

Summary

The emission spectra of toluene, ethylbenzene, *o*-, *m*- and *p*-xylene have been photographed using the Tesla discharge as a means of excitation; they are found to contain a number of bands generally accompanied by a continuous background. The numerical data are in agreement with previous measurements. A comparison of these spectra indicates that substitution produces a profound disturbance in the electrical and magnetic symmetry of the benzene ring. Further, these spectra have a limited application in qualitative analysis but are rendered less suitable for quantitative work because of the continuous background.

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THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF LITHIUM NITRATE IN CERTAIN BINARY ALCOHOLIC SYSTEMS¹

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Investigations of conductivity in mixed solvents were first made by Lenz,² and have since been extended from time to time by many other workers. Perhaps the most systematic and extensive results have been obtained by Jones³ and his co-workers using various solvents such as water, methyl alcohol, ethyl alcohol, propyl alcohol, acetone and glycerin, and a considerable number of solutes.

Data for the conductivity and viscosity of solutions of lithium nitrate in certain aqueous-alcoholic solvents have been reported in a previous paper.⁴ As a continuation of these studies data are now given for systems containing various proportions of water, ethyl alcohol, *n*-propyl alcohol and isopropyl alcohol. In some cases density data have also been included.

Materials.—The lithium nitrate, water and ethyl alcohol were prepared and purified by the methods used by Whitman and Spencer. High grade *n*- and isopropyl alcohols from the Eastman Kodak Company were purified by the same method that was used in purifying ethyl alcohol. The specific conductivities of the purified solvents were as follows: water,

¹ Prepared from a Dissertation presented to the Graduate Faculty of the State University of Iowa by D. M. Hurt, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Lenz, *Mem. V'acad. St. Petersburg*, 7, 30 (1881); Stephan, *Wied. Ann.*, 17, 673 (1883); Arrhenius, *Z. physik. Chem.*, 9, 487 (1892); Wakeman, *ibid.*, 11, 49 (1893); Zelinsky and Krapivin, *ibid.*, 21, 35 (1896); Cohen, *Wied. Ann.*, 25, 31 (1898).

³ For a summary and review of this work, see Jones and Kreider, *Am. Chem. J.*, 45, 282 (1911).

⁴ Whitman and Spencer, *THIS JOURNAL*, 50, 1840 (1928).

1.1×10^{-6} ; ethyl alcohol, 0.85×10^{-6} ; *n*-propyl alcohol, 4.96×10^{-6} ; isopropyl alcohol, 0.51×10^{-6} .

Apparatus and Measurements.—A Leeds and Northrup slide wire bridge with extension coils, tunable head phones, Curtis coil resistance boxes, adjustable air condensers and the usual shieldings and sheathings were used. A Vreeland oscillator was used as the source of alternating current. Conductivity cells similar to those described by Schlesinger and Martin⁵ were calibrated by the method of Kraus and Parker.⁶ The cell constants were checked at frequent intervals during the course of the measurements.

Temperature measurements were made with a thermometer which had been compared with one certified by the Bureau of Standards. All measurements were made at $25 \pm 0.01^\circ$. A well insulated, double-walled constant temperature bath of about 100 liters' capacity, filled with a light mineral oil, was used. Through a glass window in one side, readings were made on an Ostwald type quartz viscometer, which had a period for water of about eighteen minutes. Density determinations were made with a pycnometer of about 25 ml. capacity.

Conductivity data have been corrected for the conductivity of the pure solvent.

Experimental

Water-Ethyl Alcohol Mixtures (2).—The equivalent conductivities of solutions of lithium nitrate of various concentrations and in solvents ranging in composition from pure water to pure ethyl alcohol are recorded in Table I. This system has been previously studied by Jones and Lindsay,⁷ but it was thought best to repeat the work since they obtained but three points on the curve. The conductivity data for the 0.1 molar and the 0.00625 molar solutions are shown graphically in Fig. 1. Absolute viscosities of water-ethyl alcohol mixtures according to Noack are also shown

TABLE I
THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN THE SYSTEM WATER-ETHYL ALCOHOL, AT 25°

Molar concn.,	100% H ₂ O	90%	80%	70%	60%	50%	40%	30%	20%	10%	100% C ₂ H ₅ OH
0.1	90.56	71.61	56.25	44.39	37.68	33.49	30.39	27.90	25.44	22.51	17.47
.05	94.84	74.77	58.42	46.36	39.46	35.34	32.39	30.12	27.88	23.47	20.74
.025	98.87	77.45	60.34	48.27	40.91	36.92	34.15	32.09	30.26	28.28	24.07
.0125	102.14	79.33	62.03	49.16	41.86	37.95	33.59	32.08	31.75	29.83	27.36
.00625	105.45	81.25	63.21	49.37	43.42	39.14	34.39	32.68	33.41	32.38	30.40
Sp. cond. of pure solvent $\times 10^{-6}$	1.10	4.32	6.37	4.57	3.34	3.59	3.64	3.85	3.92	2.60	0.85

⁵ Schlesinger and Martin, *THIS JOURNAL*, **36**, 1589 (1914).

