2. The acidity of methanol solutions of sulfur dioxide is due to the monobasic acid, $CH_3O\text{-}SO_2H$, there being no indication of its acting as a "Lewis" acid with the basic form of thymol blue.

3. The addition of small quantities of water to methanol solutions of SO_2 results in the transfer of protons from methanol to water, without affecting other equilibria.

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

The Conductance of Solutions of Magnesium Perchlorate in *n*-Propyl and Isopropyl Alcohols[1]

BY PIERRE VAN RYSSELBERGHE AND GILBERT J. HUNT

The high solubilities of several alkaline earth perchlorates in a number of organic solvents have been measured by Willard and Smith.[2] The possibility of studying concentrated organic solutions of such salts is of very great interest from the point of view of the general theory of electrolytic solutions. Investigations on organic solutions of magnesium perchlorate are being carried out in this Laboratory. The conductances of aqueous solutions of this salt at 25°, heretofore missing, were recently reported by Van Rysselberghe and McGee.[3] In the present paper we report the conductances of solutions of magnesium perchlorate in *n*-propyl and isopropyl alcohols at 25°.

Experimental

Magnesium Perchlorate.—The complete dehydration of magnesium perchlorate requires extreme care. The method finally adopted was the following: the commercial G. F. Smith product ("anhydrone") or Eastman Kodak Co. white label magnesium perchlorate was changed into the hexahydrate, which was recrystallized. This salt was transferred to a quartz tube electrically heated in steps to 245° and kept at that temperature for ten hours, in vacuum (magnesium perchlorate decomposes at 250°). The dehydrated product was kept over phosphorus pentoxide. Its purity was repeatedly checked by analysis.

***n*-Propyl Alcohol.**—Eastman Kodak Co. white label *n*-propyl alcohol was refluxed for five hours over calcium oxide. The 95–98° fraction was collected by distillation from the calcium oxide and was then carefully fractionated. The specific conductance of the solvent used in the preparation of the solutions was found to be $8 \cdot 10^{-8}$ mho, in exact agreement with the value given by Scudder.[4]

Isopropyl Alcohol.—Eastman white label isopropyl alcohol was refluxed for five hours over calcium oxide. The 81–83° fraction was collected by distillation from the calcium oxide and was then carefully fractionated. The specific conductance of the solvent used in the preparation of the solutions was found to be $4 \cdot 10^{-6}$ mho, in close agreement with Scudder's value.[4]

Conductivity Bridge.—A Jones bridge of the Leeds and Northrup Company was used for all the conductance measurements. The 1000 cycle alternating current was provided by a R. C. A. beat-frequency audio oscillator and the current in the telephone receiver was amplified by means of a specially-built two-stage audio-frequency amplifier.

Conductivity Cells.—Two Jones cells of the Leeds and Northrup Company were used (constants, 9.179 and 0.2744). Concordant results were obtained with an older type of cell with spongy platinum electrodes (constant, 13.242).

Temperature Control.—An oil thermostat kept at 25 ± 0.005° by means of a toluene regulator and an electronic relay was used.

Preparation of Solutions.—Several series of solutions were prepared by successive dilutions, these dilutions being carried out on a weight basis, with the usual buoyancy corrections. The concentrations in the various series were made to overlap to a certain extent and the agreement of the conductivities so obtained was our main criterion of accuracy. Close checks were obtained with samples of salt and solvents prepared at distant intervals of time. Errors due to impurities, water in particular, have no doubt been reduced to a strict minimum.

TABLE I

CONDUCTANCE OF SOLUTIONS OF MAGNESIUM PERCHLORATE IN *n*-PROPYL ALCOHOL AT 25°

Concn. equiv. per liter	Sp. cond. mhos × 10^4	Equivalent conductance
0.0000000	0.00000	25.75
.0001814	.03647	20.105
.0004950	.08198	16.562
.001727	.1857	10.753
.003748	.2895	7.723
.005804	.3620	6.239
.009888	.5904	5.971
.01240	.6562	5.292
.01510	.6970	4.616
.02562	1.132	4.419
.03245	1.296	3.994
.04318	1.616	3.748
.05117	1.718	3.357
.05200	1.721	3.310
.08833	2.689	3.044
.1195	3.417	2.859
.1351	3.731	2.762
.1766	4.532	2.566
.2408	5.592	2.322
.2696	6.188	2.295
.4952	9.524	1.923
.5372	10.39	1.914
.8567	15.37	1.794
1.0703	18.02	1.684
1.128	18.69	1.659

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[1] From a thesis submitted by Gilbert J. Hunt in partial fulfillment of the requirements for the M.A. degree at the University of Oregon, June, 1944.

