[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

The Electrical Conductivities of Long-Chain Quaternary Ammonium Chlorides Containing Hydroxyalkyl Groups

BY A. W. RALSTON, D. N. EGGENBERGER, H. J. HARWOOD AND P. L. DU BROW

It is well known that those quaternary ammonium compounds which contain at least one long-chain hydrocarbon group function as colloidal electrolytes. Increase in the length of the hydrocarbon chain in the alkylammonium chlorides has been shown to result in a lowered equivalent conductance and a lowered concentration of electrolyte at the critical point.[1] That this is also true for the quaternary ammonium chlorides is shown by a comparison of the conductivities of hexadecyl- and octadecyltrimethylammonium chlorides reported in this paper. Although unsaturation within the hydrocarbon chain of the alkylammonium chlorides results in a higher equivalent conductivity, it does not change the concentration at the critical point.[2] Such findings are in agreement with the opinion of Hartley[3] that the critical concentration is essentially dependent upon the length of the hydrocarbon chain and not on the nature of the ionized groups.

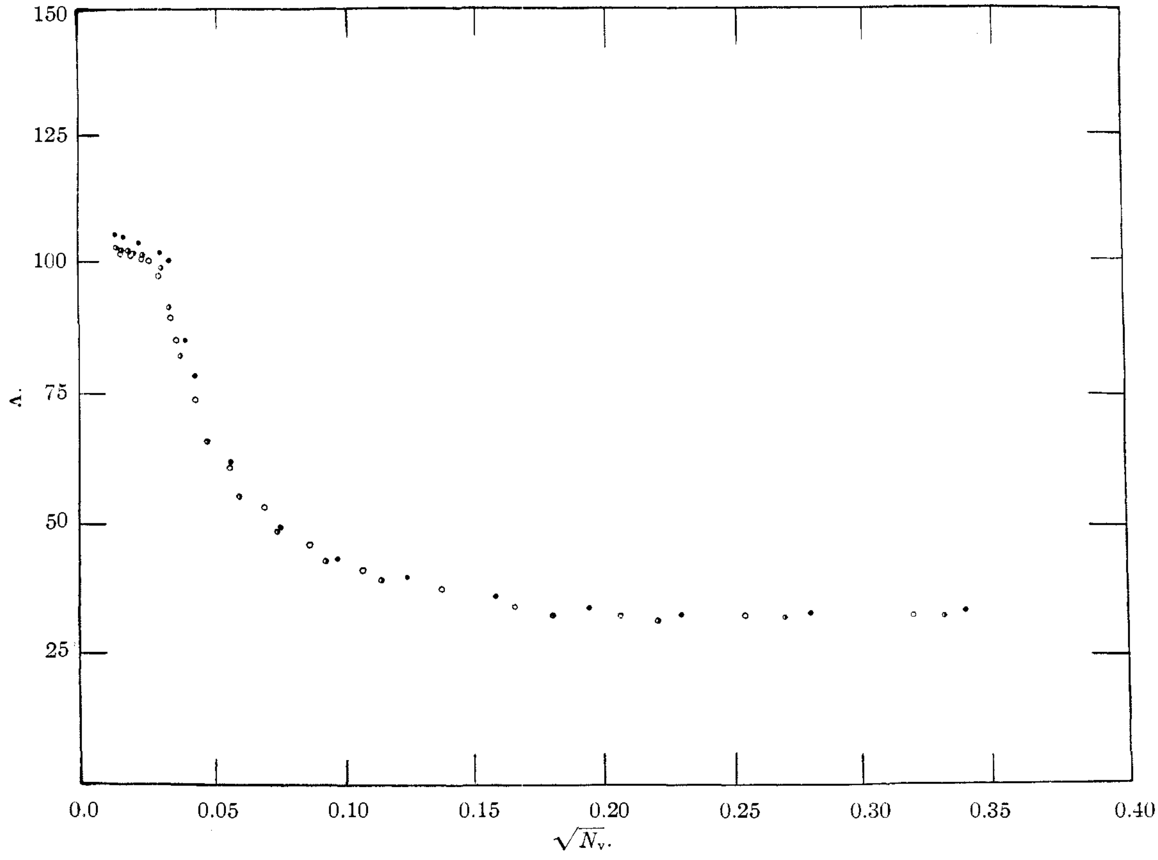

Fig. 1.—Equivalent conductivities of hexadecyl quaternary ammonium chlorides containing 2-hydroxyethyl groups: ●, 2-hydroxyethyldimethylhexadecylammonium chloride; ◑, di-(2-hydroxyethyl)-methylhexadecylammonium chloride; ○, tri-(2-hydroxyethyl)-hexadecylammonium chloride.

