iodine. An independent set of experiments also showed a change of less than 0.3% in reducing power at 50% or less reduction of the copper when the initial formal concentration of copper was increased or decreased 10% in the reagent at *p*H 9.00. The increase in the *p*H of the micro reagent accompanying the formation of the blue precipitate is given also in the middle part of Fig. 3; the total increase amounted to about 0.03 *p*H unit when equilibrium was reached.

It is worth noting that no error is made in estimating the amount of a reducing sugar even when using a reagent that has deposited blue precipitate if the solution is decanted or filtered from the precipitate and no more precipitation occurs between the time the decanted solution is calibrated and used for analysis.

The instability of the micro reagent at *p*H 9.00 does not mean that the reagent at this *p*H is not suitable for analytical purposes. Precipitation can be avoided when one uses fresh solutions made up from double strength stock solution in the manner described in this article. The reproducibility of the results is much better with the reagent at this *p*H than at higher values and the yield of cuprous oxide is higher.

Summary

1. Carbonate buffered cupritartrate reagents for estimating micro and macro quantities of reducing sugars deposit an azure blue crystalline precipitate when the *p*H is less than 9.29 and 8.75, respectively, the formal concentration of cupric sulfate is 0.02 and 0.10, respectively, the ratio of Rochelle Salt to copper is three, the formal concentration of sodium carbonate is 0.24 and the *p*H is adjusted by adding sodium bicarbonate. These values are at 25° and for concentrations in moles per liter of solution.

2. Experimental evidence indicates that the precipitate is $Na_2(CuC_4H_2O_6)\cdot 2CuCO_3\cdot 7H_2O$. It is very insoluble in water at 25°.

3. The precipitate often does not appear until the reagent has stood for several months or years. It appears overnight when the solutions are seeded, but several days are required to reach equilibrium even when the solution is shaken continuously with the crystals, and several weeks are required when the reagent stands quietly over the crystals in the dark. Precipitation can be arrested indefinitely by decanting or filtering the supernatant solution from the crystals and storing the solution in a clean Pyrex bottle.

4. The formation of the precipitate lowers the optical density of the solution and the yield of cuprous oxide produced by a sugar, and raises the *p*H. But an initial decrease of 9% in the optical density is accompanied by a decrease of only 1% in the yield of cuprous oxide produced by dextrose and by no measurable change in the *p*H of the copper reagent. The maximum error produced by ignoring the formation of the precipitate in estimating micro quantities of dextrose increases rapidly when less than 10 and more than 50% of the cupric copper is reduced.

No error is made in estimating a reducing sugar with a copper reagent that has deposited blue precipitate when the reagent is decanted or filtered from the precipitate and no more precipitation takes place between the time the decanted solution is calibrated and used for analysis.

5. The yield of cuprous oxide decreases and the probable error increases linearly as the *p*H of the copper reagent is increased. The yield decreases 11% and the probable error increases from 0.06 to 0.13 ml. of 0.005 *M* thiosulfate in an analysis when the *p*H of the micro copper reagent is changed from 9.00 to 9.30.

CAMBRIDGE, MASS. RECEIVED FEBRUARY 1, 1950

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

The Solubility of Higher Alkyl Quaternary Ammonium Salts of Fatty Acids

BY D. N. EGGENBERGER, F. K. BROOME, R. A. RECK AND H. J. HARWOOD

Inactivation of bactericidal quaternary ammonium salts by anionic colloidal electrolytes is well known.[1] This inactivation is assumed to be due to the formation of an insoluble quaternary ammonium salt of the surface-active anion involved. The formation of such insoluble salts is not always apparent to the eye because of their incorporation into the micelle. Precipitation has been demonstrated by surface-tension measurements as well as by bactericidal studies.[2]

The compatibility of quaternary ammonium compounds with soluble soaps depends upon the solubility of the quaternary ammonium salt of the fatty acid composing the soap. The present paper is concerned with the estimation of this solubility by the conductometric method.