⁶ Kraus and Parker, *ibid.*, **44**, 2422 (1922).

⁷ Jones and Lindsay, *Am. Chem. J.*, **28**, 329 (1902).

in Fig. 1.⁸ The conductivity-composition curve is here shown in complete form and is more satisfactory than the curve given by Whitman and Spencer (Ref. 4, p. 1843) as constructed from the meager data of Jones and Lindsay.

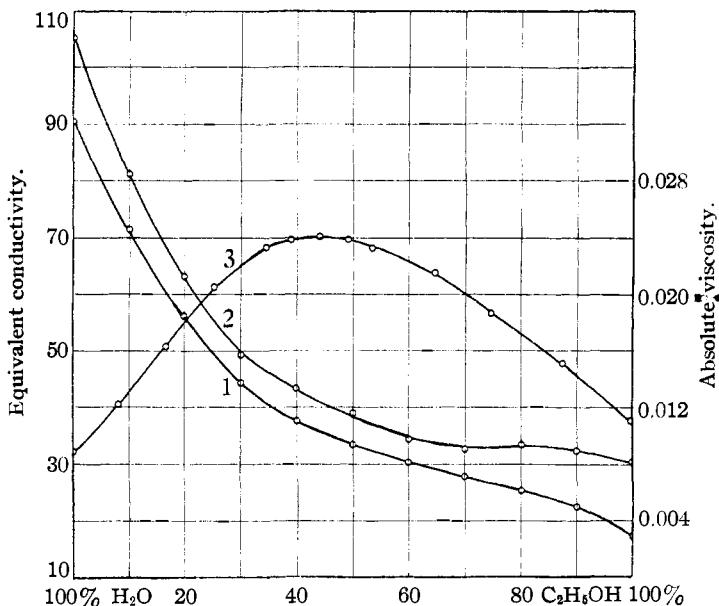


Fig. 1.—Lithium nitrate in water-ethyl alcohol mixtures. Curve 1, composition-conductivity, 0.1 *M*; Curve 2, 0.00625 *M*; Curve 3, composition-viscosity.

Water-*n*-Propyl Alcohol Mixtures (3).—Table II gives the equivalent conductivities for a series of solutions of lithium nitrate in various mixtures of water and *n*-propyl alcohol. Viscosities and densities of the various solvents are given in Table III, the values referring to water at 25°

TABLE II
THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN THE SYSTEM WATER-*n*-PROPYL ALCOHOL AT 25°

Molar concn.,	100% H ₂ O	90%	80%	70%	60%	50%	40%	30%	20%	10%	100% C ₃ H ₇ OH
0.1	90.56	69.92	53.96	45.14	38.15	31.99	26.33	21.10	16.41	11.85	5.564
.05	94.84	73.28	57.10	47.59	40.51	34.29	28.25	23.27	18.35	13.62	6.854
.025	98.87	76.93	59.53	49.93	42.64	36.72	30.49	25.37	20.25	15.94	8.381
.0125	102.14	80.50	61.53	51.73	44.17	39.05	32.63	27.28	22.00	18.13	10.10
.00625	105.45	84.63	64.26	53.18	45.66	41.23	34.44	28.80	25.07	20.72	11.85
Sp. cond. of pure solvent × 10 ⁻⁶	1.1	11.7	20.3	28.6	32.7	30.1	31.8	27.9	23.5	14.2	4.9

⁸ John C. Evans, "Physico-Chemical Tables," Griffin and Co., Ltd., London, 1911, p. 651.

TABLE III

VISCOSITIES AND DENSITIES OF WATER-*n*-PROPYL ALCOHOL MIXTURES AT 25°

H ₂ O, %	Viscosity	Density	H ₂ O, %	Viscosity	Density
100	0.008944	0.99704	40	0.02669	0.8964
90	.01233	.9853	30	.02644	.8742
80	.01668	.9730	20	.02490	.8515
70	.01944	.9626	10	.02232	.8269
60	.02362	.9372	0	.01962	.7957
50	.02575	.9170			

for which the values 0.008944 and 0.99704 were used. The corresponding curves are given in Fig. 2.

