contains free sulfur because boiling with sodium sulfite gives a considerable quantity of sodium thiosulfate. Recent work by Sauer and Steiner[12] lends support to this view. There is a definite cycle of changes which take place during the precipitation and aging of copper sulfide. During early stages of the precipitation, copper sulfide separates as a fine black sol which remains in suspension in the solution. After three or four minutes the particles begin to clump together and settle. In another five minutes the loose clumps become more compact and dense and assume a brownish color. If the flask is stoppered and allowed to stand, a definite aging process takes place. In two or three hours, the dense brownish-black aggregations begin to disperse and become greenish-black in color. In about ten hours the peptization has reached a point where secondary aggregates are so reduced in size as to be almost invisible to the unaided eye. Microscopic examination shows that minute primary particles predominate. An extremely small concentration of crotonaldehyde exerts a profound influence upon this aging process. When formed in the presence of crotonaldehyde, the precipitate does not peptize to give small primary particles, but on the contrary tends to coagulate into clumps that are even larger than those formed in the beginning. Microscopic examination shows that the clumps consist of many primary particles closely packed into opaque dense masses which show no tendency to disintegrate, even after standing for several days.

Summary

If copper sulfide is precipitated in the presence of a very small concentration of crotonaldehyde, the quantity of zinc carried down is reduced greatly. Apparently the crotonaldehyde reacts with the adsorbed hydrogen sulfide and reduces its value on the surface of the copper sulfide so that it will not cause the postprecipitation of the zinc.

COLUMBUS, OHIO RECEIVED SEPTEMBER 4, 1936

[12] Sauer and Steiner, *Kolloid-Z.*, **72**, 41 (1935).

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

The Conductivity of Various Salts in *n*-Propyl and Isopropyl Alcohols

BY FRANK HOVORKA AND JOHN COLBERT SIMMS[1]

Introduction

The conductivity of various salts has been determined in methyl and ethyl alcohols by many workers during the last few years. Since only a comparatively few measurements were made in *n*-propyl and isopropyl alcohols, it seemed desirable to carry out a series of conductivity determinations of the more common uni-univalent salts in these two solvents. The dielectric constant of the alcohols gradually decreases as they increase in molecular weight. Therefore, a study of the alcohols as a series ought to give the effect of the solvent as well as that of the dielectric constant on the nature of the electrolytic solutions.

Apparatus.—The assembly comprised a Leeds and Northrup Kohlrausch bridge and dial box type coils of low induction. All the resistances were checked against coils calibrated by the Bureau of Standards. The balance point was detected by Baldwin type telephones using two stage amplification. The other parts used in this "set up" were of the standard type generally used in accurate conductivity measurements.

The cell used in this investigation was of borosilicate glass and was made after a design of Hartley and Barrett.[2]

The thermostat was a large vacuum jar. The temperature was kept constant at 25 ± 0.005°.

Materials and Procedure.—Each of the alcohols containing a little water was refluxed for several hours over barium oxide and then distilled into a Pyrex fractionating flask and column without coming in contact with air. Each was fractionated to a boiling point of 0.05° and then treated with metallic sodium. After two further distillations they were fractionated directly into the conductivity cell which was dried previously by passing dry warm air through it. Usually about 100 g. of alcohol was distilled into the cell. The specific resistance of the *n*-propyl alcohol was 2×10^8 mhos. and of the isopropyl alcohol 9×10^9 mhos. These values were determined by using a direct current of 135 volts and were used in making the solvent correction.

The C. P. salts were recrystallized from water at least three times, dried, and analyzed for final purity. A known amount of each salt was transferred to a 100-cc. Pyrex bottle which had been baked out with a free flame. All of the handling of salts as well as of the alcohols was car-

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[1] This communication is an abstract of a portion of a thesis submitted by John Colbert Simms in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry. Original manuscript received July 24, 1933.

[2] Hartley and Barrett, *Trans. Chem. Soc.*, **103**, 789 (1913).

ried out in an atmosphere of dry air. Enough alcohol from the final purification was distilled into this bottle to give about a thirtieth normal solution. A small weight pipet was filled from this bottle and introduced through the cap of the cell while dry air was passing through the cell. The addition of about one gram of this solution to about 100 g. of the alcohol gave a solution approximately 0.0001 *N*.

