

8-hydroxyquinoline sulfate and 8-hydroxyquinoline sulfate a small amount of each of the solid substances was placed on the tongue. In the case of the first compound only a mild tingling sensation but no irritation was noted after twenty minutes. The 8-hydroxyquinoline sulfate proved to be so irritating that it had to be washed from the tongue within two minutes.

Summary

1. *o*-Amino-*p*-benzylphenol has been synthesized.

2. 5-Benzyl-8-hydroxyquinoline was prepared by a modified Skraup reaction. Bacteriological tests with the sulfate of 5-benzyl-8-hydroxyquinoline proved it to be as effective toward *B. coli* as 8-hydroxyquinoline sulfate and considerably more so than phenol. It is, moreover, considerably less irritating to mucous membrane than either of these substances.

ST. LOUIS, MO.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Mobility of the Hydrogen Ion Constituent in Aqueous Mixtures of Hydrogen Chloride and Calcium Chloride at 25°

BY L. G. LONGSWORTH¹

Introduction

The extension of the interionic attraction theory to the conductance of ternary ion mixtures has been made by Bennowitz, Wagner and K uchler² and Onsager and Fuoss.³ The theory indicates that, in an aqueous mixture of hydrogen chloride and calcium chloride, for example, at constant ionic strength, the conductance of the common ion constituent, chloride, deviates but little from the simple additive rule. In such a mixture, however, the mobility of the fast hydrogen ion constituent is less in the presence of the slow

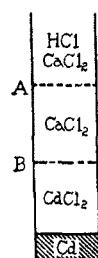


Fig. 1.

calcium ion than in a solution of pure hydrogen chloride at the same ionic strength while the mobility of the calcium ion is greater than in a solution of pure calcium chloride. Moreover the absolute decrease in the mobility of the fast ion is greater than the corresponding increase in that of the slow ion, so that the total conductance of the mixture is less than the value computed on the basis of additivity.

The experimental results which are reported in this paper show that the mobility of the hydrogen ion constituent in mixtures of hydrogen chloride and calcium chloride at a constant total concentration of 0.1 *N* decreases continuously with increasing calcium concentration, and has a value in a pure calcium chloride solution that is 6% less than in a hydrochloric acid solution of the

same ionic strength. Since the mathematical approximations which were made in the development of the theory become rather serious at the concentration at which the measurements were made, the theory can predict only the magnitude of the effect. The experimental results, however, afford an interesting qualitative confirmation of the theory.

The mobility of the hydrogen ion constituent in the mixtures was determined from a combination of conductance and transference measurements, the moving boundary method having been used for the latter. A comprehensive review of this method has been published by MacInnes and Longworth.⁴ In the application of this method to the cation constituents of the mixtures two boundaries are developed simultaneously, as is shown in Fig. 1, and move at different rates. The displacement of the leading boundary A measures directly the transference number of the hydrogen ion constituent in the mixture, while the motion of the second boundary B yields information concerning the concentration of a solution of pure calcium chloride that has been separated, by electrolysis, from the mixture originally placed in the graduated tube of the moving boundary cell. Although the data are not reported in this paper, the observed displacements of this second boundary deviated by less than 0.5%, on the average, from values that were computed with the aid of the theory developed by MacInnes and Longworth⁵ for the concentration changes on electrolysis in ternary ion mixtures.

(1) The experimental part of this work was completed while the author held a National Research Council Fellowship in Chemistry.

(2) Bennowitz, Wagner and K uchler, *Physik. Z.*, **30**, 623 (1929).

(3) Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(4) MacInnes and Longworth, *Chem. Rev.*, **11**, 171 (1932).

(5) See Ref. 4, p. 214.

Apparatus and Materials

The conductivity measurements were made on the bridge described by Shedlovsky⁶ and are based upon the value recorded in the "International Critical Tables"⁷ for 0.1 demal potassium chloride solution at 25°. The transference measurements were made in the moving boundary apparatus described by Longworth.⁸ Autogenic boundaries with a cadmium anode were used and the necessary volume corrections have been made. For the mixture in which $C_{\text{HCl}} = 0.025 N$, it was necessary to add a trace of methyl violet to the solution in order to make the leading boundary visible, but it has been shown that the minute amount of dye which is used does not measurably affect the results. No satisfactory indicator for the anion constituent of the mixtures has been found and it was impossible, therefore, to measure the transference number of this constituent as was done for the mixtures of hydrogen chloride and potassium chloride.⁹