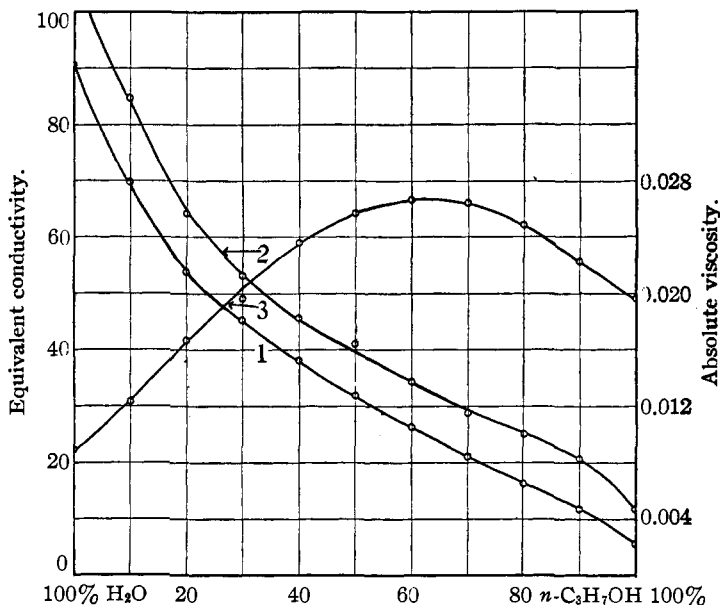


Fig. 2.—Lithium nitrate in water-*n*-propyl alcohol mixtures. Curve 1, composition-conductivity, 0.1 *M*; Curve 2, 0.00625 *M*; Curve 3, composition-viscosity.

Water-Isopropyl Alcohol Mixtures (4).—Table IV gives the conductivity data for solutions of lithium nitrate in water-isopropyl alcohol

TABLE IV

THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN THE SYSTEM WATER-ISOPROPYL ALCOHOL AT 25°

Molar concn.	100% H ₂ O	90%	80%	70%	60%	50%	40%	30%	20%	10%	100% C ₃ H ₇ OH
0.1	90.56	66.88	49.58	38.59	32.05	26.78	22.07	17.76	13.75	9.465	2.058
.05	94.84	70.39	52.36	40.76	33.77	28.56	24.01	19.53	15.54	11.07	2.447
.025	98.87	73.92	55.02	42.70	35.48	30.25	25.88	21.22	17.39	12.84	2.998
.0125	102.14	77.50	57.30	44.52	37.04	31.82	27.66	22.83	19.17	14.80	3.812
.00625	105.45	82.15	59.28	46.04	38.40	33.20	29.21	24.23	20.91	16.84	4.921

Sp. cond. of pure solvent

$\times 10^{-4}$	1.1	2.86	1.92	1.56	1.24	1.03	1.46	1.80	2.86	0.90	0.51
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TABLE V

VISCOSITIES AND DENSITIES OF WATER-ISOPROPYL ALCOHOL MIXTURES AT 25°

H ₂ O, %	Viscosity	Density	H ₂ O, %	Viscosity	Density
100	0.008944	0.99704	40	0.03139	0.8931
90	.01284	.9839	30	.03057	.8682
80	.01847	.9723	20	.02786	.8418
70	.02371	.9580	10	.02381	.8128
60	.02795	.9387	0	.02183	.7807
50	.03070	.9167			

mixtures; Table V, the viscosity and density data for the solvents. Curves are shown in Fig. 3.

