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.

CHICAGO, ILLINOIS RECEIVED OCTOBER 1, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

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

BY A. W. RALSTON, D. N. EGGENBERGER AND H. J. HARWOOD

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).

sure the product was dried *in vacuo* over calcium chloride. The tris-(2,3-dihydroxypropyl)-dodecylammonium chloride was obtained as a sticky, plastic mass. A purity of 95% was indicated by titration with standard sodium dodecyl sulfate using dichlorofluorescein as indicator.

Preparation of tris-(2,3-Dihydroxypropyl)-hexadecylammonium Chloride.—This compound was prepared from hexadecylamine according to the above procedure. It was obtained as a plastic mass with an indicated purity of 100%.

Preparation of tris-(2-Hydroxyethyl)-dodecylammonium Chloride.—This was prepared from dodecylamine and ethylene chlorohydrin in a manner similar to that described above. The product was a white, crystalline solid which was somewhat hygroscopic. The indicated purity was 100%.

The electrical conductivities of solutions of the quaternary ammonium salts were determined in the manner and with the equipment previously described.[2]

Results and Discussion

The equivalent conductivities plotted against $\sqrt{N_v}$ of dodecyltrimethylammonium chloride, tris-(2-hydroxyethyl)-dodecylammonium chloride, and tris-(2,3-dihydroxypropyl)-dodecylammonium chloride are shown in Fig. 1. Substitution of the three methyl groups of trimethyldodecylammonium chloride by hydroxyethyl groups enhances the colloidal properties as evidenced by the decrease in the critical concentration. The equivalent conductivity of tris-(2-hydroxyethyl)-dodecylammonium chloride is higher than that of trimethyldodecylammonium chloride at concentrations below the critical point; however, it is significantly lower at the higher concentrations. The difference in these curves may be explained on the basis of a greater tendency toward solubilization of the tris-(2-hydroxyethyl)-dodecylammonium chloride. Substitution of the three methyl groups by 2,3-dihydroxypropyl groups brings about a profound change in the nature of the conductance curve. Tris-(2,3-dihydroxypropyl)-dodecylammonium chloride shows a greatly decreased conductivity over the entire concentration range investigated, the curve having little similarity to those of typical colloidal electrolytes. The incorporation of the six hydroxyl groups into the molecule is therefore attended by a decided modification of the colloidal behavior as evidenced by the absence of a well-defined critical point.

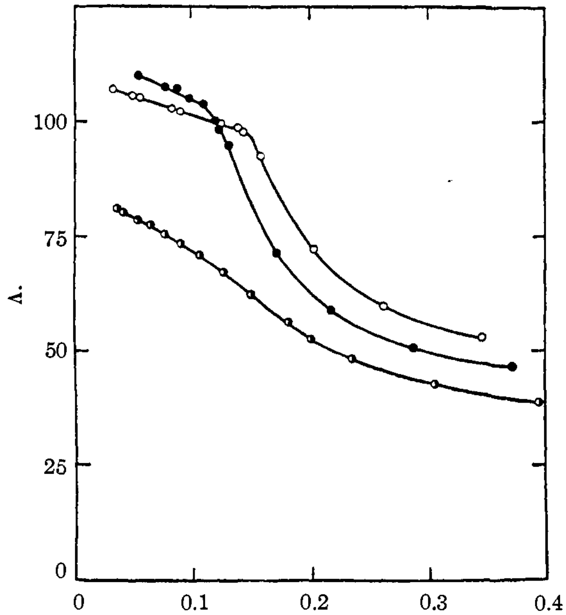

Fig. 1.—Equivalent conductivities of hydroxyalkyldodecylammonium chlorides at 30°: ○, dodecyltrimethylammonium chloride; ●, tris-(2-hydroxyethyl)-dodecylammonium chloride; ◑, tris-(2,3-dihydroxypropyl)-dodecylammonium chloride.