The solutions were prepared in calibrated volumetric flasks by dilution, with conductivity water, of the required amounts of stock solutions of hydrogen chloride and calcium chloride. The concentrations are expressed in equivalents per liter of solution at 25°. The stock solution of hydrogen chloride was the constant boiling acid prepared as directed by Foulk and Hollingsworth.¹⁰ The stock solution of calcium chloride was prepared from a salt whose purification is described elsewhere.¹¹ The concentration of this stock solution was determined by gravimetric analysis, the following values being recorded for the ratio of the weight of solution taken to that of silver chloride obtained: 1.6966, 1.6969, 1.6964. The conductances of the solutions of the pure salts are in good agreement with the values reported by Shedlovsky¹² and Shedlovsky and Brown.¹³

The Hydrogen Ion Conductance in the Mixtures.—Values of the data necessary for the computation of the equivalent conductances, $\Lambda_{\text{H}}^{\text{H}-\text{Ca}}$, of the hydrogen ion constituent in the calcium chloride, hydrogen chloride mixtures are recorded in Table I, in which are given, in order, the concentrations of hydrogen chloride and calcium chloride, the measured equivalent con-

TABLE I

HYDROGEN ION CONDUCTANCE IN HCl-CaCl₂ MIXTURES

C_{HCl}	C_{CaCl_2}	Λ	T_{H}	$\Lambda_{\text{H}}^{\text{H}-\text{Ca}}$
0.1000	0.0000	391.3	0.8314	325.3
.0750	.0250	316.3	.7619	321.3
.0500	.0500	242.8	.6518	316.5
.0250	.0750	171.5	.4537	311.2
.0000	.1000	102.6	.0000	305.2 ^a

^a Extrapolated.(6) Shedlovsky, *THIS JOURNAL*, **52**, 1793 (1930).

(7) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. VI, p. 230.

(8) Longworth, *THIS JOURNAL*, **54**, 2741 (1932).(9) Longworth, *ibid.*, **52**, 1897 (1930).(10) Foulk and Hollingsworth, *ibid.*, **45**, 1220 (1923).(11) Longworth, *ibid.*, **57**, 1185 (1935).(12) Shedlovsky, *ibid.*, **54**, 1411 (1932).(13) Shedlovsky and Brown, *ibid.*, **56**, 1066 (1934).

ductances of the mixtures and the observed values of the transference numbers. The last column contains the value of $\Lambda_{\text{H}}^{\text{H}-\text{Ca}}$ as given by the relation

$$\Lambda_{\text{H}}^{\text{H}-\text{Ca}} = \frac{T_{\text{H}} \Lambda}{C_{\text{HCl}} / (C_{\text{HCl}} + C_{\text{CaCl}_2})}$$

In Fig. 2 these values of $\Lambda_{\text{H}}^{\text{H}-\text{Ca}}$ have been plotted as ordinates against the ratio $C_{\text{CaCl}_2} / (C_{\text{HCl}} + C_{\text{CaCl}_2})$ as abscissas. The curve of this figure extrapolates to a value of 305.2 for the equivalent conductance of vanishingly small

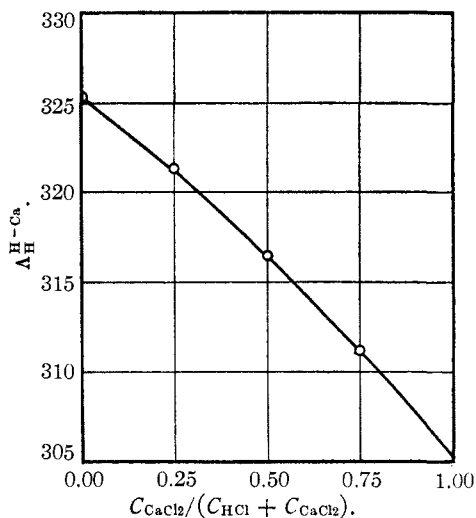


Fig. 2.—The equivalent conductance of the hydrogen ion constituent in aqueous mixtures of hydrogen chloride and calcium chloride at 25° and at a constant total concentration of 0.1 normal.

quantities of hydrogen ion in 0.1 *N* calcium chloride. The ionic strength, μ , of 0.1 *N* calcium chloride is 0.15 and the hydrogen ion conductance in a solution of pure hydrogen chloride of this ionic strength is 321.3. Hence the conductance of this constituent of the mixtures has been decreased 16.1 units in passing from a solution of hydrogen chloride to one of calcium chloride at a constant ionic strength of 0.15, that is

$$(\Lambda_{\text{H}}^{\text{HCl}} - \Lambda_{\text{H}}^{\text{CaCl}_2})_{\mu=0.15} = \Delta \Lambda_{\text{H}}^{\text{H}-\text{Ca}} (\text{obsd.}) = 16.1$$