This present investigation is concerned with the effect of the progressive substitution of hydroxyethyl groups for methyl groups upon the electrical conductivities of aqueous solutions of quaternary ammonium compounds. For the purposes of this study we have selected trimethylhexadecylammonium chloride and have determined the equivalent conductivity of aqueous solutions of this salt and of 2-hydroxyethyldimethyl-, di-(2-hydroxyethyl)-methyl- and tri-(2-hydroxyethyl)-hexadecylammonium chlorides. A comparison of these values gives an indication of the effect of the substitution of short-chain hydroxy-

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[1] Ralston and Hoerr, THIS JOURNAL, **64**, 772 (1942).

[2] Unpublished observation.

[3] Hartley, *Kolloid-Z.*, **88**, 22 (1939).

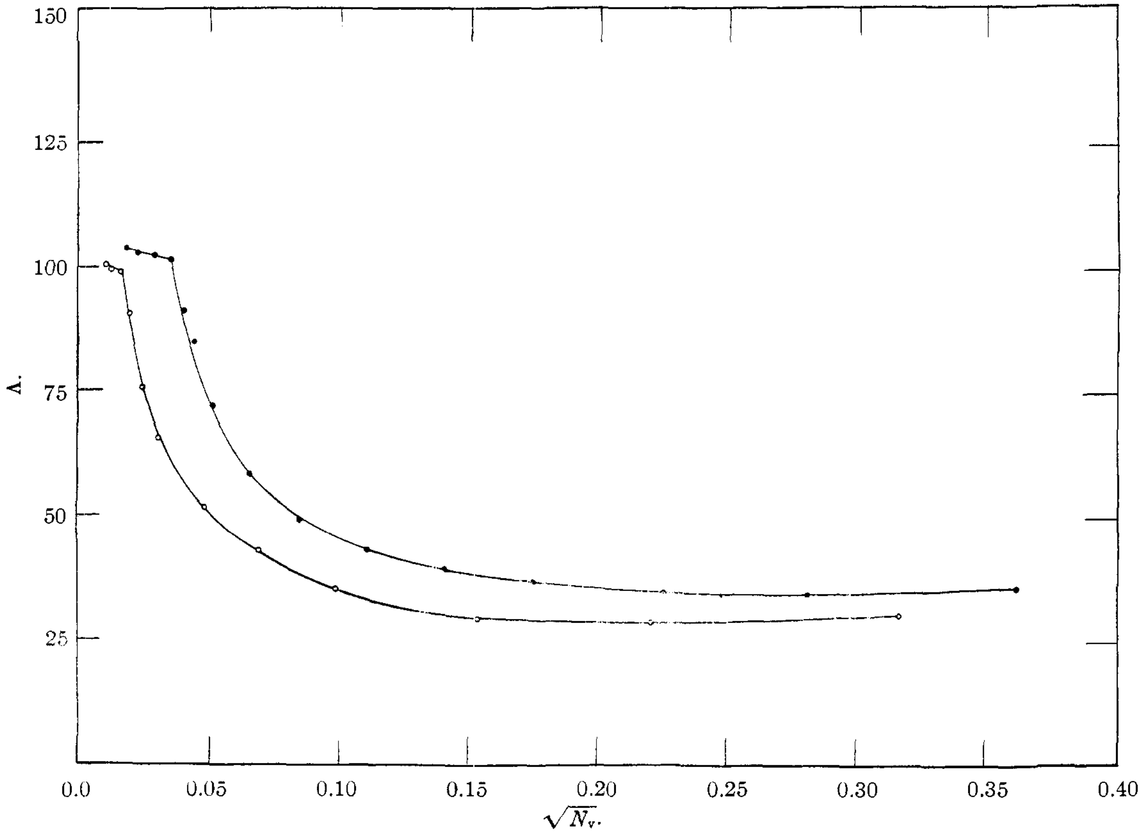

Fig. 2.—Equivalent conductivities of trimethylhexadecyl- and trimethyloctadecylammonium chlorides: ●, trimethylhexadecylammonium chloride; O, trimethyloctadecylammonium chloride.

alkyl groups for methyl groups upon the colloidal behavior of the quaternary ammonium compounds.

