^-$	3.7	17.6
$\text{Ac}^-$	.23	7.6	$\text{Br}^-$	5.6	20.0
$\text{HCO}_3^-$	.61	(?)	$\text{I}^-$	14.1	26.1

In order to compare the results obtained in this manner with the solubilities of the corresponding mercurous salts, the concentration of the mercurous ion,  $\text{Hg}_2^{++}$ , has been computed in a solution saturated with the appropriate mercurous salt. The results have been converted to a negative logarithmic scale, like  $\text{pH}$ , and called  $\text{pHg}$  in Table 1. A considerable correlation is evident, as is shown more clearly in Fig. 3. This correlation may be regarded as further evidence that the large capacities at the left of the capacity curves in Figs. 1 and 2 are associated with the type of forces operative in the crystal lattices of the corresponding mercurous salts.

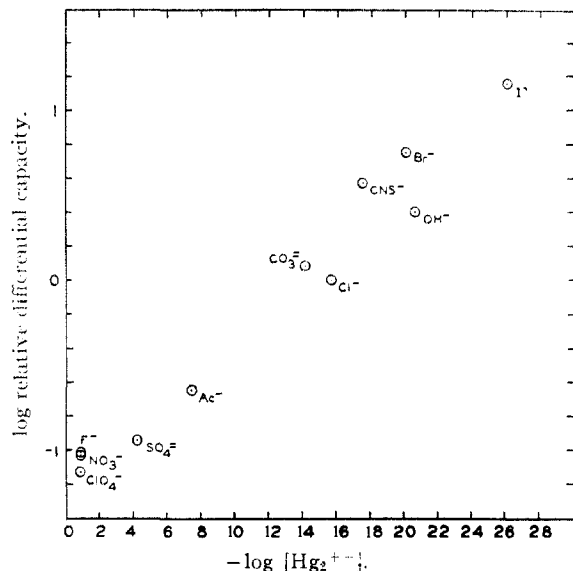


Fig. 3.—Log relative differential capacity (at limits of anodic polarization) vs.  $-\log [\text{Hg}_2^{++}]$  in saturated solution of mercurous salt in tenth normal solutions of potassium salt of anion named.

The large capacity arises, however, not from the fact of the *existence* of large metal-to-ion forces but from the fact that the magnitude of these forces *varies* with potential. The capacity (actually a differential capacity) measures the rate of change of the surface charge density with potential. The surface charge density,  $q$ , is strictly equal to the electronic charge on the metallic surface or, with change of sign, to the sum of the charges of the ions associated with the electrical double layer. The latter is a sum of two terms comprising the charge associated with the adsorbed anions and a term representing the charge associated with cations and anions in the diffuse double layer. The latter term is small under the conditions of large anodic polarization,<sup>13</sup> leaving the surface charge density,  $q$ , nearly equal to the charge associated with the adsorbed anions. The existence of a large force between metal and anions will make  $q$  large, but not  $dq/dE$ , the capacity. Only a *change with potential* in that force produces a large capa-

(13) D. C. Grahame, "Thermodynamic Properties of the Electrical Double Layer. A Summary of Recent Work." Technical Report No. 6 to the Office of Naval Research (May 25, 1951). This report will also appear in "Proceedings of the Third Meeting of the International Committee of Electrochemical Thermodynamics and Kinetics," now in press.

city, which proves the statement made at the beginning of this paragraph. This illustrates, incidentally, that the specific adsorption potential,  $\phi$ , of the Stern theory<sup>14</sup> should not be regarded as a constant.

**The Shape of the Differential Capacity Curves.**—It is interesting to note a correlation between the shapes of the curves and the solubility rules associated with anions generally, not now referring to mercurous salts in particular. Certain pairs of ions exhibit closely similar solubility rules, notably nitrate and perchlorate ions and carbonate and hydroxide ions. These pairs also exhibit very similar capacity curves. The solubilities of the halides, excluding fluorides, exhibit similar but gradually changing values, as do their capacity curves. The fluoride is like no other ion, and its capacity curve is likewise unique. The acetates are rather similar to the nitrates and perchlorates in their solubility relationships, and their capacity curves on mercury are also rather similar. In general it seems evident that the composite of properties which determines general solubility relationships also determines the form of the capacity curves. This result should be of particular interest when it becomes possible to study the capacity curves of other metals than mercury.

All of the capacity curves converge and reach a minimum ( $\sim 16.0$  mfd./cm.<sup>2</sup>) at a potential of  $-1.15$  volts<sup>15</sup> relative to a normal calomel electrode. The similarity of the curves from this point on is, of course, a reflection of the fact that the repelled anions no longer control the properties of the interface. The subsequent slow rise in the capacity (which is observed with all simple cations amenable to investigation in this region<sup>2</sup>) is not certainly understood and is not in any case a property of the anions.

The decrease in the capacity as the curves approach the minimum from the left has been discussed elsewhere.<sup>13</sup> It depends upon the nature of the anion mainly in that expulsion of the previously adsorbed anion from the double layer necessarily results in a marked decrease in capacity. Anions which are practically not at all adsorbed at the potential of the electrocapillary maximum (fluoride, sulfate, hydroxide, carbonate) naturally cannot be desorbed, and so the capacity does not fall very much as the metal is made more strongly cathodic. The small decrease which still remains is attributed in part to the fact that cations cannot approach the interface as closely as anions, which makes a thicker effective dielectric layer and so a smaller capacity, and in part to dielectric saturation in the *inner* or *non-diffuse* part of the double layer. Dielectric saturation in the *diffuse* part of the double layer appears to be of rather minor consequence.<sup>16</sup>

The surface charge density is obtained by numerical integration<sup>1</sup> of the capacity curves, taking  $q = 0$  at the potential of the electrocapillary maximum. The results are presented in condensed

(14) O. Stern, *Z. Elektrochem.*, **30**, 508 (1924). See also ref. 3, p. 486, Fig. 15.

