gate was concentrated to a sirup under reduced pressure. This sirup (67 mg.) was treated with 1 cc. of concentrated hydrochloric acid (d. 1.19) and some insoluble material removed by filtration. The filtrate was stirred at 0° for one hour with 1 cc. of ethyl mercaptan, whereupon the solution was neutralized with concentrated ammonium hydroxide, concentrated to dryness under reduced pressure and the dried residue was acetylated for twenty-four hours with acetic anhydride and pyridine (2:1). The acetylation mixture was poured into water, the water extracted with chloroform and the extract washed with 5% hydrochloric acid to remove the pyridine, then with aqueous sodium bicarbonate and water. On solvent removal from the dried chloroform solution there was obtained 10 mg. of a sirupy product that could not be brought to crystallization.

Hydrolytic Characteristics.—Crystalline barium acid heparinate (*c*, 0.25 g. per 100 cc. soln.) was hydrolyzed under reflux with 4 *N* hydrochloric acid and the rate of hydrolysis was followed in several ways. The data obtained are diagrammed in Fig. 1. The hexosamine liberation data (Curve A) have been reported previously[2] but are included for comparative purposes. They were obtained on the sodium salt (*c*, 0.8) purified through the crystalline barium acid salt. The hexuronic acid destruction (Curve B) was followed by placing the solution (*c*, 1.5) in the uronic acid assay apparatus of Burkhart, Baur and Link[7] and weighing the carbon dioxide evolved at the various time intervals. The sulfate liberated (Curve C) was determined in a separate portion to which an excess of barium acetate had been added. The anticoagulant activity (Curve D) was determined essentially according to the procedure of Foster[8] on portions of the solution that had been carefully neutralized with 2 *N* sodium carbonate and maintained at 0° until the activity was determined. The initial activity of the material used was 500 Roche ACU per mg. The reducing sugar liberated (Curve E) was determined on neutralized (by 2 *N* sodium carbonate) portions according to the method of Hagedorn and Jensen.[9] The polarimetric data (Curve F) were obtained on the neutral sodium salt, purified through the crystalline barium acid salt, employing a concentration of 1.5 g. per 100 cc. of solution.

Attempts to isolate a uronic acid by interrupting the reaction at the point of maximum reduction were without success.

We are pleased to acknowledge the advice of Dr. H. M. Wuest, director of research of Hoffmann-La Roche, Inc. We are indebted to Dr. W. H. McNeely of this Laboratory for the bioassays and for his interest and counsel.

Summary

1. The general behavior of the heparin molecule on undergoing complete acid hydrolysis has been ascertained by following the time rate of change in rotation, reducing value, free sulfate, D-glucosamine, anticoagulant activity and uronic acid destruction.

2. No other sugar derivatives than D-glucosamine and a uronic acid (not isolated) were found on hydrolysis.

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[7] B. Burkhart, L. Baur and K. P. Link, *J. Biol. Chem.*, **104**, 171 (1934).

[8] R. H. K. Foster, *J. Lab. Clin. Med.*, **27**, 820 (1942).

[9] H. C. Hagedorn and B. N. Jensen, *Biochem. Z.*, **135**, 46 (1923).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

The Conductance of Non-aqueous Solutions of Magnesium and Calcium Perchlorates[1]

BY PIERRE VAN RYSSELBERGHE AND ROBERT M. FRISTROM

The conductance data reported in the present paper were obtained in the course of the general investigation on organic solutions of metallic salts, particularly of the alkaline earth perchlorates, which is being carried out in this Laboratory. The conductances of solutions of magnesium perchlorate in *n*-propyl and isopropyl alcohols were recently reported by Van Rysselberghe and Hunt.[2] We are now presenting the conductances of the same salt in acetone, methyl alcohol and nitromethane. Since the only data on conductances of organic solutions of alkaline earth perchlorates in the literature preceding our work are the conductances of dilute solutions of barium perchlorate in acetone, measured by Walden, Ulich and Busch,[3] we have turned our attention to calcium perchlorate, and are, therefore, able to compare the conductances of the perchlorates of three alkaline earth ions, magnesium, calcium, and barium in the same solvent, acetone.

Experimental

Salts.—Most of the magnesium perchlorate used was prepared and dehydrated according to the methods previously described.[2] Some portions of this salt and all of the calcium perchlorate were dehydrated in a vacuum oven of the Abderhalden type using the vapor of boiling nitrobenzene as a source of heat. The calcium perchlorate was prepared from C. P. calcium oxide and perchloric acid. The purity of both perchlorates was checked by analysis.