The electrodes finally used were coated with a medium layer of platinum black and ignited to redness. This gave a dull gray coating. The balance was quite easily obtained and no oxidation seemed to occur as the conductivity of the solutions did not change on standing.

The value of the cell constant was determined several times during the work and no variation greater than the experimental error could be noted. The measurements were made over the same range of concentration as that of the alcohol solutions. Water was weighed in the cell and an aqueous solution of potassium chloride was added through the weight pipet. The conductivity values found compared with those calculated by the Kohlrausch and Maltby equation as corrected by Kraus and Parker:[3] $\Lambda_c = 129.91 - 80.75\sqrt{c}$.

Before the measurements on propyl alcohol were begun Frazer and Hartley's[4] measurements on potassium chloride were repeated. The results obtained checked their conductivity curve well within the experimental error.

Results

In Tables I and II C is the equivalent concentration; Λ_c the experimental equivalent conductivity; K_1, the dissociation constant as calculated from the Ostwald dilution law; and K_2, the dissociation constant as computed by the Fuoss and Kraus[5] method where

$$K_2 = c\gamma^2 f^2/1 - \gamma$$

c is the equivalent concentration, γ is equal to the average fraction of solute free to carry the current and f is the activity coefficient of the ions expressed by

$$-\ln f = \beta\sqrt{c\gamma}/(1 - \delta\sqrt{c\gamma})$$

$$\text{where } \beta = \frac{e}{2DkT}\left(\frac{8\,Ne^2}{1000\,DkT}\right)^{1/2}$$

$$\text{and } \delta = \left(\frac{8\,Ne^2}{1000\,DkT}\right)^{1/2}\alpha$$

TABLE I

CONDUCTIVITY AND DISSOCIATION CONSTANTS IN *n*-PROPYL ALCOHOL

$C \times 10^4$	Λ_c	$K_1 \times 10^3$	$K_2 \times 10^3$
	Potassium iodide		
	Series A		
2.842	22.39	1.998	3.950
5.202	21.19		
8.429	20.12		
12.260	19.07	2.980	4.229
	Series B		
2.588	22.61		
3.273	22.08		
5.068	21.33	2.393	4.082
17.980	18.09		
	Series C		
1.037	23.70		
1.581	23.23	1.778	4.166
4.122	21.75		
9.136	19.91	2.742	4.110
14.530	18.55		
16.140	18.29		
	Sodium iodide		
	Series A		
2.255	21.98	2.322	7.022
5.050	20.80		
9.133	19.66	3.445	6.985
15.770	18.42		
	Series B		
4.299	21.05	2.753	6.513
9.125	19.72		
17.240	18.12		
	Series C		
2.989	21.50		
7.399	19.95		
11.161	19.23	3.661	7.515
25.931	17.36		
	Sodium bromide		
	Series A		
1.645	16.91		
2.930	16.38	2.224	9.386
5.126	15.73		
8.410	15.08	3.235	9.548
	Series B		
2.772	16.58		
5.958	15.61	2.936	9.430
10.560	14.69	3.438	9.913
17.281	13.68	3.816	9.636
	Potassium bromide		
1.303	20.98	1.283	2.434
1.732	20.53	1.326	2.263
4.760	18.57	1.642	2.284
7.190	17.60	1.822	2.389

Each term has the usual significance. In calculating β and δ and later α the dielectric constants determined by Åkerlöf[6] were used. α, the mean value of the ionic radius, was obtained from the Stokes law.[7] The viscosities for the two solvents were obtained by evaluating the data of

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(3) Kraus and Parker, THIS JOURNAL, **44**, 2422 (1922).

(4) Frazer and Hartley, *Proc. Roy. Soc.* (London), **A109**, 351 (1925).

(5) Fuoss and Kraus, THIS JOURNAL, **55**, 476 (1933).

(6) Åkerlöf, *ibid.*, **54**, 4125 (1932).

(7) Newman, "Electrolytic Conduction," J. Wiley and Sons, Inc., New York, 1931, p. 126.