Experimental

The hydroxy quaternary ammonium compounds used in this investigation were prepared from hexadecylamine purified by fractional distillation through a Stedman packed column. The freezing point of the distilled amine was 46.04°. The quaternary salts were prepared as derivatives of dimethylhexadecylamine and di-(2-hydroxyethyl)-hexadecylamine.

The dimethylhexadecylamine was obtained from hexadecylamine by reaction with formic acid and formaldehyde. Hexadecylamine, 120.7 g. (0.5 mole), was dissolved in 150 cc. of ethanol in a three-necked flask equipped with a mercury-sealed stirrer, condenser, and dropping funnel. To this was slowly added 130 cc. of 85% formic acid, the temperature being maintained at approximately 30°. After this addition, 105 cc. of 37% formaldehyde was added and the mixture maintained at 40° until the evolution of carbon dioxide decreased. The temperature was then gradually raised to the reflux point and maintained at this temperature until the evolution of carbon dioxide ceased. The solution was then made alkaline with aqueous sodium hydroxide and sufficient water was added to produce two layers. The upper layer was drawn off, washed with water, dried over potassium carbonate, and distilled. An 80% yield of dimethylhexadecylamine, b. p. 147° (2.0 mm.), was obtained.

Trimethylhexadecylammonium chloride was prepared by treating 25 g. of dimethylhexadecylamine in 25 cc. of Skellysolve F with 10 cc. of methyl chloride (obtained by condensing the gas in a Dry Ice-bath) in a Parr hydrogenating bomb for one hour at 80°. The product was purified by crystallizing twice from ethyl acetate containing sufficient ethanol to dissolve the quaternary salt at the boiling point of the mixture.

2-Hydroxyethyldimethylhexadecylammonium chloride was obtained by treating 30 g. of dimethylhexadecylamine with 9 g. of distilled ethylene chlorohydrin at 100° for fifteen hours. The product was purified as described above. Dimethyl 2,3-dihydroxypropylhexadecylammonium chloride was similarly prepared using glycerol 1-chlorohydrin.

The di-(2-hydroxyethyl)-hexadecylamine was prepared as follows: 120.6 g. (0.5 mole) of hexadecylamine, 82 g. of freshly distilled ethylene chlorohydrin and several drops of phenolphthalein indicator were dissolved in 200 cc. ethanol in a three-necked flask. The solution was heated to the reflux temperature and an alcoholic solution of 40 g. of sodium hydroxide slowly added, at a rate sufficiently slow to maintain the solution colorless to the indicator. The reaction mixture was diluted, extracted with Skellysolve B, the solution dried and the solvent removed. Distillation gave a 70% yield of di-(2-hydroxyethyl)-hexadecylamine, b. p. 200° (0.3-0.4 mm.). The quaternary ammonium salts, di-(2-hydroxyethyl)-methylhexadecyl- and tri-(2-hydroxyethyl)-ammonium chlorides were prepared from this tertiary amine as described above.

The electrical conductivities of solutions of the quaternary ammonium salts were determined in the manner and with the equipment previously described.[4]

Results and Discussion

The equivalent conductivities at 30° of 2-hydroxyethyldimethyl-, di-(2-hydroxyethyl)-meth-

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[4] Ralston, Hoerr and Hoffman, This Journal, **64**, 97 (1942).

