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The Influence of N-Methylation upon the Electrical Conductivity of Dodecylammonium Chloride

BY A. W. RALSTON, F. K. BROOME AND H. J. HARWOOD

The substitution of the hydrogens of ammonia by alkyl groups is attended by an increase in basicity,[1] and Hall and Sprinkle[2] have shown that the introduction of one alkyl group into ammonia brings about a decided increase in basicity, a second alkyl group results in only a slight, further increase, whereas a third alkyl group produces a slight drop in basicity. The ionization constants of the tertiary amines are therefore comparable to those of the primary amines and are appreciably lower than those of the secondary amines. The long-chain, symmetrical secondary amines have been reported[3] to have much higher ionization constants than the primary amines, the values observed being essentially independent of the lengths of the hydrocarbon chains. The introduction of a fourth alkyl, or other hydrocarbon radical, into the amine molecule, with the formation of the quaternary ammonium compounds is accompanied by a profound change in the chemical and physical properties.[4] Certain of the quaternary ammonium bases, for example, tetramethylammonium hydroxide, are among the strongest bases known. In view of these facts we have undertaken a critical study of the effects of methylation upon the physical properties of dodecylammonium chloride and have studied the solubilities in water and in a number of organic solvents and also the electrical conductivities of aqueous solutions of dodecyl-, methyldodecyl-, dimethyldodecyl-, and trimethyldodecylammonium chlorides. This present paper reports the electrical conductivities of aqueous solutions of these compounds and compares their tendency toward colloid formation as portrayed by their conductivities. To our knowledge, no such studies have been previously made upon a comparable series of compounds.

Experimental

Preparation of Methyldodecylammonium Chloride.—Dodecyl chloride was prepared from dodecyl alcohol (f.p. 24.0°) by treatment with gaseous hydrogen chloride using zinc chloride as the catalyst. Methylamine was purified as the benzal derivative. The reaction of the dodecyl chloride (331 g., 1.62 moles) with 458 g. of an ethanol solution containing 218 g. (7.04 moles) of methylamine was accomplished by heating the reactants in an autoclave at 125° for eight hours. After addition of 60 g. of sodium hydroxide, the excess methylamine was removed by distillation and the methyldodecylamine extracted with Skellysolve B and dried over potassium carbonate. Distillation through a Vigreux column yielded 258 g. (80%) of methyldodecylamine, b.p. 80–85° (0.4 mm.) and 56 g. (19%) of methyldidodecylamine, b.p. 180–185° (0.4 mm.). Purification of the methyldodecylamine was accomplished by fractionation through a Stedman-packed column. A fraction of the methyldodecylamine (f. p. 16.5°) was converted to the hydrochloride by treating its benzene solution with gaseous hydrogen chloride. The salt was recrystallized from benzene containing a little methanol.

Anal. Calcd.: N, 5.94. Found: N, 5.99.

Preparation of Dimethyldodecylammonium Chloride.—Dimethyldodecylamine was prepared in the manner previously described.[5] A fraction was converted to the hydrochloride by treatment of its ether solution with gaseous hydrogen chloride. The salt was recrystallized from ethyl acetate.

Anal. Calcd.: N, 5.61. Found: N, 5.68.

The conductivities were determined in the manner and with the equipment previously described.[6]

Results and Discussion

The equivalent conductivities at 30° plotted against $\sqrt{N_v}$ of aqueous solutions of dodecyl-, methyldodecyl-, dimethyldodecyl- and trimethyldodecylammonium chlorides are shown in Fig. 1. The values for dodecylammonium chloride have been taken from a recent publication.[7] The

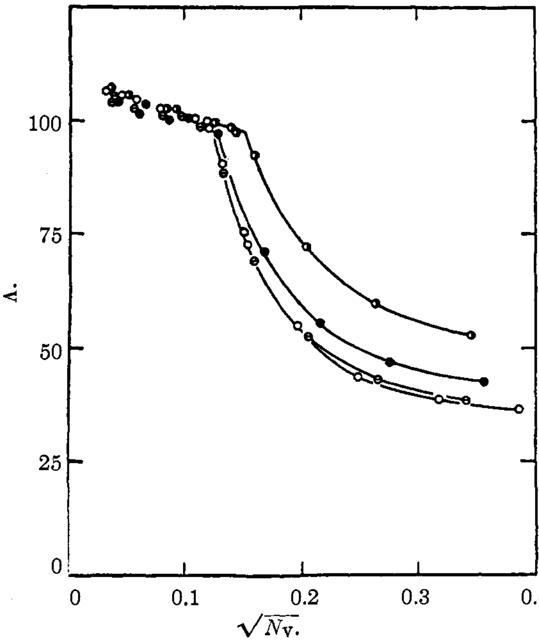

Fig. 1.—Equivalent conductivities of dodecylammonium chloride and N-methyl derivatives at 30°: ○, dodecylammonium chloride; ⊖, methyldodecylammonium chloride; ●, dimethyldodecylammonium chloride; ◑, trimethyldodecylammonium chloride.

