[CONTRIBUTION NO. 634, FROM THE CHEMISTRY LABORATORIES OF INDIANA UNIVERSITY]

Physical-chemical Studies of Solutions in Anhydrous Ethylenediamine. I.[1] Conductance Measurements of Solutions of Sodium, Silver and Tetra-N-butylammonium Nitrates and Iodides

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Relatively little work has been reported pertaining to physical-chemical properties of solutions of electrolytes in anhydrous ethylenediamine (dielectric constant 12.9). Strong electrolytes when dissolved in solvents of low dielectric constant often take on the properties of weak electrolytes, as is the case of the reciprocal salt pairs whose conductances in ethylenediamine are reported in this manuscript. Calculations have been made for the Fuoss plots for all six salts.

I. Introduction

Bromley and Luder and others[2] have reported the conductances of silver iodide, silver nitrate and potassium iodide in this solvent to concentrations low enough to permit the calculation of the limiting equivalent conductance and the thermodynamic dissociation constant.

Our value for the conductance of silver nitrate agrees fairly well with that previously measured by the above investigators. However, our value of Λ_0 for silver iodide is considerably greater than theirs in Table II. This fact is not difficult to understand since their results were obtained by a dilution procedure, rather than the concentration method here reported. The lowest specific conductance obtained by us for the pure solvent was 2×10^{-7} mho. The lowest previously reported is 0.9×10^{-7} mho[3]. However no range was given. Putnam and Kobe[3] reported a range of 1.4×10^{-6} to 2.6×10^{-6} mho.

A test of the Fuoss relationship

$$\frac{F(z)}{\Lambda} = \frac{C\Lambda f^2}{K'\Lambda_0(F(Z))} + \frac{1}{\Lambda_0}$$

was made and from which the dissociation constant K' was determined. This plot was linear for all salts used, at all concentrations less than $3 \times 10^{-7} D^3$, where D is the dielectric constant.

II. Experimental

A. Preparation of the Solvent.—The ethylenediamine used in this study was obtained from Eastman Organic Chemicals and was of 95–100% purity. A double distillation and fractionation from metallic sodium was necessary after refluxing for several days over metallic lithium. All operations were carried out in an atmosphere of dry hydrogen freed from both carbon dioxide and oxygen.

The progress of purity was followed by continued conductance measurements. When the ethylenediamine of lowest specific conductance was fractionating (lowest obtained for the solvent after many trial distillations was 2×10^{-7} mho) the solvent was allowed to run into a dried conductance cell previously flushed with hydrogen. Since the value of the solvent conductance was appreciable, it was subtracted from that of the solution in every case.

Infrared determinations of the purified solvent dissolved in pure carbon tetrachloride indicated the complete absence of CO_2 and water.

B. Preparation and Purification of the Salts.—Reagent and analytical grade silver and sodium nitrate and sodium iodide were used after one recrystallization. Silver iodide was made from analytical grade reagents, washed, and dried in the complete absence of sunlight. After drying at 100°, the silver iodide retained its bright yellow color indefinitely.

Tetra-*n*-butylammonium iodide was prepared by the method of Laitinen and Wawzonek[4] from Eastman tri-*n*-butylamine and *n*-butyl iodide. After five crystallizations from ethyl acetate, the quaternary salt melted at 144.0°.

Tetra-*n*-butylammonium nitrate was prepared by metathesis from the above iodide and silver nitrate in absolute ethanol.[5] This salt was recrystallized from pure benzene to a constant melting point.

Conductance Cells.—The conductance cells were especially prepared in this Laboratory of Pyrex glass and platinized platinum electrodes following the suggestions of Jones and Bollinger.[6]

The solvent was distilled directly into the cell. Standard taper glass caps prevent possible contamination while the cell is in the thermostated bath. Caps and stopcocks were lightly greased with Dow–Corning Silicone stopcock grease (addition of this grease to the cell contents caused no appreciable increase of the conductance). The volume of the solution contained between the electrodes was approximately 34 ml.

The cell constants were determined using the values for both 0.01 demal[7] and 0.01 normal potassium chloride solutions.

The salts were weighed out in covered Pyrex cups, made from 8 and 10 mm. tubing. The cups were made flat on the bottom and were about 1.5 cm. high. The salt was weighed by difference on a micro-balance having a sensitivity of 98 with a two-gram load on both pans.

The salt samples were added consecutively to increase the concentration through a 29/42 taper into the mixing compartment while a slight positive pressure of hydrogen was maintained in the cell through side arm. The solution could be forced into the electrode compartment at will by an increase in pressure of the hydrogen in the closed cell.