Solvents.—High-grade solvents were used: Merck C. P. acetone had, without additional purification, the correct boiling point and a conductivity in close agreement with the value given by Scudder[4]; J. T. Baker C. P. methyl alcohol was refluxed over calcium oxide and fractionated, the final product having, again, a conductivity in close agreement with Scudder's value[4]; Eastman Kodak Co. white label nitromethane was treated with sodium amalgam and calcium oxide, then fractionated, the final product having the correct boiling point but a conductivity somewhat higher than Scudder's value.[4] Corrections for solvent conductivity were made whenever necessary.

Conductivity Bridge, Conductivity Cells, Temperature Control, Preparation of Solutions.—The equipment used was the same as that previously described.[2] Conductiv-

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[1] Based in part upon a thesis submitted by Robert M. Fristrom in partial fulfillment of the requirements for the M.A. degree at the University of Oregon, August, 1944.

[2] P. Van Rysselberghe and G. J. Hunt, THIS JOURNAL, **66**, 1488 (1944).

[3] P. Walden, H. Ulich and G. Busch, *Z. physik. Chem.*, **123**, 429 (1926). Data available in W. A. Roth and K. Scheel, Landolt-Börnstein, "Physikalisch-chemische Tabellen," Erster Ergänzungsband, 1927, p. 636.

[4] H. Scudder, "The Electrical Conductivity and Ionization Constants of Organic Compounds," D. Van Nostrand Co., New York, N. Y., 1914.

ity cells of the Jones type but of smaller capacity than the Leeds and Northrup Co. ones and a Shedlovsky flask permitting gradual dilution of the solutions without removal from the cell were used in the measurements reported in this paper. The temperature control of our oil thermostat was narrowed down to 25 ± 0.002°.

Results

In Tables I, II, and III we give, for 25°, the specific and equivalent conductances of magnesium perchlorate in acetone, methyl alcohol and nitromethane, respectively. In Table IV we give, for 25°, the specific and equivalent conductances of calcium perchlorate in acetone. The limiting equivalent conductances reported in the first lines of the tables were obtained by extrapolations of plots of equivalent conductance against the square root of the equivalent concentration. In all cases the Kohlrausch type of behavior holds in the range of very low concentrations.

TABLE I

CONDUCTANCE OF SOLUTIONS OF MAGNESIUM PERCHLORATE IN ACETONE AT 25°

Concn. equiv. per liter	Sp. cond., mhos × 10^4	Equivalent conductance
0.0000000	0.0000	185.5
.0004520	.6127	135.6
.0004958	.6594	133.0
.0005498	.7162	130.3
.0006168	.7844	127.2
.0007024	.8698	123.9
.0008156	.9805	120.2
.0009728	1.132	116.4
.001205	1.335	110.8
.001581	1.661	105.0
.002088	2.044	97.90
.002278	2.183	95.85
.002500	2.351	94.05
.002778	2.546	91.65
.003124	2.797	89.50
.003572	3.109	87.05
.004164	3.509	84.26
.004222	3.522	83.44
.004998	4.058	81.15
.006248	4.831	77.32
.008332	6.055	72.68
.01250	8.264	66.12
.02542	13.28	52.24
.05798	20.84	35.94
.1407	37.00	26.30
.3732	84.02	22.52
.6538	117.2	17.93
1.553	195.2	12.57

TABLE II

CONDUCTANCE OF SOLUTIONS OF MAGNESIUM PERCHLORATE IN METHYL ALCOHOL AT 25°

Concn. equiv. per liter	Sp. cond., mhos × 10^4	Equivalent conductance
0.0000000	0.0000	83.2
.0001145	.8980	81.03
.002186	1.625	74.34
.004002	2.857	71.39
.007926	4.905	61.88
.01189	7.066	59.43
.01439	8.130	56.49
.02378	12.99	54.63
.04762	22.52	47.29
.2196	79.45	36.18
.5854	171.3	29.26

TABLE III

CONDUCTANCE OF SOLUTIONS OF MAGNESIUM PERCHLORATE IN NITROMETHANE AT 25°

Concn. equiv. per liter	Sp. cond., mhos × 10^4	Equivalent conductance
0.0000000	0.0000	115.7
.0005858	.5524	94.30
.0006982	.6516	93.33
.0008644	.7868	91.03
.001134	.9820	86.57
.001649	1.321	80.09
.003590	1.928	53.70
.004488	2.242	49.96
.005981	2.688	44.93
.008976	3.385	37.71
.01795	3.997	22.27
.05702	8.197	14.38
.08556	10.44	12.20
.1222	11.82	9.671
.1711	12.57	7.347
.2140	14.80	6.916
.2852	14.09	4.941
.3914	14.59	3.728
.8556	19.67	2.299