TABLE II

CONDUCTIVITY AND DISSOCIATION CONSTANTS IN ISOPROPYL ALCOHOL

$C \times 10^4$	Λ_c	$K_1 \times 10^3$	$K_2 \times 10^3$
	Potassium iodide		
	Series A		
2.478	19.61		
3.407	18.77		
7.522	16.55	1.274	1.441
9.732	15.71	1.323	1.539
	Series B		
1.420	20.57		
2.848	19.20	1.054	1.394
5.566	17.52	1.229	1.469
11.931	15.16		
	Sodium iodide		
	Series A		
1.988	16.61	1.498	4.124
3.856	15.59		
6.137	14.78		
10.191	13.75	2.147	3.762
	Series B		
2.680	16.21	1.599	3.897
7.371	14.44	1.998	3.701
20.040	11.82		
	Sodium bromide		
	Series A		
3.276	15.24	1.196	1.839
6.200	13.96		
8.291	13.21	1.426	1.871
12.880	12.04	1.515	1.856
25.830	9.99		
	Series B		
5.351	14.16	1.281	1.772
17.711	11.12		
18.561	10.87		
	Potassium bromide		
	Series A		
2.308	13.65	3.524	3.679
3.634	12.26	3.650	3.653
5.134	11.18		
	Series B		
3.160	12.57	3.482	3.511
4.161	11.66	3.424	3.442

Gartenmeister,[8] Thorpe and Rodger,[9] and Dunston and Thole.[10]

Series A, B, etc., indicate results of entirely independent runs.

Table III gives the values of the constants used for various salts in the two solvents.

TABLE III

CONSTANTS FOR CONDUCTANCE CURVES AT 25°

Solute	α	β	$a \times 10^8$	δ
n-Propyl alcohol				
Diel. constant = 20.1 Viscosity = 0.0199				
Potassium iodide	98.52	3.907	3.222	2.093
Sodium iodide	96.21	3.907	3.397	2.206
Sodium bromide	86.37	3.907	4.408	2.864
Potassium bromide	95.18	3.907	3.480	2.260
Isopropyl alcohol				
Diel. constant = 18.0. Viscosity = 0.02072				
Potassium iodide	109.86	4.612	3.328	2.286
Sodium iodide	100.11	4.612	4.149	2.851
Sodium bromide	98.28	4.612	4.351	2.989
Potassium bromide	101.23	4.612	4.034	2.772

In Table IV Λ_0 is the limiting conductivity obtained by extrapolating $\Lambda_c - \sqrt{c}$ experimental curves. Λ_0' was obtained by using the Fuoss and Kraus[5] equation

$$\gamma' = \frac{\Lambda/\Lambda_0}{1 - \alpha\Lambda_0^{-3/2}\sqrt{C\Lambda}}$$

and determining for what value of Λ_0, γ will converge to a constant value as successive substitutions are made. α in the last expression is computed by Onsager[11] as $\alpha = \frac{8.18 \times 10^5}{(DT)^{3/2}}\Lambda_0 + \frac{82}{\eta(DT)^{1/2}}$

This is probably the best method for obtaining accurately the limiting equivalent conductivity. A greatly simplified method for estimating γ suggested later by Fuoss[12] was found to be very useful but was not as accurate for the determination of Λ_0 as the original method which was used in all of the calculations in this paper. K_1 and K_2 are the averages of those given in Tables I and II. K_3 is a dissociation constant obtained by plotting $f\sqrt{c} - \sqrt{1 - \gamma}/\gamma$ for various values of Λ_0 until a straight line is obtained which passes through the origin. The slope of this line is equal to K_3.

Discussion

When $\Lambda_c - \sqrt{c}$ curves are plotted the points fall quite well on a straight line up to a concentration of about 0.0003 N. Above this concentration region the equivalent conductivity decreases at a considerably lower rate with the increase in concentration. Many of the curves intersect, illustrating rather marked differences between the electrolytes. These differences become more evident with the increasing molecular weight of the alcohols. In methyl alcohol, for instance,

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[8] Gartenmeister, *Z. physik. Chem.*, **6**, 524 (1890).

[9] Thorpe and Rodger, *Trans. Roy. Soc.* (London), **A185**, 397 (1895).

[10] Dunston and Thole, *J. Chem. Soc.*, **95**, 1556 (1909).

[11] Onsager, *Physik. Z.*, **28**, 277 (1927).