Figure 2, which compares the equivalent conductivities of trimethylhexadecylammonium chloride and tris-(2,3-dihydroxypropyl)-hexadecylammonium chloride, shows that both these compounds function as typical cationic electrolytes. This behavior is in sharp contrast to that of the dodecyl homologs and indicates that the paraffin nature of the hexadecylammonium ion is not decidedly modified by the introduction of three 2,3-dihydroxypropyl groups.

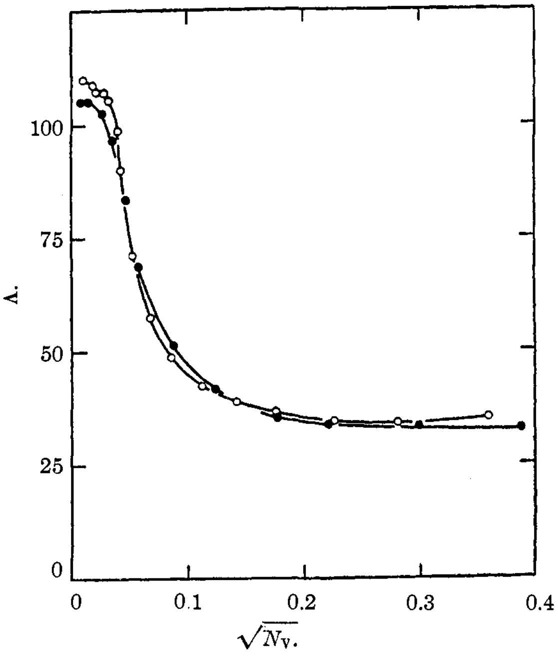

Fig. 2.—Equivalent conductivities of hexadecyltrimethylammonium chloride and tris-(2,3-dihydroxypropyl)-hexadecylammonium chloride at 30°: ○, hexadecyltrimethylammonium chloride; ●, tris-(2,3-dihydroxypropyl)-hexadecylammonium chloride.

Summary

1. The equivalent conductivities of trimethyldodecyl-, tris-(2-hydroxyethyl)-dodecyl-, tris-(2,3-dihydroxypropyl)-dodecyl-, trimethylhexadecyl-

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[2] Ralston, Hoerr and Hoffman, *ibid.*, **64**, 97 (1942).

and tris-(2,3-dihydroxypropy)-hexadecylammonium chlorides have been compared.

2. The substitution of hydroxyethyl groups for methyl groups in trimethyldodecylammonium chloride does not greatly modify the colloidal properties; however, the substitution of 2,3-dihydroxypropyl groups results in a decided modification. A similar substitution in trimethylhexadecylammonium chloride is without a significant effect.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Dissociation Constants of Some Mono-substituted Benzeneseleninic Acids[1]

BY JAMES D. MCCULLOUGH AND EDWIN S. GOULD

Introduction

The benzeneseleninic acids are white crystalline solids analogous to benzenesulfinic acids in the sulfur series. They are weak acids of strengths comparable to that of acetic acid. A series of thirteen of these compounds has been prepared, six members of which have not been previously described in the literature. Acidic dissociation constants were determined by titration of approximately $0.005F$ solutions of the acids with standard ($0.1N$) carbonate-free sodium hydroxide using a model H Beckman *p*H meter. The dissociation constants thus obtained have been correlated with the Hammett ρ–σ treatment[2] and a ρ value for the ionic dissociation observed. The effects of small temperature changes on the dissociation constants have been noted for a number of the acids and have been found to be similarly small.

Experimental

I. **Syntheses.**—The seleninic acids were prepared from the corresponding diselenides through oxidation with concentrated hydrogen peroxide.

$$R_2Se_2 + 3H_2O_2 = 2RSeO_2H + 2H_2O \qquad (1)$$

A. **Preparation of Diselenides.**—The diselenides were prepared by the two methods described by Campbell and McCullough.[3] The numbers in Table I refer to the numbering of the methods used by those authors.