Experimental

The preparation of trimethylhexadecylammonium chloride has been previously described.[3] N-Dodecyl-N-methylmorpholinium methosulfate was prepared from N-dodecylmorpholine and dimethyl sulfate according to the method of Niederl.[4] The morpholinium chloride was prepared in the usual manner using methyl chloride.[3] Solu-

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[1] Baker, Harrison, and Miller, *J. Exptl. Med.*, **74**, 621 (1941); Lawrence, *J. Am. Pharm. Assoc., Sci. Ed.*, **37**, 57 (1948).

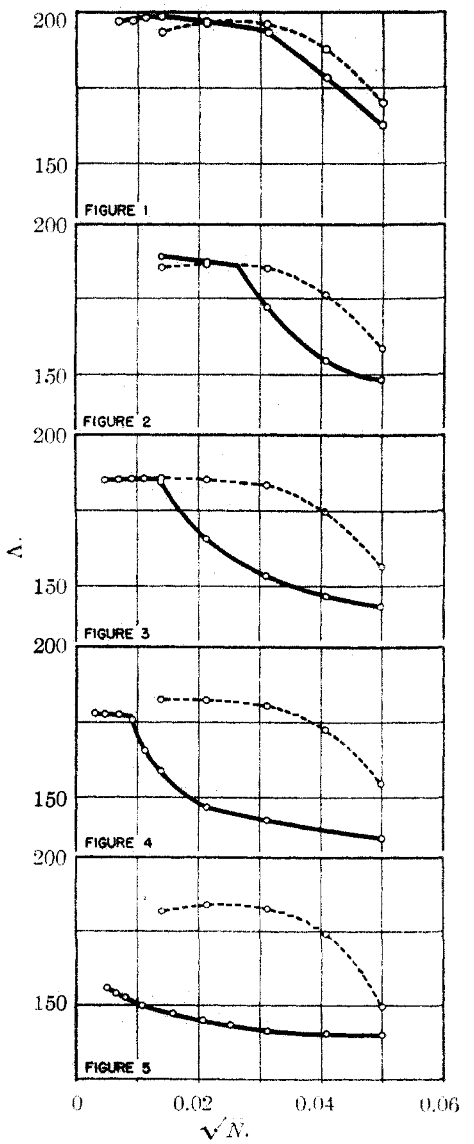
[2] Alexander and Tomlinson, "Surface Chemistry," Interscience Publishers, Inc., New York, N. Y., 1949, p. 325.

[3] Ralston, Eggenberger, Harwood and Du Brow, THIS JOURNAL, **69**, 2095 (1947).

[4] Niederl, *ibid.*, **70**, 618 (1948).

tions of the sodium salts of caproic, caprylic, capric and oleic acids were prepared by addition of the calculated quantities of standard sodium hydroxide solution to the fatty acids. Purified fatty acids were used except in the case of the oleic acid which was a commercial grade of 90% purity.

Measurements of solution resistances were made in a cell with a constant of 0.0877. The electrodes were unplatinized to prevent adsorption of solute. A connection between the cell and a mixing flask, both of which were mounted in the constant-temperature bath, made it possible to transfer the solution from one to the other by air pressure. The air for these transfers was freed of carbon dioxide and saturated with water vapor at the temperature of the bath. A buret containing concentrated solution was fitted into the mixing flask by means of a rubber stopper.

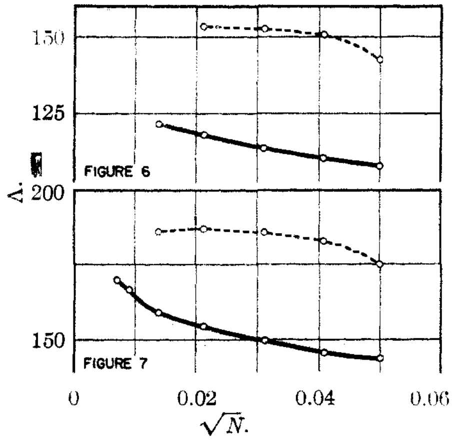


Figs. 1–5.—Equivalent conductances: solid lines, trimethylhexadecylammonium chloride in equimolar mixture with sodium salts of fatty acids; broken lines, sums of the conductances of the individual salts; Fig. 1, with sodium acetate; Fig. 2, caproate; Fig. 3, caprylate; Fig. 4, caprate; Fig. 5, oleate.