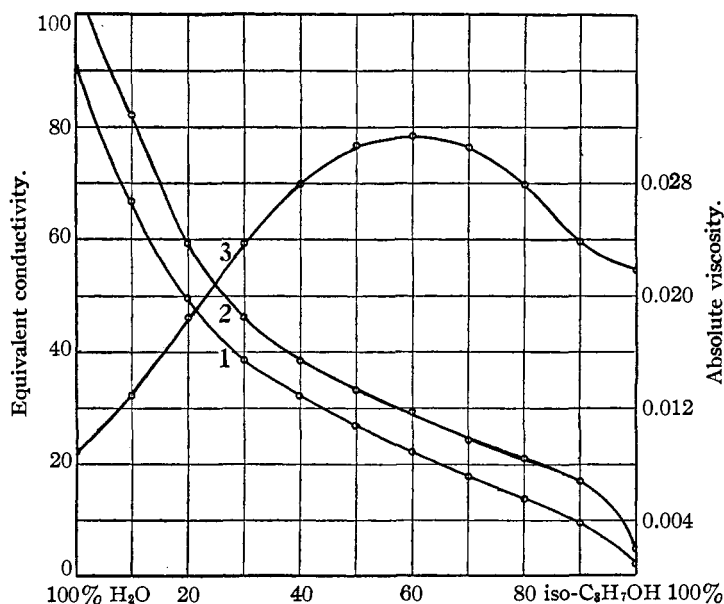


Fig. 3.—Lithium nitrate in water-isopropyl alcohol mixtures. Curve 1, composition-conductivity, 0.1 *M*; Curve 2, 0.00625 *M*; Curve 3, composition-viscosity.

Ethyl Alcohol-*n*-Propyl Alcohol Mixtures (6).—Conductivity data are given in Table VI. Viscosity data are according to Herz,⁹ the corresponding volume percentages having been calculated from his weight percentages by means of the necessary density data. Curves are given in Fig. 4.

Ethyl Alcohol-Isopropyl Mixtures (7).—Conductivity data are given in Table VII; viscosity and density data in Table VIII. Curves are shown in Fig. 5.

⁹ "Tables Ann. Internat. de Constantes," Vol. V, Gauthier-Villars et Cie., Paris, 1925, p. 54.

TABLE VI

THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN THE SYSTEM ETHYL ALCOHOL-
n-PROPYL ALCOHOL AT 25°

Molar concn.	100% C ₂ H ₅ OH	90%	80%	70%	60%	50%	40%	30%	20%	10%	100% C ₃ H ₇ OH
0.1	17.47	15.66	14.04	12.86	11.73	10.50	9.427	8.375	7.370	6.455	5.564
.05	20.74	18.66	17.11	15.72	14.41	12.87	11.52	10.28	9.081	7.971	6.854
.025	24.07	22.14	20.26	18.80	17.27	15.42	13.94	12.41	11.02	9.724	8.381
.0125	27.36	25.62	23.46	21.86	20.22	18.10	16.48	14.68	13.23	11.66	10.10
.00625	30.40	28.31	26.30	24.78	22.99	20.71	18.96	16.84	15.38	13.58	11.85
Sp. cond. of pure solvent											
× 10 ⁻⁴	0.85	4.95	5.86	6.66	6.85	7.30	6.87	6.52	6.09	5.68	4.96

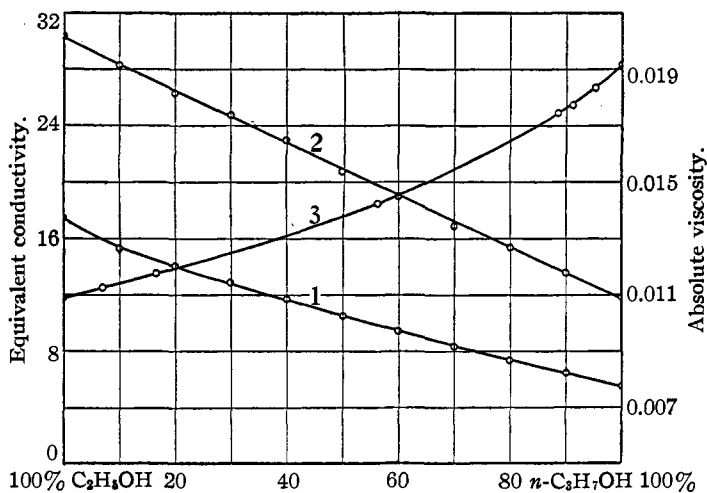


Fig. 4.—Lithium nitrate in ethyl alcohol-*n*-propyl alcohol mixtures. Curve 1, composition-conductivity, 0.1 *M*; Curve 2, 0.00625 *M*; Curve 3, composition-viscosity.

