[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Chemistry of Persulfate. III. The Reaction of Persulfate with Mercaptans Solubilized in Sodium Laurate Solutions in the Presence of Unsaturated Compounds[1]

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RECEIVED MARCH 8, 1952

Aliphatic mercaptans, containing 6 to 12 carbon atoms, solubilized in sodium laurate solution in the presence of potassium persulfate add to unsaturated compounds by a chain reaction. Free radicals capable of initiating the reaction may be formed by thermal decomposition of the persulfate or by reaction of persulfate with the laurate or unsaturated compound.

Because of the wide use of persulfate as an initiator of vinyl polymerizations in emulsion systems it is of interest from the viewpoint of establishing the mechanism of persulfate initiated emulsion polymerizations to study the mechanism of the reaction of persulfate with water insoluble compounds solubilized in soap solutions. This paper deals with the reaction of *n*-hexyl, *n*-octyl and *n*-dodecyl mercaptans with sodium oleate, isoprene, styrene and 2,5-dimethylhexadiene 1,5-solubilized in sodium laurate solutions in the presence of potassium persulfate.

Experimental

Materials.—The *n*-dodecyl mercaptan used was a product obtained from Dr. C. S. Marvel of the University of Illinois, b.p. 114–116° (6.5 mm.), n^{20}_{D} 1.4589. Research grade *n*-octyl mercaptan was obtained from the U.S. Rubber Co. and research grade *n*-hexyl mercaptan was obtained from the Humphrey Wilkenson Company. Eastman Kodak Co. lauric acid, Esso isoprene and Dow styrene were used. The 2,5-dimethylhexadiene-1,5 used was a product obtained from the University of Illinois, b.p. 111–112°, n^{20}_{D} 1.4289. The styrene, isoprene and dimethylhexadiene were distilled under vacuum before use. The oleic acid was a specially pure product obtained from Dr. W. C. Ault of Eastern Regional Research Laboratories, Philadelphia, Pa. Merck and Co., Inc., potassium persulfate was recrystallized twice from conductivity water and dried in a vacuum desiccator at room temperature. Other products used were reagent grade chemicals.

Analytical Methods.—Mercaptans were determined by amperometric titration with silver nitrate in ammoniacal ethanol solution according to the method of Kolthoff and Harris.[3] Interference by persulfate in the mercaptan determination was prevented in two ways depending upon the amount of persulfate present. (1) Soap solutions containing solubilized mercaptans and small amounts of persulfate (up to 0.01 *M*) were added to 90% ethanol containing ferrous iron in about fivefold excess over the persulfate present. After stirring for 15 minutes an excess of ammonia was added and the amperometric titration with silver nitrate was performed. (2) In the presence of larger amounts of persulfate (0.01 to 0.1 *M*) it was necessary to separate the mercaptan from the aqueous persulfate solution prior to titration of the mercaptan. This was accomplished by extraction of the fatty acid and mercaptan from an acidified sample of the soap solution into benzene. The benzene solution was added to an excess of ethanol, ammonia was added and the mercaptan titrated by the amperometric method. Disul-

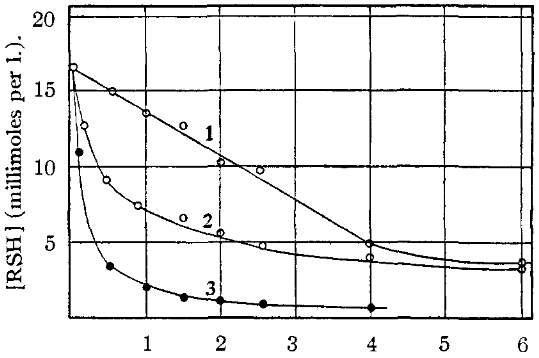

Fig. 1.—The effect of sodium oleate on the rate of mercaptan consumption in sodium laurate solution containing persulfate at 50°: 1, no oleate; 2, 0.01 *M* oleate; 3, 0.02 *M* oleate.

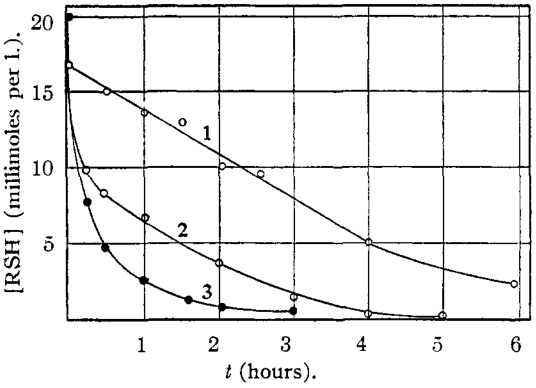

Fig. 2.—The effect of 2,5-dimethylhexadiene-1,5 on the rate of mercaptan consumption in sodium laurate solution containing persulfate at 50°: 1, no hexadiene; 2, 0.01 *M* hexadiene; 3, 0.02 *M* hexadiene.