Solutions of increasing concentration were prepared by adding measured portions of concentrated solution from the buret into the solution already present in the system. The concentrated solutions of the quaternary ammonium salts of the fatty acids were prepared by mixing equal volumes of 0.01 N solutions of the quaternary ammonium chloride (or methosulfate) and the sodium soaps.

Results and Discussion

Conductance curves for equimolar mixtures of trimethylhexadecylammonium chloride with the sodium salts of acetic, caproic, caprylic, capric and oleic acids, together with curves representing the sum of the conductances of the component salts, are shown in Figs. 1 to 5. It has previously been shown[5] that the critical point of a cationic colloidal electrolyte in the presence of inorganic electrolytes is determined by the solubility of the least-soluble colloidal salt capable of being formed in the mixture. Examination of Figs. 1 to 5 reveals that according to the above criterion the solubilities of trimethylhexadecylammonium salts of fatty acids decrease with increase in chain length of the fatty acid. In these figures the sum of the equivalent conductances for the quaternary ammonium chloride and the sodium salt of the fatty acid, and the conductance of the mixture of the two, have been plotted against the square root of the normality of the individual salts. Values for the sums give the theoretical conductance curves for the mixtures in the absence of any precipitation. The critical concentration for the system trimethylhexadecylammonium chloride–sodium acetate (Fig. 1) (0.0012 N) is slightly below that for the pure quaternary ammonium chloride (0.0013 N).[3] This is to be expected since the system contains added electrolyte.[5] Figure 2, depicting the effect of sodium caproate, shows a still-lower critical point (0.0007 N). Similarly, in the systems containing



Figs. 6 and 7.—Equivalent conductances: solid lines, N-dodecyl-N-methylmorpholinium salts in equimolar mixture with sodium oleate; broken lines, sums of the conductances of the individual salts; Fig. 6, quaternary morpholinium methosulfate; Fig. 7, quaternary chloride.

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[5] Ralston, Eggenberger and Broome, This Journal, **71**, 2145 (1949).

sodium caprylate (Fig. 3) and caprate (Fig. 4), the critical points are at 0.0002 and 0.00008 *N*, respectively. The values for the equivalent conductance of the mixtures below the critical concentration in each case approximate the sum of the values for the original quaternary ammonium chloride and the sodium salt. In the system containing sodium oleate (Fig. 5), the critical point is evidently below the lowest concentration investigated (0.000005 *N*).

A recent report[6] on the compatibility of N-alkyl-N-methylmorpholinium methosulfates with soaps prompted investigation of this type of compound as well as the corresponding chloride. Conductance curves for mixtures of the N-dodecyl-N-methylmorpholinium salts with sodium oleate are shown in Figs. 6 and 7 together with curves for the sums. Extrapolation of the curves for the mixtures indicates a critical concentration not greater than 0.000025 *N*. On the basis of this value the morpholinium salts cannot be considered as compatible with sodium oleate.

Summary

A conductometric method for estimating the solubility of slightly soluble quaternary ammonium salts has been presented.

Solubilities, as indicated by the critical concentrations, of trimethylhexadecylammonium salts of fatty acids in the presence of equimolecular quantities of sodium chloride are as follows: acetate 0.0012 *N*, caproate 0.0007 *N*, caprylate 0.0002 *N*, caprate 0.00008 *N*, and oleate < 0.000005 *N*.

Evidence is presented that N-dodecyl-N-methylmorpholinium salts are not compatible with sodium oleate.