General Procedure.—The cell was cleaned, dried and weighed. Pure solvent was distilled into the cell and conductance determined at constant temperature. Resistance values were checked for constancy for a period of ten minutes after obtaining temperature equilibrium. After this the cell was withdrawn from the bath and self-rinsed. Content of the electrode chamber was allowed to mix again with the content of the main part of the cell. After self-rinsing two or three times, displacement being accomplished by force of gravity and dry hydrogen pressure, the cell was returned to the bath. If the resistance of the sample showed no appreciable change, the above procedure was repeated until three consecutive resistance values agreed, within one part in ten thousand.

Densities of the solutions were obtained at 25.00 ± 0.01° with a 25-ml. picnometer. The over-all precision of the results is better than one part in 1000. The data are reported to four significant figures.

Bridges and Accessories.—A Jones Conductivity Bridge, Leeds and Northrup Catalog Number 4666 with oscillator Catalog Number 9842 was used. The oscillator frequency

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[1] The work described in this manuscript was presented before the 124th Meeting of the American Chemical Society at Chicago, Illinois, September, 1953, and is abstracted from the dissertation presented by Billy B. Hibbard to the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, February, 1952.

(2) W. H. Bromley and W. F. Luder, THIS JOURNAL, **66**, 107 (1944).

(3) G. L. Putnam and K. A. Kobe, *Trans. Electrochem. Soc.*, **74**, 609 (1939).

(4) H. A. Laitinen and S. J. Wawzonek, *ibid.*, **64**, 1865 (1942).

(5) N. L. Cox, C. A. Kraus and R. M. Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

(6) G. Jones and G. Bollinger, THIS JOURNAL, **53**, 411 (1931).

(7) G. Jones, K. J. Mysels and W. Juda, *ibid.*, **62**, 2919 (1940).

was calibrated against the National Bureau of Standards frequency of 400 and 600 cycles per second as broadcast by Radio WWV. Correction settings for 500, 1000 and 2000 cycles per second were determined and resulted in a maximum possible error of less than one cycle per second. The exactness of the frequency had a minor effect on the results since the resistance values were appreciably the same at all frequencies. This fact indicated that there were no polarization effects and that the electrodes had been satisfactorily platinized.

The null point of balanced resistance and capacitance was indicated by a horizontal line on the screen of an oscilloscope instead of by phones. Accuracy of detection of resistance settings by this method was greater than the stated accuracy of the Jones bridge, 0.02%.

Kerosene, Fuel Oil No. 1, was used in the constant temperature bath to reduce stray capacitance. The temperature of the bath was measured by a Beckmann differential thermometer calibrated against a National Bureau of Standards calibrated mercury in glass thermometer and also against a platinum resistance thermometer previously calibrated by the Bureau of Standards. The temperature was controlled by means of a DeKhotinsky Thermoregulator in conjunction with a Thyratron tube regulator. The bath temperature was maintained at 25.000 ± 0.003°.

Discussion.—The plots of specific conductance *versus* molality for each of the six salts studied produces a smooth curve.

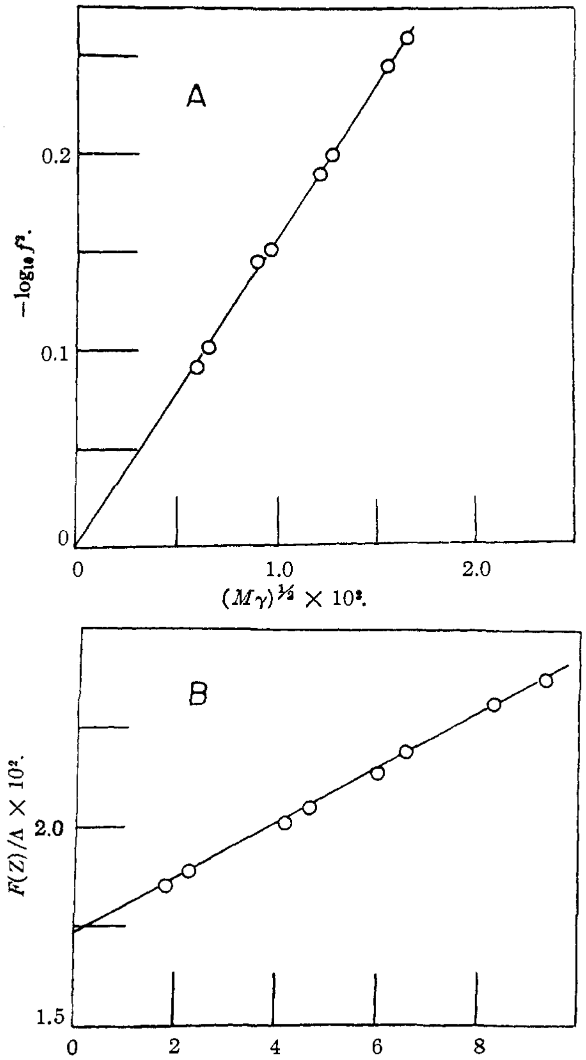

Fig. 1.—Fuoss plots for Bu_4NNO_3.

