[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

The Electrical Behavior of Hexyl- and Dodecylammonium Chlorides in Various Dilutions of Aqueous Ethanol

BY A. W. RALSTON AND C. W. HOERR

In a previous article[1] it has been shown that the solubility of a typical cationic electrolyte, dodecylammonium chloride, in mixtures of ethanol and water exhibits a distinct maximum dependent upon both the composition of the solvent and the temperature. That this is a manifestation of a colloidal phenomenon was shown by the fact that hexylammonium chloride possesses a normal solubility behavior in all compositions of ethanol and water. This present paper discusses the electrical conductivity of solutions of these two amine salts in various compositions of aqueous ethanol and presents an interpretation of their behavior based upon the micelle theory.

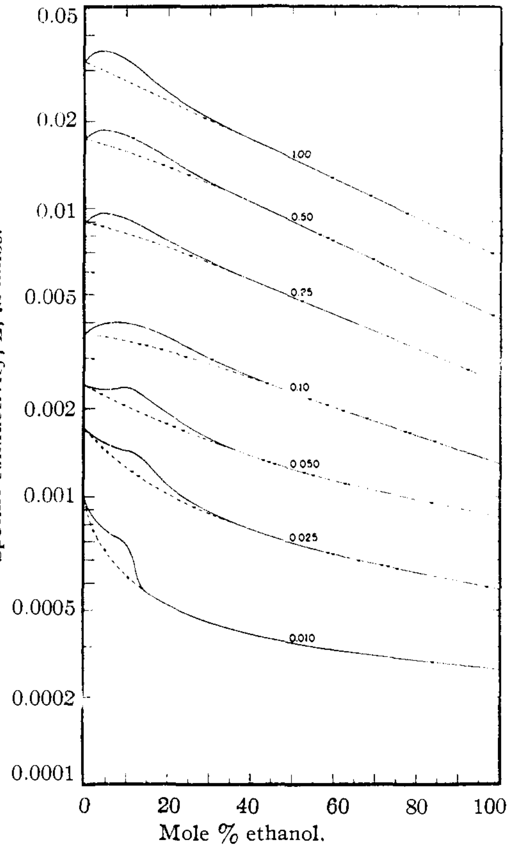

Fig. 1.—Variation of specific conductivity of dodecylammonium chloride at 30.0° with increased ethanol content of solutions. The numbers on the curves refer to the molarity of the amine salt.

Experimental

The hexyl- and dodecylammonium chlorides employed in this investigation were those used in the previous solubility measurements.[1] The aqueous ethanol solutions were prepared by diluting pure absolute ethanol with freshly distilled conductivity water. The compositions of these solvents were determined accurately by comparison of their densities with those reported in the "International Critical Tables." The amine salt solutions were prepared by diluting weighed portions of amine salt in calibrated volumetric flasks.

The electrical conductivities were determined in the manner and with the equipment described previously,[2a] as were the transference numbers.[2b]

Results

Table I shows the specific conductivities of solutions of dodecylammonium chloride at 30° as a function of the molarity in various dilutions of aqueous ethanol.

TABLE I

SPECIFIC CONDUCTIVITIES[a] OF DODECYLAMMONIUM CHLORIDE IN AQUEOUS ETHANOL AT 30.0°

Mole % ethanol	Molarity[b] of amine salt. $L \times 10^4$						
	0.001	0.005	0.01	0.05	0.1	0.5	1.0
0.00	1.22	5.38	10.10	24.0	37.7	170	320
4.17	1.09	4.28	7.72	23.1	39.2	185	350
8.80	..	3.85	6.97	23.4	40.0	176	322
14.37	..	2.72	4.68	20.9	36.8	164	291
20.68	..	2.25	4.19	19.6	35.0	146	244
28.12	..	2.06	3.75	16.5	31.7	125	211
47.68	..	1.79	3.16	12.9	23.4	95.1	156
61.05	..	1.67	2.87	11.2	19.9	75.0	124
100.0	..	1.46	2.49	8.6	12.5	41.5	...

[a] For the sake of brevity, the experimental values were plotted on large scale logarithmic paper from which these values have been obtained. The accuracy of the tabulated results approximates that of the experimental conditions. [b] The critical concentrations of dodecylammonium chloride in these solvents, as based upon change of specific conductivity with concentration, are as follows: in pure water, 0.0129 molar; in 4.17 mole % ethanol, 0.0138 molar; in 8.80 mole % ethanol, 0.0152 molar; in 14.37 mole % ethanol, 0.021 molar; in 20.68 mole % ethanol, 0.043 molar; in 28.12 mole % ethanol, 0.103 molar.