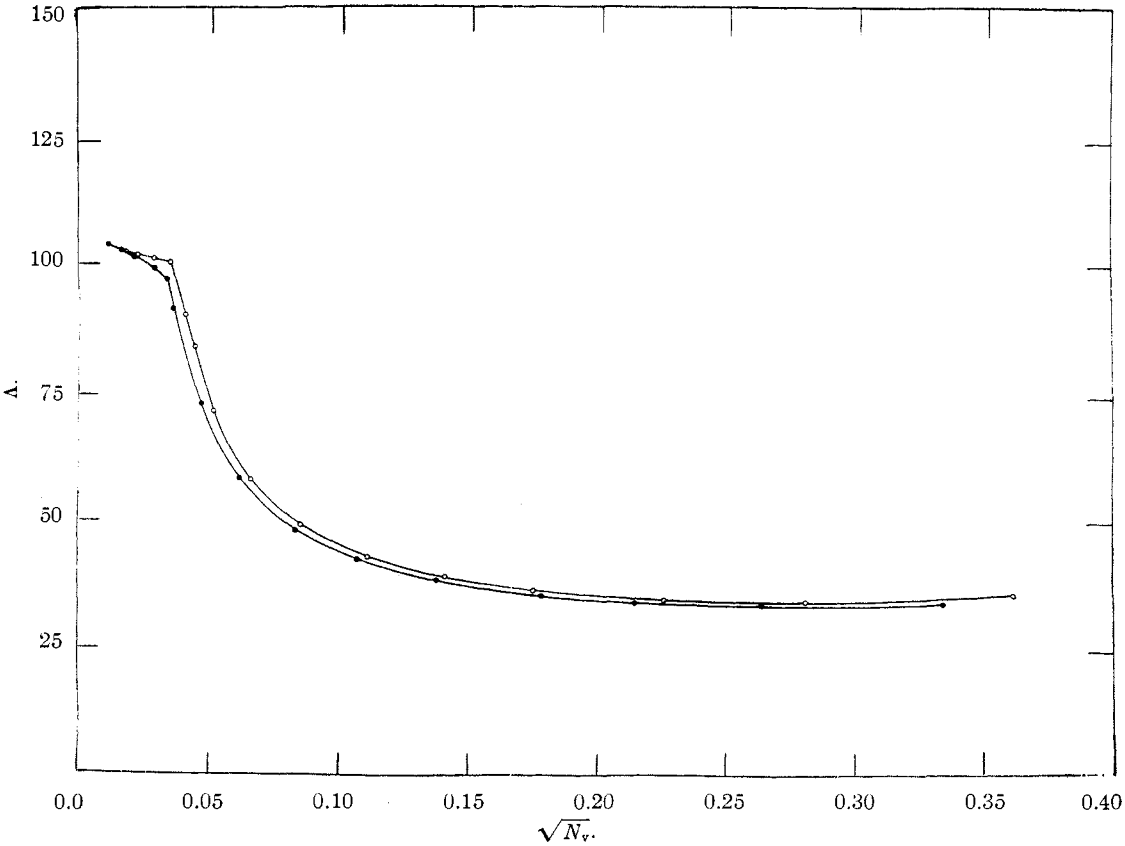

Fig. 3.—Equivalent conductivities of trimethylhexadecyl- and 2,3-dihydroxypropyldimethylhexadecylammonium chlorides: ●, trimethylhexadecylammonium chloride; ○, 2,3-dihydroxypropyldimethylhexadecylammonium chloride.

yl- and tri-(2-hydroxyethyl)-hexadecylammonium chlorides plotted against $\sqrt{N_v}$ are shown in Fig. 1. Figure 2 shows the equivalent conductivities at 30° of trimethylhexadecylammonium chloride and of trimethyloctadecylammonium chloride plotted against $\sqrt{N_v}$. A comparison of these two figures shows that although the addition of two carbon atoms to the long chain of the quaternary compound is attended by an appreciable reduction in the equivalent conductivities and by a shifting of the critical point toward a lower concentration, the progressive substitution of hydroxyethyl for methyl groups does not bring about a decided change in these values. Figure 3 shows the equivalent conductivity at 30° of 2,3-dihydroxypropyldimethylhexadecylammonium chloride compared to that of trimethylhexadecylammonium chloride. It is evident that the substitution of a 2,3-dihydroxypropyl group for a methyl group is not attended by a significant change in either the equivalent conductivity or the concentration at the critical point. Table I contains a comparison of certain of the data shown in Figs. 1, 2 and 3.

TABLE I

CONDUCTIVITY DATA AT 30° OF ALKYL- AND HYDROXYALKYLAMMONIUM CHLORIDES

Quaternary chloride	Λ_0	$\Lambda_{\text{crit.}}$	$\Lambda_{0.09}$	N_v at crit. concn.
Trimethylhexadecyl	104	100	34	0.0013
2-Hydroxyethyldimethylhexadecyl	109	102	33	.0012
Di-(2-hydroxyethyl)-methylhexadecyl	105	102	32	.0010
Tri-(2-hydroxyethyl)-hexadecyl	106	100.5	33	.0010
2,3-Dihydroxypropyldimethylhexadecyl	106	98	33	.0016
Trimethyloctadecyl	102	97	29	.0004

Acknowledgment.—The authors wish to express their appreciation to Mr. E. F. Binkerd for the preparation of the drawings.

Summary

1. The equivalent conductivities of trimethyl-, 2-hydroxyethyldimethyl-, di-(2-hydroxyethyl)-methyl-, tri-(2-hydroxyethyl)- and 2,3-dihydroxypropyldimethylammonium chlorides and of trimethyloctadecylammonium chloride have been compared.

2. The substitution of hydroxyethyl for methyl groups does not materially change the conductivities or the concentration of electrolyte at the critical point for micelle formation.

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