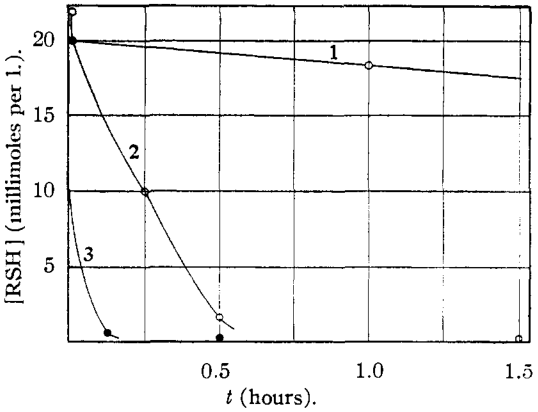

Fig. 3.—The effect of styrene and isoprene on the rate of mercaptan consumption in sodium laurate solution containing persulfate at 50°: 1, no unsaturate; 2, 0.1 *M* isoprene; 3, 0.1 *M* styrene.

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(1) This work was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, Synthetic Rubber Division of the United States Government.

(2) From a thesis submitted by I. K. Miller to the Graduate School of the University of Minnesota, 1950.

(3) I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).

TABLE I

CONSUMPTION OF PERSULFATE AND *n*-DODECYL MERCAPTAN AT 50° IN 10% SODIUM LAURATE SOLUTION AT *p*H 10 IN THE PRESENCE AND ABSENCE OF UNSATURATED COMPOUNDS (OXYGEN NOT REMOVED)

1. 0.110 *M* $K_2S_2O_8$, 0.017 *M* mercaptan, no unsaturate			2. 0.111 *M* $K_2S_2O_8$, 0.024 *M* mercaptan, 0.05 *M* sodium oleate			3. 0.011 *M* $K_2S_2O_8$, 0.02 *M* mercaptan, 0.05 *M* styrene		
Reaction, hours	Mercaptan consumed[a]	Persulfate consumed[a]	Reaction, hours	Mercaptan consumed[a]	Persulfate consumed[a]	Reaction, hours	Mercaptan consumed[a]	Persulfate consumed[a]
0	0	0	0	0	0	0	0	0
1.5	5.4	4.0	0.03	(1.6)	(0.5)	0.75	8.4	.21
2.5	9.8	6.0	0.5	18.8	1.2	3.0	17.5	.30
6.0	15.4	8.0	1.0	21.6	1.9	8.0	19.5	.82
			2.0	23.0	3.9			

[a] Millimoles per liter.

fides were determined by reduction to mercaptans according to the method of Kolthoff, *et al.*,[4] followed by amperometric titration of the mercaptan. Persulfate was determined polarographically[6] after extraction of the fatty acid and mercaptan from the acidified soap solution with benzene.

Experimental Method.—The reaction of persulfate with solubilized mercaptans in the presence of unsaturated compounds was studied using 10% sodium laurate solutions containing approximately 0.02 *M* solubilized mercaptan, 0.01 to 0.111 *M* potassium persulfate and varying amounts of sodium oleate, styrene, isoprene or 2,5-dimethylhexadiene-1,5. The solutions were buffered at a *p*H of 10 by addition of 0.2 g. of sodium bicarbonate and 0.3 g. of sodium carbonate per 100 g. of solution. The experiments were carried out at 50° in a reaction vessel described in an earlier paper of the series.[6] The mercaptan was first solubilized in an oxygen-free solution of sodium laurate and buffer at 50°. The olefin was then added and after stirring the mixture for 30 to 60 minutes the persulfate was added. In some cases the reaction mixture was saturated with air when the persulfate was added and in other cases the mixture was kept oxygen-free throughout the experiment.

Reaction Rate.—The influence of various unsaturated compounds on the rate of mercaptan consumption in sodium laurate solutions in the presence of persulfate is shown by the data plotted in Figs. 1–3. These results show that the rate of mercaptan consumption in sodium laurate solutions containing persulfate is considerably greater in the presence than the absence of unsaturated compounds.

Stoichiometry of Persulfate–Mercaptan Reaction.—The data in Table I give the relative amounts of persulfate and *n*-dodecyl mercaptan consumed when persulfate reacts with mercaptan solubilized in 10% sodium laurate solution in the presence and absence of unsaturated compounds.