The values recorded in Table I show quite clearly that the critical point for micelle formation is shifted toward higher concentration with increase in the alcoholic content of the solvent. While the addition of alcohol lowers the specific conductivities at all concentrations *below* the critical concentration for micelle formation, the specific conductivities of the more concentrated solutions are actually increased by the addition of small amounts of alcohol. This effect is so marked that a plot of the values recorded in Table I shows that the conductivity curves for this electrolyte in solvents containing less than 14.37 mole % of ethanol cross those in pure water in the higher concentration ranges. Figure 1 illustrates the effect of increasing ethanol con-

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(1) Ralston and Hoerr, THIS JOURNAL, **68**, 851 (1946).

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

(2b) Hoerr and Ralston, *ibid.*, **65**, 976 (1943).

tent of the solvent upon the specific conductivities at 30° of various concentrations of dodecylammonium chloride. It will be noted that at all concentrations of electrolyte investigated the addition of small amounts of ethanol results in specific conductivities higher than the expected values and that at the high concentrations of electrolyte the curves exhibit maximum values. These maxima shift toward lower alcoholic content of the solvent with increasing concentration of electrolyte.

The equivalent conductivities of solutions of dodecylammonium chloride in solvents varying from pure water to pure ethanol are shown in Fig. 2. These curves illustrate several interesting observations relative to the behavior of this colloidal electrolyte in aqueous ethanol. In pure water dodecylammonium chloride shows the conductivity behavior of a typical colloidal electrolyte,[3-5] the equivalent conductivity first falling linearly with increase in concentration to a certain critical point after which it falls quite abruptly and finally remains essentially constant. In pure ethanol, on the other hand, the equivalent conductivity falls along a smooth curve with concentration, there being no abrupt change of slope. The conductivity behavior of this electrolyte in those solvents intermediate between pure water and pure ethanol is highly significant. It would normally be anticipated that the addition of alcohol to the solvent would result in lowered conductivities at all concentrations of electrolyte and that the resulting curves would be intermediate between those of pure water and of pure ethanol. This is decidedly not the case since an abnormal behavior is observed in those solvents which contain small percentages of alcohol and this behavior persists up to relatively high alcoholic concentrations.

The progressive addition of alcohol to the solvent results in a shifting of the critical point toward a higher concentration of electrolyte. This shift, which is at first slight, is quite abrupt between 14.37 and 20.68 mole per cent. of alcohol, the concentration of electrolyte almost doubling in going from the former to the latter. Micelle formation is evidenced even in those solvents which contain relatively high percentages of alcohol, an abrupt change of slope occurring at 0.10 molar in a solvent containing 28.12 mole per cent. of alcohol. The downward slope of the curves after the critical point is much reduced by the addition of small amounts of alcohol and this effect is so pronounced that the curves for the solutions in 4.17 and 8.80 mole per cent. of alcohol lie above those for pure water over an appreciable range of concentration. In order to evaluate this behavior it is necessary to compare it with that of a structurally similar compound which functions

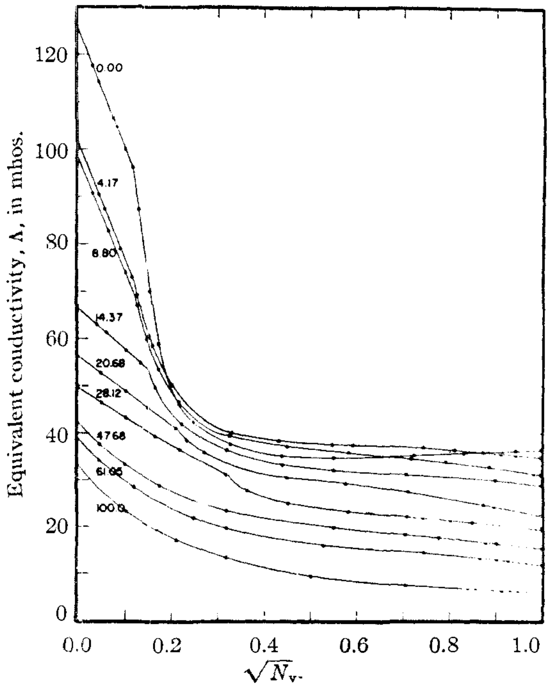

Fig. 2.—Equivalent conductivity of dodecylammonium chloride in various concentrations of ethanol at 30.0°. The numbers on the curves refer to the mole per cent. of ethanol in the solvent.