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(1) Bredig, *Z. physik. Chem.*, **13**, 191 (1894).

(2) Hall and Sprinkle, THIS JOURNAL, **54**, 3469 (1932).

(3) Hoerr, McCorkle and Ralston, *ibid.*, **65**, 328 (1943).

(4) Flürscheim, *J. Chem. Soc.*, **95**, 718 (1909).

(5) Reck, Harwood and Ralston, *J. Org. Chem.*, **12**, 517 (1947).

(6) Ralston, Hoerr and Hoffman, THIS JOURNAL, **64**, 97 (1942).

(7) Ralston and Eggenberger, *ibid.*, **70**, 436 (1948).

curves show that the conductivities of dodecyl- and methyldodecylammonium chlorides are almost identical, indicating that the transition from the primary to the secondary amine salt is not accompanied by a significant change in solution behavior. The tertiary amine salt, dimethyldodecylammonium chloride, has a somewhat higher concentration at the critical point and a higher equivalent conductivity at concentrations beyond the critical point. A much larger difference is encountered in going from the tertiary amine hydrochloride to the quaternary ammonium chloride. Trimethyldodecylammonium chloride has a significantly higher critical concentration and a much higher equivalent conductivity beyond this point. The values of Λ_o, Λ_c, $\sqrt{N_c}$, and N_c for these four salts are shown in Table I.

TABLE I

Compound, chloride	Λ_o	Λ_c	$\sqrt{N_c}$	N_c
Dodecylammonium	108.5	100.0	0.121	0.0146
Methyldodecylammonium	107.9	99.1	.121	.0146
Dimethyldodecylammonium	109.2	98.1	.127	.0161
Trimethyldodecylammonium	109.8	97.8	.151	.0228

These values together with the curves in Fig. 1 show that for this series of salts the greatest change in conductivity behavior occurs in going from the tertiary amine salt to the quaternary ammonium salt. The colloidal state, as evidenced by the values of N_c, is assumed at the same concentration for the salts of the primary and secondary amines, at a somewhat higher concentration for the tertiary amine salt and at a materially higher concentration for the quaternary ammonium salt. The values of Λ_c undergo a progressive, small decrease in going from the primary to the quaternary ammonium salt. The conductivities of these four salts at concentrations lower than the critical concentration are not significantly different as shown by the small differences in the values of Λ_o.

Summary

1. The equivalent conductivities of aqueous solutions of dodecyl-, methyldodecyl-, dimethyldodecyl-, and trimethyldodecylammonium chlorides have been determined.

2. The greatest difference in these values is observed in going from dimethyldodecylammonium chloride to trimethyldodecylammonium chloride.

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The Electrical Conductivities of Tris-(hydroxyalkyl)-alkylammonium Chlorides

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The substitution of short-chain hydroxyalkyl groups for methyl groups in trimethylalkylammonium chlorides renders the long-chain cations more hydrophilic and should result in a modification of the colloidal properties portrayed by the electrical conductivities of aqueous solutions. In contrast to this expectation, it recently has been shown[1] that the progressive substitution of 2-hydroxyethyl groups for methyl groups in trimethylhexadecylammonium chloride does not bring about a significant change in either the equivalent conductivity or the concentration at the critical point. Substitution of one of the methyl groups in trimethylhexadecylammonium chloride by a 2,3-dihydroxypropyl group is likewise not attended by a noticeable change in the critical concentration. The critical concentration of trimethyldodecylammonium chloride is materially greater than that of trimethylhexadecylammonium chloride, thus manifesting that the colloidal state is not so readily assumed with the former salt as with the latter. As a consequence, the incorporation of hydroxyalkyl groups into a trimethyldodecylammonium salt should have a greater relative effect upon its colloidal properties than a similar incorporation into a trimethylhexadecylammonium salt. The present paper discusses the effect of the substitution of the methyl groups in trimethyldodecylammonium chloride by hydroxyethyl and 2,3-dihydroxypropyl groups and compares these effects with similar substitutions in the hexadecyl homolog.

Experimental

Preparation of tris-(2,3-Dihydroxypropyl)-dodecylammonium Chloride.—To a solution of 38 g. of sodium hydroxide in 400 cc. of ethanol was added 80 g. of dodecylamine (f. p. 28.2°). The solution was cooled to 15° and to it was added 120 g. of glycerol 1-chlorohydrin. The reaction which occurred was accompanied by an appreciable rise in temperature. After standing overnight the sodium chloride was filtered off and the ethanol distilled, the last traces of solvent being removed under reduced pressure. Without purification, the bis-(2,3-dihydroxypropyl)-dodecylamine was treated with 47.8 g. of glycerol 1-chlorohydrin and the mixture heated on the steam-bath at 100° for sixteen hours. Attempts to purify the product by crystallization from a number of solvents were unsuccessful. Some purification was achieved by dissolving the quaternary ammonium salt in ethyl acetate (700 cc.) containing methanol (35 cc.) and cooling the solution to −10°. The upper layer was decanted and the process repeated. After removal of the solvent under reduced pres-

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