From the equations derived by Bennewitz, Wagner and K uchler² on the basis of the interionic attraction theory the following value for this difference may be computed

$$\Delta \Lambda_{\text{H}}^{\text{H}-\text{Ca}} (\text{calcd.}) = 36.50$$

This computation involves, in addition to certain universal constants, the temperature, and the dielectric constant and viscosity of water, the limiting mobilities of the three ion constituents of

the mixture. The following values were used in this computation, $\Lambda_{Ca}^{\circ} = 59.48$, $\Lambda_{Cl}^{\circ} = 76.32$ and $\Lambda_{H}^{\circ} = 349.72$.¹⁴ The formulas which have been used in this computation are limiting laws, strictly valid only at very low concentrations. As suggested in the introduction values computed for an ionic strength of 0.15 can consequently indicate little more than the order of magnitude of the effect.

The following comparison of the results presented in this paper with those for mixtures of hydrogen chloride and potassium chloride⁹ may possibly be significant. For the latter mixtures, also at a total concentration of 0.1 normal, the observed decrease of the equivalent conductance of the hydrogen ion constituent in passing from a solution of hydrogen chloride to one of potassium chloride is $\Delta\Lambda_{H}^{H-K}$ (obsd.) = 10.96 and the corresponding computed value is $\Delta\Lambda_{H}^{H-K}$ (calcd.) = 24.79, giving 0.442 as the ratio of the observed to the computed value. The value of the corresponding ratio for the mixtures of hydrogen chloride and calcium chloride is 0.441. The agreement between these two ratios may indicate that the same phenomena which produce devia-

tions from the limiting equations are operative in the two cases.

I am glad to acknowledge my indebtedness to Dr. D. A. MacInnes for constructive criticism and to Dr. Theodore Shedlovsky for placing the conductivity bridge at my disposal during the course of the measurements.

Summary

The transference numbers of the hydrogen ion constituent in aqueous mixtures of hydrogen chloride and calcium chloride at a constant total concentration of 0.1 normal have been measured at 25°. The conductances of the same mixtures have also been determined and from a combination of these data with the transference numbers the mobility of the hydrogen ion constituent in each of the mixtures has been computed. The observed decrease in the mobility of this constituent in passing from the solution of pure hydrogen chloride to one of pure calcium chloride has been compared with the value computed from the interionic attraction theory of electrolytic conductance and also with a similar effect that was observed in mixtures of hydrogen chloride and potassium chloride.

(14) MacInnes, Shedlovsky and Longworth, *ibid.*, **54**, 2758 (1932).

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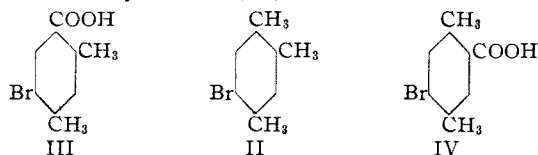
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Xylic Acids Obtained in the Oxidation of 5-Bromo and 5-Nitropseudocumene

BY C. HAROLD FISHER AND CHEVES T. WALLING

It has been reported¹ that the compound (I, m. p. 172–173°) produced in the oxidation of 5-bromopseudocumene (II) is 5-bromo-2,4-xylic acid (III). This oxidation has been repeated, and it was shown by direct comparison that the product (I) is not 5-bromo-2,4-xylic acid.²

A further study of this oxidation has indicated that the melting point of the oxidation acid (I) may be raised to 173–174° by prolonged purification, and that this substance is a sharply-melting mixture of 5-bromo-2,4-xylic acid (III) and 4-bromo-2,5-xylic acid (IV).



(1) Sussenguth, *Ann.*, **215**, 244 (1882).

(2) Fisher and Grant, *THIS JOURNAL*, **57**, 718 (1935).

Separation of the oxidation product (I) into its components (III and IV) could not be effected by numerous crystallizations, and an identical substance was prepared by crystallizing a mixture of equal amounts of III and IV.

Both bromoxylic acids (III and IV) were synthesized for comparison by methods that leave no doubt as to their structures. At the beginning of this work it was expected that I would be identical with 4-bromo-2,5-xylic acid, since the methyl group para to the bromine atom is attacked preponderantly in the oxidation³ of 4-bromo-*o*-xylene.

The oxidation of 5-nitropseudocumene has been claimed⁴ to give 5-nitro-2,4-xylic acid, but no proof of structure was offered. The oxidation of a compound having ortho, meta and para

(3) Keuning and Evenhuis, *Rec. trav. chim.*, **54**, 73 (1935).

(4) Schaper, *Chem. Centr.*, **39**, 837 (1868).