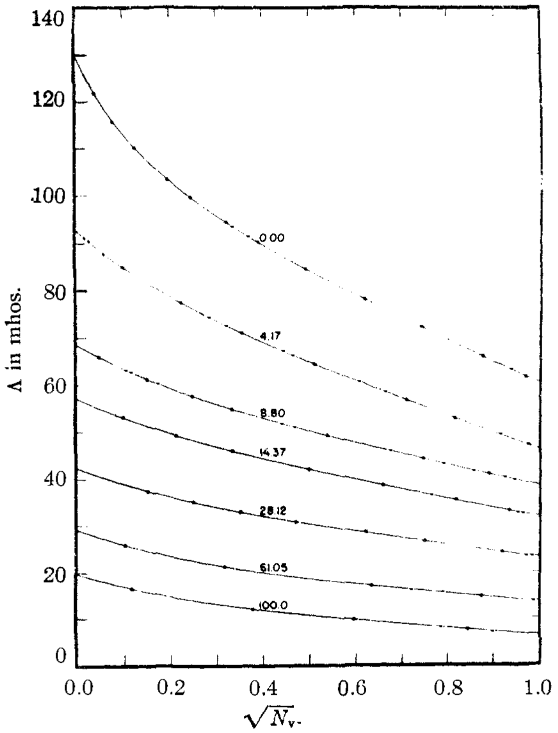

Fig. 3.—Equivalent conductivity of hexylammonium chloride in various concentrations of ethanol at 30.0°. The numbers on the curves refer to the mole per cent. of ethanol in the solvent.

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(3) McBain, Laing and Titley, *J. Chem. Soc.*, **115**, 1279 (1919).

(4) McBain and Betz, THIS JOURNAL, **57**, 1905 (1935).

(5) Ralston and Hoerr, *ibid.*, **64**, 772 (1942).

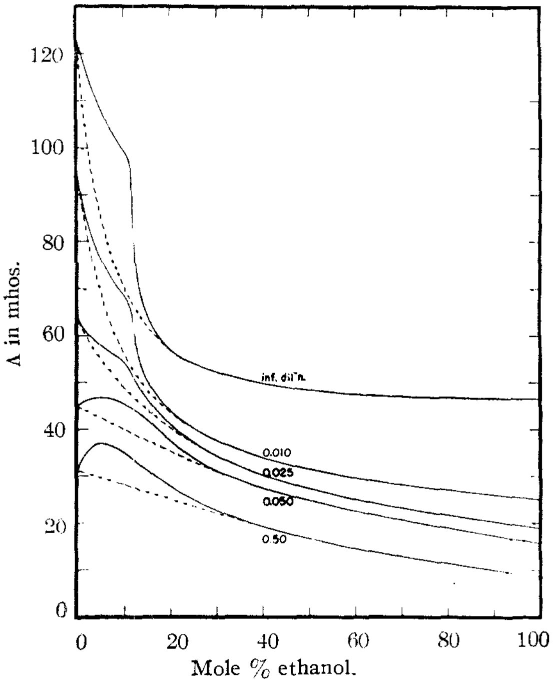

Fig. 4.—Variation of equivalent conductivity of dodecylammonium chloride at 30.0° with increased ethanol content of the solvent. The numbers on the curves refer to the molarity of the amine salt.

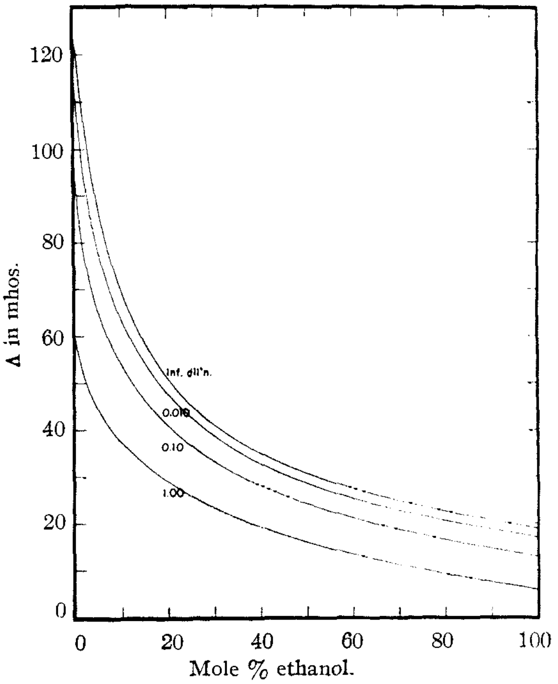

Fig. 5.—Variation of equivalent conductivity of hexylammonium chloride at 30.0° with increased ethanol content of the solvent. The numbers on the curves refer to the molarity of the amine salt.