TABLE IV

CONDUCTANCE OF SOLUTIONS OF CALCIUM PERCHLORATE IN ACETONE AT 25°

Concn. equiv. per liter	Sp. cond., mhos × 10^4	Equivalent conductance
0.0000000	0.0000	198.9
.0004798	.6574	137.0
.0006296	.8147	129.4
.0009158	1.134	123.9
.001993	2.221	111.5
.002492	2.629	105.5
.003322	3.299	99.31
.004984	4.561	91.52
.04068	16.78	41.25
.1221	38.79	31.78
.1831	52.53	28.69
.3662	89.25	24.37
.7324	148.9	20.33

Discussion

In Table V we present a comparison between the limiting conductances Λ_0 of magnesium perchlorate in the various solvents used in our work,[2,5] the empirical slopes A in the formula

$$\Lambda = \Lambda_0 - A\sqrt{C}$$

in which Λ is the equivalent conductance and C the equivalent concentration, the dielectric constants D and the viscosities η of the solvents, the products $\Lambda_0\eta$, the ratios $\Lambda_0\eta/D$ and the theoretical

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[5] P. Van Rysselberghe and J. M. McGee, THIS JOURNAL, **65**, 737 (1943).

Onsager slopes A_0 obtained on the basis of hypothetical transport numbers corresponding to equal limiting equivalent conductances for the two ions of the salt.[6] We note that the products $\Lambda_0\eta$ are not constant, as Walden's rule might have led one to expect.[7] It is also interesting to note that the ratios $\Lambda_0\eta/D$ are much closer to constancy than the products $\Lambda_0\eta$, these ratios being practically identical for water, methyl alcohol, and isopropyl alcohol. The Onsager A_0 value for water is in remarkable agreement with the experimental slope A. The other cases speak for themselves: the disagreement in the case of methyl alcohol is particularly conspicuous. The theoretical Onsager slope A_0 for an unsymmetrical electrolyte depends in a rather sensitive manner on the transport numbers. One can calculate the transport numbers at infinite dilution which would bring into exact agreement the experimental slopes A and the theoretical ones A_0,[8] but the resulting values of the limiting transport number of the magnesium ion for the cases reported in Table V are impossibly large in the cases of nitromethane (1.44), acetone (1.15), and *n*-propyl alcohol (1.36), negative in the case of isopropyl alcohol (−1.14), imaginary in the case of methyl alcohol (the transport number is obtained from a quadratic equation). In the case of water alone do we get a reasonable value (0.42) which, for the time being, in the absence of experimental transport data, can be regarded as the true value of the transport number of magnesium in an infinitely dilute aqueous solution of magnesium perchlorate at 25°.

TABLE V

COMPARISON OF CONDUCTANCES OF MAGNESIUM PERCHLORATE IN VARIOUS SOLVENTS AT 25°

Solvent	Λ_0	A	D	η, poises	$\Lambda_0\eta$	$\Lambda_0\eta/D$	A_0
Water	128.5	244	78.5	0.00895	1.15	0.0146	248
Nitromethane	115.7	873	37	.00620	0.717	.0194	584
Methyl alcohol	83.2	190	30.3	.00546	.454	.0150	661
Acetone	185.5	2350	21	.00316	.586	.0280	1816
n-Propyl alcohol	25.8	412	20.1	.0199	.513	.0255	281
Isopropyl alcohol	13.5	189	18.0	.0207	.279	.0155	229

TABLE VI

COMPARISON OF CONDUCTANCES OF MAGNESIUM, CALCIUM AND BARIUM PERCHLORATES IN ACETONE AT 25°

Salt	Λ_0	A	$\Lambda_0\eta$	A_0
$Mg(ClO_4)_2$	185.5	2350	0.586	1816
$Ca(ClO_4)_2$	198.9	2817	.629	1885
$Ba(ClO_4)_2$	201.3	1603	.636	1898

In Table VI we present a comparison between the limiting conductances Λ_0 of magnesium, calcium and barium perchlorates in acetone, the empirical slopes A, the products $\Lambda_0\eta$ and the theoretical Onsager slopes A_0. Calculating as above the transport number of the positive ion which would bring A and A_0 into exact agreement, we again find impossible values: 1.15 for magnesium as already indicated above, 1.34 for calcium and −0.25 for barium. Evidently we are dealing with a set of conditions quite different from those postulated in the foundations of the Onsager theory. Equilibria between simple ions, neutral molecules and complex ions very likely affect the limiting slope A in the Kohlrausch formula.

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Summary

The conductances of solutions of magnesium perchlorate in acetone, methyl alcohol and nitromethane, and of solutions of calcium perchlorate in acetone have been measured from high to very low concentrations. The significance of the results has been discussed.

The limiting slopes in the Kohlrausch formula have been reported and compared with the theoretical Onsager slopes. Remarks have been made concerning the limiting transport numbers.

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[6] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, see pp. 127–129.

[7] Ref. 6, see the discussion on pp. 183–186.

[8] H. S. Harned and B. B. Owen, ref. 6, see formula (5-3-9), p. 129.