TABLE VII

THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN THE SYSTEM ETHYL ALCOHOL-
ISOPROPYL ALCOHOL AT 25°

Molar concn.	100% C ₂ H ₅ OH	90%	80%	70%	60%	50%	40%	30%	20%	10%	100% C ₃ H ₇ OH
0.1	17.47	14.88	12.99	11.30	9.741	8.282	6.854	5.498	4.179	3.071	2.058
.05	20.74	17.42	15.99	13.92	12.01	10.22	8.513	6.853	5.233	3.981	2.447
.025	24.07	21.31	18.24	16.80	14.59	12.47	10.50	8.478	6.573	5.078	2.998
.0125	27.36	24.25	22.05	19.92	17.35	14.98	12.66	10.48	8.264	6.478	3.812
.00625	30.40	27.80	25.36	22.94	20.19	17.56	15.21	12.84	10.31	8.222	4.921
Sp. cond. of pure solvent											
× 10 ⁻⁴	0.85	2.56	2.60	2.54	2.04	1.57	1.23	0.88	0.60	0.46	0.51

n-Propyl Alcohol-Isopropyl Alcohol Mixtures (8).—Conductivity data are given in Table IX; viscosity and density data, in Table X. Curves are shown in Fig. 6. Fewer mixtures were used in this system since it was expected that a very nearly linear relationship would be found. Results show this to be true.

TABLE VIII

VISCOSITIES AND DENSITIES OF ETHYL ALCOHOL-ISOPROPYL ALCOHOL MIXTURES AT 25°

C ₂ H ₅ OH, %	Viscosity	Density	C ₂ H ₅ OH, %	Viscosity	Density
100	0.01095	0.7852	40	0.01605	0.7827
90	.01150	.7849	30	.01709	.7823
80	.01224	.7843	20	.01856	.7819
70	.01302	.7839	10	.01985	.7822
60	.01388	.7835	0	.02183	.7807
50	.01485	.7832			

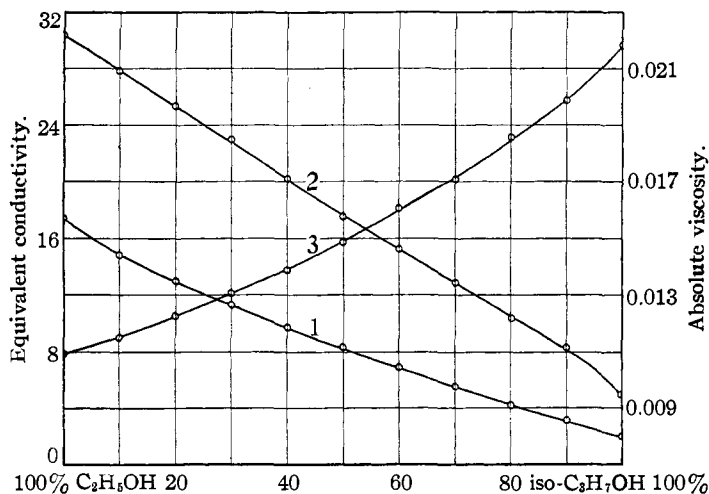


Fig. 5.—Lithium nitrate in ethyl alcohol-isopropyl alcohol mixtures. Curve 1, composition-conductivity, 0.1 *M*; Curve 2, 0.00625 *M*; Curve 3, composition-viscosity.

TABLE IX

THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN THE SYSTEM *n*-PROPYL ALCOHOL-ISOPROPYL ALCOHOL AT 25°

Molar concn.	100% <i>n</i> -C ₃ H ₇ OH	80%	60%	40%	20%	100% iso-C ₃ H ₇ OH
0.1	5.564	4.886	4.174	3.452	2.782	2.058
.05	6.854	6.023	5.133	4.267	3.419	2.447
.025	8.381	7.389	6.349	5.325	4.276	2.998
.0125	10.10	8.998	7.853	6.664	5.349	3.812
.00625	11.85	10.76	9.518	8.272	6.792	4.921
Sp. cond. of pure solvent × 10 ⁻⁶	4.96	4.12	3.16	2.29	1.39	0.51

TABLE X

VISCOSITIES AND DENSITIES OF *n*-PROPYL ALCOHOL-ISOPROPYL ALCOHOL MIXTURES AT 25°

<i>n</i> -C ₃ H ₇ OH, %	Viscosity	Density	<i>n</i> -C ₃ H ₇ OH, %	Viscosity	Density
100	0.01962	0.7957	40	0.02082	0.7889
80	.02004	.7962	20	.02130	.7852
60	.02040	.7924	0	.02183	.7807

Discussion

The various systems studied have been numbered and will subsequently be referred to by number. Nos. 1 and 5 are the water-methyl alcohol and methyl alcohol-ethyl alcohol systems, respectively, previously reported by Whitman and Spencer.