as an ordinary uni-univalent electrolyte. Since the conductivity behavior of aqueous solutions of hexylammonium chloride has been shown[5-7] to be that of an ordinary electrolyte, its electrical behavior in aqueous ethanol was investigated. Figure 3 plots the equivalent conductivities of solutions of hexylammonium chloride in solvents varying from pure water to pure ethanol. It will be noted that these curves contain none of the irregularities shown by those of the higher homolog. Figures 4 and 5 show the effect of the addition of alcohol upon the equivalent conductivities at 30° of various concentrations of dodecylammonium chloride and of hexylammonium chloride, respectively. The dissimilarity in the effect of the alcohol upon solutions of these two electrolytes is clearly evidenced. The addition of alcohol to solutions of hexylammonium chloride is attended by an abrupt drop in equivalent conductivity, the effect being most pronounced at the lower concentrations of alcohol and electrolyte. With dodecylammonium chloride, for concentrations of electrolyte between 0.025 and 0.50 molar the equivalent conductivity rises upon the addition of alcohol, the curves exhibiting a maximum in the vicinity of four mole per cent. of alcohol and then slowly falling, as shown in Fig. 4. At lower concentrations of this electrolyte the addition of alcohol lowers the equivalent conductivity, the maximum effect being observed between 10 and 15 mole per cent. of alcohol. The curves exhibit a marked change of slope in the neighborhood of 10 mole per cent. of alcohol and another at approximately 15 mole per cent. of alcohol. Since the two salts investigated are representative of a colloidal electrolyte and a uni-univalent electrolyte it follows that the peculiar electrical behavior of the former in aqueous ethanol must be associated with its colloidal properties.

The addition of alcohol to solutions of dodecylammonium chloride results in a lowering of the cationic transference numbers at the concentrations of amine salt investigated, namely, 0.1 and 0.3 molar, as shown by the values recorded in Table II.

TABLE II

CATIONIC TRANSFERENCE NUMBERS OF DODECYLAMMONIUM CHLORIDE IN AQUEOUS ETHANOL AT 30.0°

Molarity of amine salt	t at mole % of ethanol			
	0.00[2a]	8.80	28.12	61.05
0.013	0.310	...	...	...
.024	.850	...	...	...
.10	.872	0.515	0.200	0.130
.30	.870	.515	.270	.105
.52	.855	...	...	...

This phenomenon probably results from several factors which will be subsequently discussed.

Discussion

It is generally accepted that many of the physical properties of aqueous solutions of polar molecules which contain long chain ions are de-

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(6) Paquette, Lingafelter and Tartar, THIS JOURNAL, 65, 686 (1943).

(7) Scott and Tartar, *ibid.*, 65, 692 (1943).

pendent upon the presence of associated particles. The exact nature of these particles is, however, somewhat controversial. The contention of McBain and others[8–11] has been that at least two types of micelles exist, an associated ion, or ionic micelle, which is highly ionic and spherical in shape, and an associated molecule, or lamellar micelle, which is feebly ionic. The former may exist in quite dilute solutions while the latter exists in conjunction with the former in the more concentrated solutions. Hartley and others,[12,13] on the other hand, maintain that only one type of particle is present, an associated ion to which are attached a number of oppositely charged ions, termed gegen ions. This particle is formed at a certain critical concentration below which the solute acts as an ordinary electrolyte. Most investigators agree that these associated particles must be highly hydrated and that this bound water constitutes an integral part of the micelle. Since the associated particle must be in equilibrium with its surroundings, it can be assumed that such particles possess varying degrees of hydration depending upon their external environment. It can further be postulated that some bound water is a necessary prerequisite for the formation and continued existence of either associated ions or molecules of colloidal electrolytes.