TABLE I

$M \times 10^5$	$Ls \times 10^5$	Λ	γ	f^2	$\frac{F(Z)}{\Lambda} \times 10^2$	$\frac{M\Lambda f^2}{F(Z)} \times 10^3$
			$AgNO_3$			
31.16	1.374	49.45	0.8682	0.5806	1.873	8.614
59.96	2.273	42.52	.7659	.4925	2.123	12.40
65.59	2.465	42.10	.7623	.4773	2.133	13.10
99.49	3.473	39.14	.7308	.4102	2.225	16.36
154.60	4.864	35.29	.6726	.3446	2.417	19.65
181.30	5.318	32.87	.6316	.3269	2.574	20.34
192.60	5.755	33.51	.6500	.3106	2.503	21.30
216.20	6.013	31.16	.6066	.3020	2.681	21.74
			AgI			
5.48	0.1507	30.96	0.4267	0.8525	3.162	1.312
7.33	.1794	27.54	.3803	.8400	3.548	1.542
14.08	.2800	22.39	.3110	.8039	4.339	2.317
16.12	.2956	20.64	.2869	.7991	4.703	2.433
17.72	.3235	20.55	.2861	.7907	4.717	2.639
29.65	.4268	16.21	.2268	.7630	5.951	3.376
33.66	.4758	15.92	.2232	.7513	6.046	3.714
76.18	.7366	10.89	.1542	.6995	8.754	5.405
			$NaNO_3$			
5.574	0.2873	57.87	0.8106	0.8009	1.678	2.369
10.63	.4711	49.77	.7032	.7516	1.935	3.677
15.03	.6478	48.39	.6886	.7145	1.976	4.666
22.88	.8440	41.43	.5939	.6805	2.290	6.055
44.03	1.386	35.34	.5137	.6086	2.648	7.606
55.09	1.587	32.35	.4732	.5868	2.875	10.01
95.67	2.296	26.95	.4006	.5240	3.396	13.14
128.8	2.793	24.36	.3650	.4883	3.718	15.06
			NaI			
6.214	0.3045	54.94	0.9475	0.7759	1.759	2.445
7.361	.3560	54.35	.9419	.7596	1.769	2.812
15.93	.7239	51.07	.9010	.6733	1.850	5.160
27.19	1.201	49.52	.8884	.5983	1.876	7.735
40.88	1.689	46.33	.8442	.5413	1.974	9.996
58.85	2.236	42.71	.7895	.4909	2.111	12.17
60.16	2.321	43.25	.8017	.4840	2.079	12.49
			Bu_4NNO_3			
4.503	0.2172	54.30	0.9200	0.8087	1.788	1.810
6.079	.2867	53.16	.9042	.7831	1.818	2.323
12.66	.5616	49.97	.8629	.7084	1.906	4.177
14.88	.6535	48.76	.8451	.6910	1.946	4.686
20.73	.8643	46.94	.8208	.6504	2.004	5.976
24.08	.9740	45.60	.8006	.6327	2.055	6.578
34.90	1.327	42.85	.7612	.5844	2.161	8.376
42.07	1.562	41.82	.7483	.5571	2.198	9.466
			Bu_4NNI			
5.478	0.2622	53.67	0.9247	0.7905	1.802	2.143
6.511	.2933	50.74	.8759	.7815	1.903	2.374
13.28	.5730	48.40	.8479	.7042	1.966	4.241
14.67	.6150	47.20	.8284	.6952	2.012	4.502
24.41	.9631	44.43	.7907	.6311	2.108	6.490
34.72	1.299	42.13	.7584	.5856	2.198	8.217
38.27	1.413	41.41	.7481	.5716	2.228	8.755
54.69	1.893	38.84	.7116	.5210	2.342	10.84

The equivalent conductance *versus* the square root of the concentration gives curves which are typical of weak electrolytes. The slopes are extremely steep for the low concentrations measured. A similar plot for a strong electrolyte in water would give a range of possibly two Λ units, while

TABLE II

Λ_0 AND K' FOR VARIOUS SALTS IN ETHYLENEDIAMINE AT 25°

Salt	Λ_0	Λ_0[8] Other investigators	$K' \times 10^{-4}$
$AgNO_3$	63.5	(61.4)	5.740
AgI	72.8	(48.8)	0.168
$NaNO_3$	75.1		1.120
NaI	61.4		6.860
Bu_4NNO_3	59.3		5.110
Bu_4NI	57.8		5.320

in the case of the same electrolytes in ethylenediamine a range of 10 to 30 of these same units would be found over the same concentration range.