B. **Oxidation of Diselenides.**—Two methods were employed depending on whether the diselenide was liquid or solid.

1. **Solid Diselenides.**—Ten grams of the diselenide was added to 10 ml. of 1,4-dioxane and the mixture warmed to about 60° to dissolve as much solid as possible. It was then cooled to below 5° and C. P. concentrated hydrogen peroxide (20–28%) was added dropwise, stirring the mixture and cooling externally to keep the temperature under 10°. After addition of a threefold excess of peroxide, fifteen grams of ice was added and the resulting solid (which was almost white) was filtered off and washed with 10 ml. of ice water.

2. **Liquid Diselenides.**—Ten grams of the diselenide was dissolved in 15 ml. of diethyl ether. Concentrated hydrogen peroxide was added dropwise; but after each five or six drops, the solution was swirled vigorously over a warm water-bath at 45° to ensure as complete a reaction as possible. If the temperature of the mixture rose above 38°, it was cooled to below 34°, ether being added from time to time to replace that lost by evaporation. After addition of a threefold excess of peroxide, the ether was stripped off at room temperature with a water pump, leaving a mixture of white seleninic acid and orange oil impurities.

If the amount of orange oil was excessive, 30 cc. of $6N$ ammonia was added to the residue, dissolving the acid. The solution was washed twice with 20-ml. portions of ether, removing a large part of the orange residue. The aqueous layer was acidified with dilute sulfuric acid, and an excess of potassium iodide was added along with an additional 15 ml. of ether to reduce the acid back to the original diselenide. The mixture was shaken thoroughly, and just enough sodium thiosulfate solution was added to reduce the I_3^- formed. The ether layer, containing the diselenide, was separated, washed twice with dilute sodium hydroxide, twice with distilled water, and reoxidized with hydrogen peroxide as before.

C. **Purification Method.**—One of two methods was used, depending upon the solubility in water of the seleninic acid involved.

1. **Slightly Soluble Acids.**—A ten per cent. excess of $15N$ ammonia was added to the solid acid, and the solution was stirred until no white solid remained. The solution was filtered, decolorized twice with Norite, and the acid reprecipitated by slow addition of C. P. 6 N hydrochloric acid. The solid was washed with ice water, dissolved in a minimum volume of methanol, and the methanolic solution added dropwise to boiling water until cloudiness formed. At that point, 25% more boiling water was added, the solution filtered hot, decolorized if necessary, then cooled rapidly with scratching to 0°. After thirty minutes, the crystallized acid was filtered off and recrystallized as before, this time cooling very slowly. The crystals, usually needles, were filtered off, dried in a vacuum desiccator over calcium chloride for two days, and a preliminary melting point taken. If the melting point was above 120°, the acid was dried in an oven for an hour at 90°. If the melting point was below 120°, the solid was kept in the vacuum desiccator for three additional days. Difficulty was encountered in removing the last traces of water from the solid; for if it were dried too persistently, the product turned pink, indicating decomposition. For this reason, the equivalent weights of some of the acids were as much as 1% low while some were 3 or 4% high. This difficulty should not, however, affect the accuracy of the dissociation constants.

2. **Soluble Acids.**—If the acid was quite soluble in cool water, treatment with ammonia was omitted, the crude product dissolved directly in a minimum quantity of hot (but not boiling) water (80°), the solution filtered hot, decolorized with norite until a pale yellow, and the acid reprecipitated by cooling. A second recrystallization was then made. The drying procedure was that described above.

D. **Special Method.**—*m*-Nitrobenzeneseleninic acid was prepared by nitration of benzeneseleninic acid nitrate as described by Friend.[4] The procedure was modified by

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[1] Based on research carried out under Task Order I of Contract N6onr-275, between the Office of Naval Research and the University of California, Los Angeles. Presented at the Chicago meetings of the American Chemical Society, April, 1948.

[2] Louis P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1941.

[3] Tod W. Campbell and James D. McCullough, THIS JOURNAL, **67**, 1965 (1945).

[4] Friend, "Text-book of Inorganic Chemistry," Vol. XI, Charles Griffin and Company, Ltd., London, 1937, p. 48.