[12] Fuoss, THIS JOURNAL, **57**, 488 (1935).

which resembles water in its behavior, the curves are almost parallel.

The experimental slopes of the conductivity curves are greater in every case than those predicted by Onsager. The deviation is in the neighborhood of 100% or more indicating a rather incomplete dissociation. The comparison of the values of experimental Λ_c (Tables I and II) with those calculated from the Debye–Hückel–Onsager equation show differences of about 5 to 10% in the more dilute regions.

The limiting equivalent conductivity (Table IV) of each salt is considerably less than its conductivity in ethyl alcohol. However, if methyl, ethyl, and the propyl alcohols are considered as a series, the values obtained cannot be explained on the ground of viscosity and the dielectric constant differences. Further, there seems to exist no relation in the order of conductivities of the salts in propyl and isopropyl alcohols, nor does the principle of additivity apply in either alcohol. Either the chemical nature of the solvent plays an important part or the viscosity and the dielectric constant are not accounted for correctly or both. It is of interest to note that the values of Λ_0 obtained by the extrapolation of $\Lambda_c - \sqrt{c}$ curves and those obtained by the Fuoss and Kraus method differ in some cases by as much as 3%. The importance, of course, of obtaining correct Λ_0 for various calculations cannot be overemphasized.

TABLE IV

LIMITING CONDUCTIVITY AND DISSOCIATION CONSTANTS

Solute	Alcohol solvent	Λ_0	Λ_0'	$K_1 \times 10^3$	$K_2 \times 10^3$	$K_3 \times 10^3$
KI	*n*-Propyl	25.42	25.16	2.378	4.107	4.053
NaI	*n*-Propyl	24.12	23.94	3.046	7.010	7.039
NaBr	*n*-Propyl	18.58	18.31	3.054	9.582	9.140
KBr	*n*-Propyl	23.54	22.93	1.518	2.343	2.373
KI	Isopropyl	23.64	23.45	1.220	1.461	1.461
NaI	Isopropyl	18.96	18.58	1.811	3.846	3.798
NaBr	Isopropyl	18.08	18.65	1.354	1.835	1.853
KBr	Isopropyl	19.50	19.81	0.352	0.357	0.354

There seem to be data available only for sodium iodide in propyl[13] and isopropyl alcohols.[14] The value of 18.87 obtained for Λ_0 by Brown for sodium iodide in isopropyl alcohol is in good agreement with the value obtained here. However, the value of 21.04 for Λ_0 obtained by Keyes and Winninghoff for sodium iodide in propyl alcohol is in considerable disagreement with the value found here.

The dissociation constants (Table IV) show that all of the salts used here may be considered as weak electrolytes in propyl and isopropyl alcohol. The values of these constants fit in rather well with those recorded for the lower and higher alcohols as well as for related solvents.[15]

The variation of the dissociation constant with concentration is shown in Tables I and II. The method of Fuoss and Kraus yields much greater but quite constant values. The Ostwald dilution law gives values for dissociation constants that increase considerably with the increase in concentration. The former is expected while the latter is inconsistent for weak electrolytes.

Summary

The conductivities of potassium iodide and bromide and of sodium iodide and bromide have been determined in propyl and isopropyl alcohols.

The limiting equivalent conductivities were calculated by the Fuoss and Kraus method and were compared with those obtained by extrapolation of $\Lambda_0 - \sqrt{C}$ curves.

The dissociation constants were calculated by the Fuoss and Kraus, and Ostwald methods for each electrolyte. It was shown that the former method yields greater but quite constant values. Furthermore, the values of the dissociation constants indicate that all of the salts used here may be considered as weak electrolytes in propyl and isopropyl alcohols.

There seems to exist no relation in the order of conductivities of the salts in these two alcohols nor does the principle of additivity apply in either alcohol.

CLEVELAND, OHIO RECEIVED NOVEMBER 17, 1936

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[13] Keyes and Winninghoff, THIS JOURNAL, 38, 1178 (1916).

[14] Brown, Thesis, Yale University, 1929.

[15] See Davies, "The Conductivity of Solutions," J. Wiley and Sons. Inc., New York. 1930, pp. 197–199, for a complete bibliography of accurate conductivity measurements in non-aqueous solutions.