[2] H. H. Willard and G. F. Smith, THIS JOURNAL, **45**, 286 (1923).

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

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

Results

The specific and equivalent conductances of magnesium perchlorate in *n*-propyl alcohol at 25° are reported in Table I. The specific and equivalent conductances of magnesium perchlorate in isopropyl alcohol at 25° are reported in Table II.

TABLE II

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

Concn. equiv. per liter	Sp. cond. mhos × 10^4	Equivalent conductance
0.0000000	0.00000	13.50
.0002910	.02985	10.258
.0008490	.06782	7.988
.002359	.1157	4.905
.005520	.1973	3.574
.01447	.3037	2.122
.02512	.4964	1.976
.06496	.7637	1.176
.1559	1.132	0.7261
.3877	2.006	.5174
.5272	2.676	.5076
1.2041	5.531	.4593

Discussion

The most striking characteristic of these data is that the conductances of magnesium perchlorate in *n*-propyl alcohol are about twice as large as in isopropyl alcohol. This is no doubt largely due to the different structures of the solvated magnesium and perchlorate ions in the two solvents. The molecules of *n*-propyl alcohol are probably attached to the magnesium ion through the oxygen at the end of the three-carbon chain, while the isopropyl alcohol molecules would be attached through the oxygen in the middle of the chain, with a resulting structure and a shape likely to offer a greater resistance to motion in the electric field. A similar difference would exist in the case of the solvated perchlorate ion. It is unlikely that the degrees of dissociation would be sufficiently different to account for the difference in conductance: the dielectric constants are quite similar[5] (20.1 for *n*-propyl and 18.0 for isopropyl), and so are the viscosities[5] (0.0199 for *n*-propyl and 0.0207 for isopropyl alcohol). Plots of the equivalent conductance against the square root of the equivalent concentration indicate, in both cases, that the Kohlrausch type of behavior very nearly holds in the range of high dilutions, the empirical formulas being

$$\Lambda = 25.75 - 412\sqrt{C}$$

for the solutions in *n*-propyl alcohol, and

$$\Lambda = 13.50 - 189\sqrt{C}$$

for the solutions in isopropyl alcohol, Λ being the equivalent conductance and C the equivalent concentration. The coefficients, when interpreted on the basis of the Onsager formula for the conductance of unsymmetrical electrolytes,[6] lead to impossible values of the ionic conductances, but the conductances in isopropyl alcohol are closer to agreement with the Onsager theory than the conductances in *n*-propyl alcohol. The situation is of course obscured by the probable presence of unknown amounts of neutral molecules of magnesium perchlorate and of various complex ions. The Ostwald dilution law values are by no means constant. On the other hand, the lack of information about transport numbers (required in the case of an unsymmetrical electrolyte) prevents a detailed calculation of the dissociation constants on the basis of the Onsager[6] and Fuoss–Kraus[7] theories, as was done by Hovorka and Simms[5] for solutions of the chlorides and iodides of potassium and sodium in *n*-propyl and isopropyl alcohols. We hope to come back to this point when transport numbers are available. It is interesting to note that both our conductance curves approach the Kohlrausch limiting tangent from above.

Kraus and Bishop[8] measured the conductances of calcium nitrate in *n*-propyl alcohol. These are smaller than the conductances of magnesium perchlorate. Desai, Naik and Desai[9] found that the conductances of chlorides, iodides and nitrates of the alkali and alkaline earth metals in *n*-propyl alcohol do not agree with the Onsager theory. Hovorka and Simms[5] concluded from their measurements that the chlorides and iodides of potassium and sodium should be regarded as weak electrolytes in both *n*-propyl and isopropyl alcohols. They found no relation in the order of the conductances and no additivity of ionic conductances.

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Summary

The conductances of solutions of magnesium perchlorate in *n*-propyl and isopropyl alcohols have been measured from high to very low concentrations. The significance of the results has been discussed.

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(5) F. Hovorka and J. C. Simms, THIS JOURNAL, **59**, 92 (1937).

(6) L. Onsager, *Physik. Z.*, **28**, 277 (1927).

(7) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476 (1933); R. M. Fuoss, *ibid.*, **57**, 488 (1935); H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943.

(8) C. A. Kraus and J. E. Bishop, THIS JOURNAL, **43**, 1568 (1921).

(9) H. N. Desai, D. B. Naik and B. N. Desai, *Indian J. Physics*, **8**, 323 (1934).