CHICAGO, ILLINOIS RECEIVED FEBRUARY 13, 1950

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[6] Hart, McGreal and Niederl, Abstracts of the Atlantic City Meeting of the American Chemical Society, September 19–23, 1949.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

The System Ammonium Fluoride–Potassium Fluoride–Water at 25°[1]

BY HELMUT M. HAENDLER AND ALBERT W. JACHE

Few complete studies have been made of systems involving two inorganic fluorides and water. Kurtenacker, Finger and Hey[2] have reported several systems with ammonium or potassium

TABLE I

ANALYSES OF SOLUTIONS AND WET RESIDUES

Solutions, weight %			Wet residues, weight %		
NH_4F	KF	H_2O	NH_4F	KF	H_2O
0.00	48.96	51.04	...	...	...
1.70	48.76	49.54	0.27	63.08	36.65
3.49	48.63	47.88	0.69	60.31	39.00
6.53	48.15	45.32	1.41	59.32	39.27
8.04	48.42	43.44	1.32	61.80	36.88
8.75	48.44	42.40	1.60	62.93	35.47
8.97	47.63	43.40	5.79	53.01	41.20
10.08	47.88	42.04	2.99	58.65	38.30
10.77	47.93	41.30	52.39	25.96	21.95
10.94	47.04	42.02	43.46	29.58	26.96
11.09	47.39	41.52	43.69	30.03	26.28
11.98	44.88	43.04	67.94	16.57	15.49
12.14	45.09	42.77	52.41	25.83	21.76
12.92	42.93	44.15	61.14	19.50	19.30
13.12	43.28	43.60	58.57	19.13	22.30
13.62	41.45	44.93	55.08	20.79	24.13
13.77	41.26	44.97	59.74	18.37	21.65
13.93	40.82	45.15	70.00	14.96	15.04
14.41	39.29	46.30	56.24	20.03	23.73
14.85	38.63	46.52	60.34	18.01	21.65
16.88	35.43	47.69	64.50	15.02	20.48
17.07	35.01	47.92	60.53	16.43	23.04
18.60	31.41	49.94	77.90	10.15	11.95
20.37	29.92	49.71	70.48	10.99	18.63
22.52	27.57	49.91	78.64	10.23	11.23
26.44	23.76	49.80	41.23	18.83	39.94
28.49	19.65	51.84	67.61	11.25	21.14
31.59	16.85	51.66	76.99	5.43	17.68
36.03	10.69	53.28	79.04	4.00	10.36
41.27	4.57	54.16	80.74	1.64	17.66
42.92	1.48	55.60	78.50	0.61	20.59
44.85	0.00	55.15	...	...	...

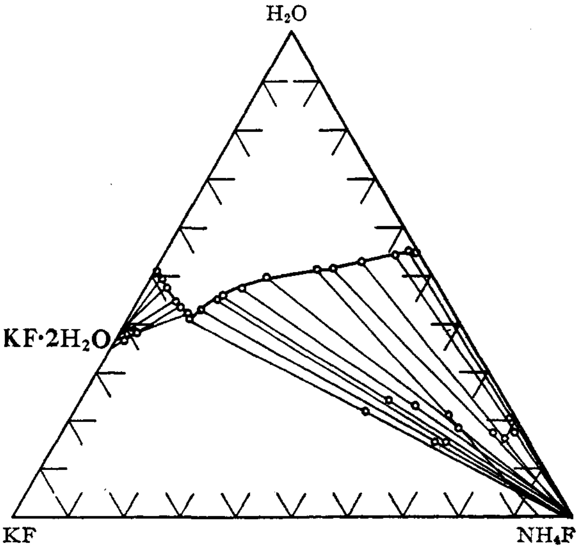

Fig. 1.—The system ammonium fluoride–potassium fluoride–water at 25°.

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[1] This work was part of a program of fluoride research supported by a Research Corporation grant-in-aid and is taken in part from the M.S. thesis of A. W. Jache.

[2] Kurtenacker, Finger and Hey, *Z. anorg. allgem. Chem.*, **211**, 281 (1933).