The addition of alcohol to an aqueous solution of an electrolyte normally results in a lowering of the conductivity since the resulting solvent is a poorer ionizing medium. That this occurs with those ammonium salts which function as uni-univalent electrolytes is shown in Figs. 3 and 5. The abnormal effects observed upon the addition of alcohol to aqueous solutions of dodecylammonium chloride (Fig. 4) must, therefore, involve the micelles.

In discussing the effect of alcohol upon the conductivities and transference numbers of solutions of colloidal electrolytes it is necessary to realize that the observations are the result of several factors. These involve not only the change in composition of the micelles, but also the equilibrium between free ions, ionic micelles and lamellar micelles brought about by the increased solvent power of the solvent for the hydrocarbon chains. Attending these effects is the decreased ionization of the simple molecules due to the lowering of the dielectric constant of the solvent. All of these influences will manifest themselves in a departure from the electrical properties observed when water alone is the solvent.

That the increased solvent power of the alcohol for the hydrocarbon portion of the molecule is antagonistic to micelle formation is shown by the shift in critical concentrations as evidenced by the change of slopes of the equivalent conductivity curves (Figs. 2 and 6). The addition of small amounts of alcohol shifts the critical point to higher concentrations and large amounts of alcohol (above 28.12 mole per cent.) completely inhibit micelle formation. These findings are in agreement with those of Ward[14] who observed that micelles are not formed in solutions of sodium dodecyl sulfate containing 40 or more per cent. of ethanol. Since the presence of alcohol is antagonistic to micelle formation as evidenced by its influence on the critical concentration it is reasonable to assume that it also influences the equilibrium between lamellar micelles, ionic micelles and simple ions. The addition of alcohol to concentrated solutions of dodecylammonium chloride brings about an increase in both specific and equivalent conductances, one of the contributing factors to such an increase being a shift in the equilibrium toward ionic micelles and simple ions. Although the conductivity values fall upon the addition of alcohol to dilute solutions of dodecylammonium chloride (Figs. 2 and 4) the initial drop is not as abrupt as with solutions of hexylammonium chloride (Fig. 5). Since fewer micelles are present in the dilute solutions it is evident that the shift in equilibrium is not sufficient to overcome the reduced ionizing power of the solvent. The abnormal behavior of very dilute solutions of dodecylammonium chloride upon the addition of alcohol shows that associated particles must be present in solutions containing less than the critical concentration of electrolyte. In such solutions we have, therefore, an equilibrium between simple ions and ionic micelles as originally postulated by McBain.[15]

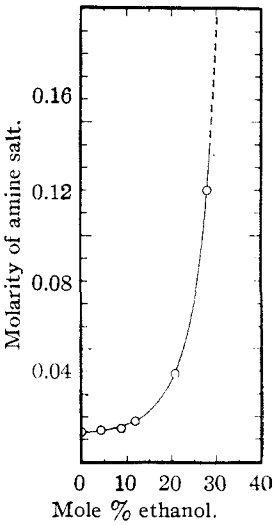

Fig. 6.—Variation of critical concentration for micelle formation with increased ethanol content of the solvent.

The above considerations adequately explain the drop in cationic transference numbers upon the addition of alcohol to aqueous solutions of dodecylammonium chloride. A shift in the equilibrium toward free ions, at any concentration of this solute, would be attended by a drop in the cationic transference number.

While a shift in the equilibrium between free

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[8] McBain and Jenkins, *J. Chem. Soc.*, **121**, 2325 (1922).

[9] McBain and McBain, *Proc. Roy. Soc.* (London), **139A**, 26 (1933).

[10] Hess and Gundermann, *Ber.*, **70B**, 1800 (1937).

[11] Hess, Philippoff and Kiessig, *Kolloid Z.*, **88**, 40 (1939).

[12] Hartley, "Aqueous Solutions of Paraffin-Chain Salts," Hermann et Cie., Paris, 1936.

[13] Reychler, *Kolloid Z.*, **12**, 277 (1913).

[14] Ward, *Proc. Roy. Soc.* (London), **A176**, 412 (1940).