The data show that in the absence of an unsaturated compound, about two moles of mercaptan are consumed per mole of persulfate reacting while in the presence of sodium oleate or styrene much more than two moles of mercaptan react per mole of persulfate consumed. In the absence of persulfate and oxygen, *n*-dodecyl mercaptan undergoes no reaction in 10% sodium laurate solution containing 0.05 *M* peroxide-free sodium oleate after 24 hours at 50°. In a similar solution saturated with oxygen but containing no persulfate mercaptan is oxidized to disulfide at a rate of about 0.3 millimole per liter per hour at 50°. This rate is much smaller than when persulfate is also present. Apparently (*v.i.*) the small amount of oxygen present in the above experiments hardly affects the reaction brought about by persulfate.

Reaction Products.—The results in Table II show the amount of *n*-dodecyl disulfide formed by the reaction of persulfate with *n*-dodecyl mercaptan solubilized in 10% sodium laurate solution in the presence and absence of unsaturated compounds. The disulfide was determined quantitatively by reduction to mercaptan and was isolated and identified qualitatively by a mixed melting point with a sample of pure *n*-dodecyl disulfide.

TABLE II

DISULFIDE FORMED BY REACTION OF PERSULFATE (0.111 *M*) WITH *n*-DODECYL MERCAPTAN IN 10% SODIUM LAURATE SOLUTION IN THE PRESENCE AND ABSENCE OF UNSATURATES AT 50°. REACTION ALLOWED TO PROCEED 10 HOURS IN AIR-SATURATED SOLUTION AT *p*H 10

Initial mercaptan concn., mole per liter	Unsaturated compound	Concentration of unsaturate, mole per liter	*n*-Dodecyl disulfide formed, mole per liter
0.0172	None	..	0.0086
.0175	Sodium oleate	0.01	.0053
.0175	Sodium oleate	.02	.0018
.0191	Styrene	.10	.0024
.0244	Isoprene	.10	.0055
.0200	2,5-Dimethylhexadiene-1,5-	.01	.0046
.0200	2,5-Dimethylhexadiene-1,5-	.02	.0023

Although the disappearance of persulfate and mercaptan and the formation of disulfide in the reaction mixture could be easily measured, no satisfactory method for quantitative determination of the unsaturates in the reaction mixture was found. The fact that *n*-octyl and *n*-hexyl mercaptans add to sodium oleate in the presence of persulfate was established by measurement of the increase in weight of the oleate caused by combination with the mercaptan.

n-Octyl and *n*-hexyl mercaptans solubilized in 2% sodium oleate solution were allowed to react with persulfate at 50° and the unreacted oleic acid together with the addition product of the mercaptan and oleic acid was isolated in the following way.

A portion of the reaction mixture was acidified with sulfuric acid and the unreacted oleic acid, addition product of oleic acid and mercaptan, disulfide and unreacted mercaptan were extracted into benzene. An equal volume of ethanol was added to the benzene solution and enough water was added to cause turbidity. The turbidity was removed with a few drops of ethanol and the solution boiled to remove the benzene. The remaining solution was diluted with water containing enough sodium hydroxide to dissolve the oleic acid and addition product. An excess of barium nitrate was then added, the solution was allowed to stand for 4 hours at room temperature, then filtered. The precipitate was washed with cold ethanol to dissolve any disulfide and mercaptan present, then dried at 50° in a vacuum oven. The amount of mercaptan added to the oleate was calculated

TABLE III

ADDITION OF *n*-OCTYL AND *n*-HEXYL MERCAPTANS TO OLEATE IN A SOLUTION 0.0658 *M* IN SODIUM OLEATE, 0.06 *M* IN MERCAPTAN AND 0.10 *M* IN $K_2S_2O_8$ BUFFERED AT *p*H 10

	n-Octyl mercaptan		*n*-Hexyl mercaptan	
Experiment No.	1	2	3	4
Init. mercaptan concn.	0.0612	0.0594	0.0814	0.0814
Final mercaptan concn.	.0062	.0074	.0050	.0032
Disulfide formed	.0210	.0280	.0358	.0362
Mercaptan consumed but not converted to disulfide	.0340	.0240	.0406	.0420
Mercaptan added to oleate[a]	.0325	.0240	.0404	.0433

[a] Calculated from increase in weight.

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(4) I. M. Kolthoff, D. R. May, P. Morgan, H. A. Laitinen and A. S. O'Brien, *Ind. Eng. Chem., Anal. Ed.*, **18**, 442 (1946).