In systems 1, 2, 3 and 4, *i. e.*, those which contain water as one of the components of the solvent, a maximum viscosity is found for some composition. In only one of these, No. 1, does the conductivity-composition curve exhibit a minimum. In systems 5, 6, 7 and 8, *i. e.*, those systems which contain two alcohols as the components of the solvent, no maxima or minima are observed in either the viscosity or the conductivity curves.

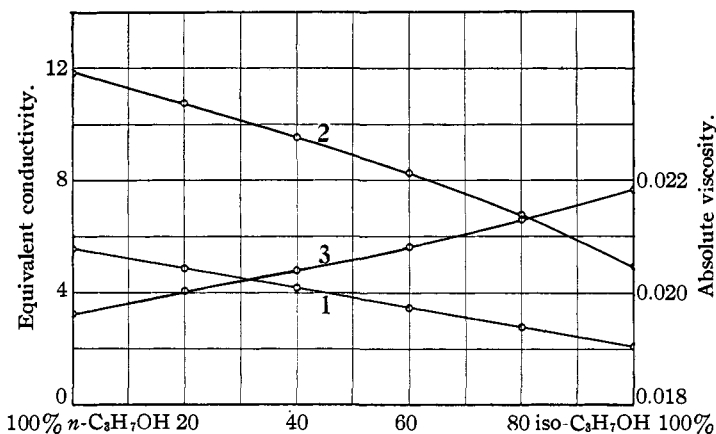


Fig. 6.—Lithium nitrate in *n*-propyl-isopropyl alcohol mixtures. Curve 1, composition-conductivity, 0.1 *M*; Curve 2, 0.00625 *M*; Curve 3, composition-viscosity.

In several of the latter cases the curves are very nearly straight lines, as might be expected since the components of the solvent are very similar chemically.

Jones concluded that a minimum in the conductivity curve was the direct result of the increase in viscosity. However, in attempting to explain this minimum other factors must also be considered, such as change in degree of dissociation with change in composition of solvent. But Jones¹⁰ found that the degree of dissociation in a solvent containing 50% water and 50% methyl alcohol was greater than that in either pure solvent. This factor should therefore cause an increase in conductivity. It is thus evident that the viscosity explanation alone is far from satisfactory as a means of explaining the observed conductivity changes.

The viscosity data here recorded are believed to be accurate to ap-

¹⁰ Jones and Carroll, *Am. Chem. J.*, **32**, 521 (1904).

proximately 0.05%. For the viscometer used the time of outflow for water was approximately 1000 sec., while the stop-watch used was accurate to 0.2 sec. An error of 0.4 sec. in time would thus introduce an error of 0.04%. If the weighings involved were accurate to only 1 mg., then the errors of weighing for the pycnometer used (about 25 g. capacity) would amount to only 0.004%. According to the "International Critical Tables," Vol. V, p. 10, the change in viscosity of water per 0.01° at 25° is approximately 0.02%. Thus the appreciable errors will total not more than 0.06% and it is believed that an error of 0.05% represents the reasonable degree of precision of results obtained.

It should be noted that the values recorded for the water-*n*-propyl alcohol system are probably the least accurate of the conductance data, since the solvent corrections for this system are unusually large.

Summary

1. Measurements have been made of the conductivities of lithium nitrate in the mixed solvents containing various proportions of the following components: water, ethyl alcohol, *n*-propyl alcohol and isopropyl alcohol.

2. Viscosity and density determinations have also been made on the same pure solvent systems.

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THE EFFECT OF LIGHT ON THE FERROCYANIDE-FERRICYANIDE IODINE-IODIDE EQUILIBRIUM

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It is well known that ferric salts oxidize iodides in aqueous solution at a moderate rate and that ultimately an equilibrium, $2\text{Fe}^{+++} + 2\text{I}^- \rightleftharpoons 2\text{Fe}^{++} + \text{I}_2$, is reached. Sasaki¹ investigated the effect of light on systems containing the substances involved in this equilibrium. Using sunlight and light from an incandescent lamp, he found that the illuminated systems always contained less titratable iodine than similar unilluminated systems. He further adduced evidence that the effect of the light was a displacement of the equilibrium rather than some other mode of disappearance of iodine. Further photochemical experiments were made by Rideal and Williams² who concluded, among other things, that the region of visible photoactive radiation was within the range 5500-6500 Å., and that one quantum of absorbed radiant energy caused one molecule of iodine to react. However,

¹ N. Sasaki, *Z. anorg. Chem.*, **122**, 61 (1922).

² E. K. Rideal and E. G. Williams, *J. Chem. Soc.*, **127**, 258 (1925).