[15] McBain, *Trans. Faraday Soc.*, **9**, 99 (1913).

ions, ionic micelles and lamellar micelles explains much of our data it is believed that the addition of alcohol is accompanied by other effects which contribute to the observed values. Prominent among these effects is the decreased hydration of the micelles occasioned by the lowered partial pressure of the water in the solvent. Since the bound water contained in both the ionic and lamellar micelles must be in equilibrium with the free water in the solvent, a lowering of the partial pressure of the latter will be attended by a loss of water from the micelles. This loss of water will result in increased mobilities which, in the case of ionic particles, will manifest itself in increased conductivities. Such an effect may contribute to the increased conductivities which result upon the addition of alcohol to concentrated aqueous solutions of dodecylammonium chloride and to the abnormal behavior of the more dilute solutions upon such additions. The lowered cationic transference values, however, indicate that this effect is not determinative as regards the general properties of the system.

That the composition of the lamellar micelle is influenced by external factors has been shown recently by Ross and McBain[16] who observed marked increases in the long spacings of hexanolamine oleate upon dilution as shown by X-rays, their results thus confirming those previously reported upon soap solutions.[17] Contemporaneously with this work Harkins, Mattoon and Corrin[18] published an extensive investigation of the structure of soap micelles as shown by X-rays. Their results also confirmed that the long spacing is a function of the concentration, the spacing increasing materially upon lowering the concentration. It has been observed that the addition of salt to a solution of a colloidal electrolyte brings about a decrease in the specific conductivity attributable to the colloidal electrolyte and is also attended by a shift in the critical point toward a *lower* concentration.[19] Such observations are, however, not antagonistic to our findings since the addition of salt is undoubtedly attended by a decrease in hydration of the micelles. On the other hand, the presence of an electrolyte and the common ion effect must greatly reduce ionization and favor the formation of associated molecules as evidenced by the shift in critical concentration.

Summary

The electrical behavior of hexyl- and dodecylammonium chlorides in pure water, pure ethanol and in various concentrations of aqueous ethanol has been studied.

The addition of ethanol to aqueous solutions of hexylammonium chloride lowers the conductivities at all concentrations investigated. The conductivities of concentrated solutions of dodecylammonium chloride are increased by the addition of small amounts of alcohol. The addition of alcohol to more dilute aqueous solutions of this salt is accompanied by an irregular decrease in the conductivities.

Micelle formation is completely inhibited by the addition of large amounts of alcohol to aqueous solutions of dodecylammonium chloride.

The difference in behavior of these two salts has been ascribed to micelle formation in solutions of dodecylammonium chloride. The behavior of these salts in such solvents has been discussed in the light of the present micelle theory

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[16] Ross and McBain. THIS JOURNAL, **68,** 296 (1946).

[17] References to this work are given by Ross and McBain.[16]

[18] Harkins. Mattoon and Corrin, *ibid.*, **69**, 220 (1946).

[19] Wright, Abbott, Sivertz and Tartar, *ibid.*, **61**, 549 (1939).

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[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Copolymerization of Vinyl Compounds with Dienes[1]

BY TURNER ALFREY, JR., A. I. GOLDBERG AND W. P. HOHENSTEIN

When two vinyl monomers (A and B) are polymerized together, the composition of the resulting copolymer has been shown theoretically and experimentally,[2] to be governed by a "copolymer composition equation" of the form

$$\frac{b}{a} = \frac{B}{A}\,\alpha\,\frac{\beta B + A}{\alpha B + A}$$

where b and a are the molar proportions of the respective monomer groups in the initial copolymer, B and A are the molar proportions of the monomers in the monomer mixture, and α and β are ratios of rate constants for chain propagation

$$\alpha = k_{ab}/k_{aa},\ \beta = k_{bb}/k_{ba}$$

In this investigation the copolymerization of styrene with chloroprene and dichlorostyrene with styrene has been studied.

Experimental

Monomers.—Styrene, Dow N99, was washed, dried and distilled *in vacuo*; 2,5-dichlorostyrene, Monsanto, was washed with dilute alkali, water, and dried over calcium chloride; chloroprene (2-chlorobutadiene-1,3), du Pont,

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[1] This paper is from the doctoral dissertation submitted by A. I. Goldberg to the Polytechnic Institute of Brooklyn and was presented in part at the Atlantic City Meeting of the American Chemical Society, April, 1946.

[2] (a) Alfrey and Goldfinger. *J. Chem. Phys.*, **12**, 205 (1944); (b) Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944); (c) Wall. *ibid.*, **66**, 2050 (1944); (d) Alfrey, Merz and Mark, *J. Polymer Research*, **1**, 37 (1946); (e) Lewis, Mayo and Hulse, THIS JOURNAL, **67**, 1701 (1945); (f) Alfrey and Harrison, *ibid.*, **68**, 299 (1946).