(5) I. M. Kolthoff, L. S. Guss, D. R. May and A. I. Medalia, *J. Polymer Sci.*, **1**, 340 (1946).

(6) I. M. Kolthoff and I. K. Miller, THIS JOURNAL, **73**, 5118 (1951).

from the weight of the precipitate and the weight of oleate initially present in the reaction mixture. Data obtained with *n*-hexyl and *n*-octyl mercaptans solubilized in 0.0658 *M* sodium oleate solution containing 0.10 *M* persulfate are given in Table III.

Reaction of Persulfate with Sodium Oleate.—In the second paper[6] of this series it was shown that persulfate reacts with caprate, laurate and palmitate ions in mildly alkaline solution (*p*H 10). Although the over-all process is quite complex, the chief reaction appears to be the decarboxylation of the fatty acid salts. The reaction of persulfate with sodium oleate at 50° in a solution buffered at a *p*H of 10 by a borate buffer has been studied using the analytical techniques described[6] to follow the disappearance of persulfate and oleate from the solution and the formation of sulfate ion. The oxygen-free reaction mixtures were allowed to stand for 3 days at 50°. The results are given in Table IV.

TABLE IV

THE REACTION OF PERSULFATE WITH SODIUM OLEATE AT 50° IN A BORAX BUFFER SOLUTION AT *p*H 10 (OXYGEN ABSENT)

	Initial concentration[a]		Final concentration[a]		ΔC	
	I	II	I	II	I	II
Persulfate	50.0	48.5	0.10	0.00	49.9	48.5
Oleate[b]	53.1	48.0	32.3	25.8	20.8	22.2
CO_2	0.5	...	5.5	...	5.0	..
Sulfate	..	0.00	...	96.6	..	96.6

[a] Millimoles per liter. [b] Carboxyl.

No water soluble organic acids were formed by the reaction and no organic peroxides were formed.

The fact that all of the persulfate which was consumed formed sulfate ion shows that under the conditions studied persulfate does not attack the double bond of the oleate by adding a sulfate group to the oleate.

The Reaction of Persulfate with Styrene.—Smith and Campbell[7] gave evidence that persulfate initiation of styrene polymerization occurs by addition of an SO_4^- radical to the monomer. Further evidence in favor of this type of initiation was given by Bartlett and Nozaki[8] who found sulfate groups in persulfate initiated polyallyl acetate.

Considering the high molecular weight of persulfate initiated polystyrene, the amount of sulfur introduced into the polymer by the initiation reaction is so small that it can be determined only by use of persulfate containing radioactive sulfur.[7]

Work being carried out in this Laboratory on the emulsion polymerization of styrene with radioactive sulfur containing persulfate as initiator has shown that the sulfur content of the polymer greatly depends on the method of its purification. This work will be reported on in a future paper. In the present work low molecular weight polystyrene was obtained by using inactive persulfate as an initiator and *p*-benzoquinone as inhibitor of the polymerization.

An aqueous oxygen-free solution of 0.01 *M* potassium persulfate containing 5 g. of styrene per 100 g. of solution and 0.01 *M* *p*-benzoquinone was shaken in a thermostat at 50° for 100 hours. The amount of sulfate ion formed by the reaction was determined by amperometric titration in 30% ethanol solution with lead nitrate by the method of Kolthoff and Pan.[9] Before analysis for sulfate the sample was acidified and shaken with liquid zinc amalgam to reduce any remaining persulfate. The amount of persulfate remaining in the solution at the end of the reaction period could not be determined polarographically due to interference by quinone and its reaction products. Bartlett and Nozaki[8] found that the sulfate groups introduced into allyl acetate by the reaction with persulfate could be converted to sulfate by acid hydrolysis. Accordingly, samples of persulfate–styrene reaction mixtures were hydrolyzed in hydrochloric acid solution and the amount of sulfate formed by the hydrolysis was determined by precipitation with barium chloride. For this analysis a 20-ml. sample of the reaction mixture was acidified with 1 ml. of 6 *N* hydrochloric acid and shaken with liquid zinc amalgam to reduce any remaining persulfate, then 2 ml. of concentrated hydrochloric acid was added and the solution heated at 85° for 24 hours. After addition of 5 ml. of 0.1 *M* barium chloride the mixture was again heated at 85° for 24 hours and then evaporated to dryness to remove excess acid. The residue was taken up in 25 ml. of water and the precipitate was collected by filtration, dried and weighed.