(15) Except KI and KCNS for which the curves reach a minimum at  $-1.20$  volts because of the incomplete desorption of anions at  $-1.15$  volts. The minimum capacity is then slightly higher.

(16) D. C. Grahame, *J. Chem. Phys.*, **18**, 903 (1950).

TABLE II

SURFACE CHARGE DENSITY,  $q$ , OF Hg IN 0.1 N SOLUTIONS OF POTASSIUM SALTS AT 25°. POTENTIALS MEASURED RELATIVE TO NORMAL CALOMEL ELECTRODE CORRECTED FOR LIQUID JUNCTION POTENTIAL BETWEEN 0.1 N KCl AND THE SOLUTION NAMED

$-E$ rel. to $N$ cal. volts	KCl	KCNS	KOH	KAc	KBr	$K_2CO_3$	$KClO_4$	$KF$	$KHCO_3$	KI	$KNO_3$	$K_2SO_4$
	Microcoulombs per sq. cm.											
-0.19				23.37			17.91	18.16			19.38	23.67
- .11				18.32			15.68	15.30			16.74	20.12
- .03				14.87			13.67	13.83			14.56	16.94
.04	18.77			12.58			12.02	10.81	14.88		12.82	14.32
.12	14.71			10.24		13.19	10.16	8.57	11.26		10.92	11.35
.20	11.50	20.20	8.03	7.99	21.58	9.02	8.28	6.43	8.37		9.01	8.32
.28	8.44	14.89	5.00	5.70	14.69	5.51	6.30	4.38	5.67		6.97	5.38
.36	5.30	10.92	2.781	3.40	10.19	2.866	4.15	2.449	3.07		4.72	2.805
.44	2.199	7.50	0.834	1.218	6.26	0.762	1.889	0.661	0.807		2.303	0.700
.52	-0.408	4.25	- .950	-1.753	2.417	-.997	-0.340	-1.001	-1.070	16.73	-0.098	-1.045
.60	-2.440	1.031	-2.640	-2.547	-1.043	-2.623	-2.353	-2.624	-2.758	9.08	-2.228	-2.646
.68	-4.17	-2.035	-4.26	-4.22	-3.68	-4.21	-4.12	-4.22	-4.36	3.31	-4.05	-4.22
.80	-6.49	-5.84	-6.56	-6.54	-6.44	-6.49	-6.49	-6.51	-6.64	-3.72	-6.43	-6.49
.90	-8.26	-8.15	-8.32	-8.32	-8.29	-8.26	-8.27	-8.28	-8.40	-7.64	-8.22	-8.26
1.00	-9.94	-10.01	-9.99	-10.00	-9.98	-9.94	-9.96	-9.95	-10.07	-10.00	-9.89	-9.93
1.10	-11.56	-11.68	-11.61	-11.62	-11.61	-11.57	-11.57	-11.57	-11.68	-11.77	-11.51	-11.54
1.20	-13.16	-13.30	-13.22	-13.22	-13.22	-13.16	-13.17	-13.17	-13.27	-13.40	-13.12	-13.14
1.30	-14.78	-14.92	-14.83	-14.84	-14.85	-14.79	-14.79	-14.79	-14.88	-15.03	-14.74	-14.76
1.40	-16.45	-16.59	-16.50	-16.50	-16.52	-16.45	-16.45	-16.45	-16.54	-16.70	-16.41	-16.42
1.50	-18.19	-18.31	-18.23	-18.23	-18.26	-18.19	-18.19	-18.18	-18.25	-18.44	-18.15	-18.14
1.60	-20.03	-20.12	-20.05	-20.06	-20.09	-20.01	-20.02	-20.00	-20.06	-20.27	-19.99	-19.96
1.70	-21.97	-22.05	-21.99	-21.99	-22.03	-21.95	-21.96	-21.94	-21.98	-22.21	-21.93	-21.88
1.80	-24.05	-24.11	-24.08	-24.07	-24.13	-24.03	-24.05	-23.66	-24.05	-24.31		-23.96
1.90	-26.36	-26.37	-26.38	-26.36	-26.43		-26.34	-26.30	-26.31	-26.61		-26.24
e.c. max. volts	-0.506	-0.626	-0.477	-0.488	-0.574	-0.473	-0.507	-0.471	-0.473	-0.732	-0.517	-0.471

form<sup>17</sup> in Table II. They are of interest partly on their own account but mostly as a necessary first step in other calculations relating to the electrical double layer.

It does not necessarily follow from the convergence of the capacity curves that the  $q$ -values must also converge, although this is what one expects from the fact that on strong cathodic polarization the anion no longer controls the properties of the interface. The results are in agreement with this expectation to within the experimental uncertainty.

One could extend the argument one step further to the conclusion that the *interfacial tension*, which is the integral with respect to potential of the  $q$ -values, should also be independent of the nature

of the anion, and this is what was found by Gouy<sup>18</sup> to the limits of accuracy attainable by his method. If one assumes the validity of this conclusion, it becomes possible to find by electrical measurements alone not only the *shape* of the electrocapillary curve (by integration of the  $q$ -values) but also the height of one curve relative to another. This enables one to ascertain, again by the aid of electrical measurements only, such quantities as  $\Gamma_{max}^{salt}$  (see ref. 5), and  $\Gamma^+$  (or  $\Gamma^-$ ), the concentration of cations (or anions) in the double layer. A start has been made in this direction (see ref. 13), and further work is in progress.

The authors are grateful to the Research Corporation and to the Office of Naval Research for financial support of this work.

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

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(17) More detailed tables are contained in the tables mentioned in footnote 11.