The plots of the reciprocal of the equivalent conductance against M gives a straight line with the intercepts at $1/\Lambda_0$. The values of Λ_0 obtained from these curves are slightly lower than those obtained from the Fuoss calculation. The cause of this deviation is, no doubt, the fact that no correction has been made for incomplete dissociation.

The plots of $-\log f^2$ *versus* $\sqrt{M\gamma}$ yield a straight line, an example of which is shown in Fig. 1 for tetra-*n*-butylammonium nitrate.

When $F(Z)/\Lambda$ is plotted against $M\Lambda f^2/F(Z)$ a straight line results (Fig. 1) whose slopes and intercepts were calculated by the method of least squares yielding Λ_0 and the dissociation constant, K', as shown in Table II.

The possibility of finding a solute possessing strong electrolytic properties in ethylenediamine is quite unlikely.

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[CONTRIBUTION FROM THE LEWIS FLIGHT PROPULSION LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

Flame Propagation. V. Structural Influences on Burning Velocity. Comparison of Measured and Calculated Burning Velocity

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The fundamental burning velocities of thirty-one hydrocarbons of which two contained deuterium, six oxygenated compounds, isopropylamine and acrylonitrile have been determined. The burning velocities of twelve of the normally liquid hydrocarbons were measured in a burner type apparatus at elevated initial temperatures, and the fundamental burning velocities at 298°K. were determined by extrapolation of these data. With the exception of acrylonitrile, all other burning velocity measurements were made in a horizontal, open end tube. Some qualitative conclusions are drawn as to the effect of the molecular structures of the fuels on the burning velocities. Burning velocity trends previously established for 56 other pure hydrocarbons are in the main borne out, and are extended to include the general behavior of the cyclic hydrocarbons. The behavior of the oxygen and the nitrogen compounds is discussed. Equilibrium flame temperatures and active particle concentrations for the mixtures at which the maximum burning velocities occurred were calculated for thirty-seven of the compounds. The Tanford–Pease "square root law" of burning velocity, which relates active particle concentration with burning velocity, was used in a modified form to calculate the burning velocities for all but the deuterated compounds. An empirical average "rate constant" determined from the hydrocarbon data with the modified square root law equation had a value of 2.57×10^{-13} ml. molecule^{-1} sec.$^{-1}$ The burning velocities of the pure hydrocarbon compounds correlate better with relative active particle concentrations than do those compounds containing oxygen or nitrogen. This is reflected in the values of the calculated burning velocities for the latter compounds.

Introduction

One of the major problems of high speed flight propulsion research involves the behavior of the fuel–air mixture during the combustion process. In order to gain some basic understanding of this phenomenon, a program of study of fundamental combustion properties was undertaken at this laboratory. One of the properties investigated has been the rate of flame propagation of various gaseous hydrocarbons in air, and the relation of these rates to the molecular structures of the fuels. Previously published results include laminar burning velocities determined by both the tube[1,2] and the Bunsen burner method[3,4] and consideration of these data in terms of existing theories of flame propagation.[3–7] A simplified theoretical equation based on an active particle diffusion mechanism has been used to calculate burning velocities for a large number of pure hydrocarbons in air.[5,6] In the present work burning velocities in air of twenty nine pure hydrocarbons, two deuterated hydrocarbons, six oxygenated hydrocarbons, acrylonitrile and isopropylamine are presented and the semi-theoretical calculations are extended to include the majority of these latter data. Burning velocity measurements were made in either a horizontal tube, or in a Bunsen burner type apparatus.

Ideally, a comprehensive theory of flame propagation[8] should be used to calculate burning velocities. However, the information needed for the solutions of the differential equations in such a treatment is available for only the very simplest of systems. A less exact but more convenient approach is to use equations derived from either a thermal or an active particle diffusion model of the combustion mechanism. The thermal theory is based on the assumption that the rate at which heat

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(4) G. L. Dugger and D. D. Graab, "Fourth Symposium on Combustion," Williams and Wilkins, Baltimore, Maryland, 1953, p. 302.

(5) D. M. Simon, THIS JOURNAL, **73**, 422 (1951).

(6) D. M. Simon, *Ind. Eng. Chem.*, **43**, 2718 (1951).

(7) G. L. Dugger and D. M. Simon, "Fourth Symposium on Combustion," Williams and Wilkins, Baltimore, Maryland, 1953, p. 336.

(8) Such a theory would include processes of diffusion, heat transfer and chemical kinetics in addition to the more general hydrodynamic considerations. A detailed treatment of the characteristics of steady state one-dimensional flames is given by J. O. Hirschfelder and C. F. Curtiss, *J. Chem. Phys.*, **17**, 1076 (1949).