The data in Table V show the amount of sulfate ion formed by the reaction of persulfate with styrene in the presence of *p*-benzoquinone at 50° in an unbuffered solution and also the total amount of sulfate present after acid hydrolysis of the reaction mixture.

TABLE V

SULFATE FORMED BY THE REACTION OF PERSULFATE (0.01 *M*) WITH STYRENE IN THE PRESENCE OF *p*-BENZOQUINONE AT 50°

	Solution	Sulfate formed, *M*	%	Total sulfate after hydrolysis Concn.	%
I	0.01 *M* Quinone	0.0194	97	....	...
II	0.01 *M* Quinone,[a] 5% styrene	.0167	84	....	...
III	As II	.0163	82	0.0202	101
IV	0.01 *M* Quinone,[b] 5% styrene	.0131	66	.0202	101
V	0.01 *M* Quinone,[c] 5% styrene	.0104	52	.0200	100
VI	As V	.0091	46	.0200	100

[a] Quinone dissolved in persulfate solution, pure styrene added. [b] Quinone dissolved in styrene. [c] Quinone added to styrene layer in 4 equal increments at beginning of reaction and after 4, 8 and 20 hours.

These data show that persulfate, in its reaction with styrene, does not form sulfate ion quantitatively but apparently adds sulfate groups to the styrene molecule. Upon heating the organic sulfate in acid medium the sulfate groups are split off forming sulfate ions.

Further evidence that an organic sulfate is formed by the action of persulfate on styrene is provided by the reaction of methylene blue with the persulfate–styrene–quinone reaction product. Anionic detergents, like sodium dodecyl sulfate, react with methylene blue to form compounds soluble in chloroform. Methylene blue was added to a portion of reaction mixture V (see Table V) after the mixture had been allowed to react for 100 hours at 50°. Upon shaking the methylene blue-containing solution with carbon tetrachloride an intense blue color was extracted into the carbon tetrachloride layer providing a qualitative indication that the solution contained a compound of the type $RO\text{-}SO_3^-$. The methylene blue test applied to reaction mixture I of Table V was negative.

Discussion.—The data presented above indicate that aliphatic mercaptans react with unsaturated compounds in sodium laurate solutions in the presence of persulfate according to a chain reaction initiated by persulfate. The following equations, in which XH is an unsaturate which does not polymerize and M is a polymerizable monomer, account for the mechanism of the over-all reaction.

$$S_2O_8^{=} \longrightarrow 2SO_4\cdot^- \quad (1)$$

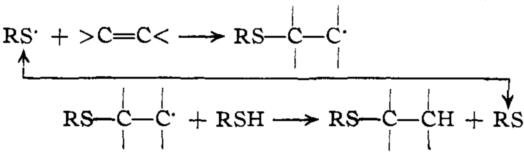
$$S_2O_8^{=} + XH \longrightarrow HSO_4^- + X\cdot + SO_4\cdot^- \quad (2)$$

$$SO_4\cdot^- + XH \longrightarrow X\cdot + HSO_4^- \quad (3)$$

$$(SO_4\cdot^- + M \longrightarrow {}^-O_4SM\cdot) \quad (3a)$$

$$X\cdot + RSH \longrightarrow XH + RS\cdot \quad (4)$$

$$(SO_4M\cdot + RSH \longrightarrow MSO_4H + RS\cdot) \quad (4a)$$



$$RS\cdot + {>}C{=}C{<} \longrightarrow RS{-}C{-}C\cdot \quad (5)$$

$$RS{-}C{-}C\cdot + RSH \longrightarrow RS{-}C{-}CH + RS\cdot \quad (6)$$

$$2RS\cdot \longrightarrow RSSR \quad (7)$$

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(7) W. Smith and H. N. Campbell, *J. Chem. Phys.*, **15**, 338 (1947); W. Smith, THIS JOURNAL, **71**, 4077 (1949).

(8) P. D. Bartlett and K. Nozaki, *J. Polymer Sci.*, **3**, 216 (1948).

(9) I. M. Kolthoff and Y. D. Pan, THIS JOURNAL, **62**, 3332 (1940).

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 $R\overset{O}{\overset{\|}{C}}O^{\cdot}$ are formed by the reaction of persulfate with sodium laurate has been presented in a previous paper.[6] That persulfate can attack a double bond to form a free radical of the type $R\underset{|}{\overset{|}{C}}\text{-}\underset{|}{\overset{\bullet}{C}}OSO_3^-$ (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[6] 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.[1] Certain results obtained by this method have already been presented.[2] 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[3] and also in numerous subsequent publications.[4–6] 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[2] 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.[1,2] 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-

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[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.