[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LELAND STANFORD JUNIOR UNIVERSITY.]

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS IN DIMETHYLAMINE, TRIMETHYLAMINE, ETHYLAMINE, DIETHYLAMINE, TRIETHYLAMINE, AND PROPYLAMINE.[1]

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Introduction.

The work described in this paper was undertaken as a contribution to our knowledge of the properties of the ammono alcohols[2] and ethers (alkyl amines) as electrolytic solvents.

It seemed desirable to gather data on the properties of solutions in that class of ammono alcohols of which dimethylamine is a representative member and also to study the ammono ethers or tertiary amines. Though it was to be expected, from the low dielectric constants of the solvents,[3] that the solutions would have very high resistances the improved type of apparatus available made it possible to measure the conductivity with a high degree of accuracy. In fact, it was found that the conductivity of a given solution could be measured very much more accurately than the solution could be duplicated.

The surprising observations of Shinn[4] that potassium iodide is insoluble in ethylamine led to a study of the solubility of salts in the amines, preliminary to beginning the other work. Potassium iodide is very soluble in liquid ammonia, Franklin[5] having measured the conductivity of a 7.1 molar solution. The salt is also very soluble in methylamine, Fitzgerald[6] having measured the conductivity of a 1.7 molar solution. As accurate data[7] for the conductivity of potassium iodide in liquid ammonia through a wide range of concentrations is already available for comparison, this solute would have been most desirable to work with in the amines.

The solubility tests[8] were disappointing in that they showed that only a very few salts were sufficiently soluble to be of any value for use in making conductivity measurements, though in a surprising number of cases on the introduction of the solvent an "addition" compound was

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[1] Submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Stanford University.

[2] For the development of the ammonia system of compounds, together with the nomenclature. See Franklin, *Am. Chem. J.*, **47**, 285 (1912).

[3] Schlundt, *J. Phys. Chem.*, **5**, 503 (1901).

[4] Shinn, *ibid.*, **11**, 537 (1907).

[5] Franklin, *Z. physik. Chem.*, **69**, 272 (1909).

[6] Franklin, Gibbs and Fitzgerald, THIS JOURNAL, **29**, 1389 (1907).

[7] *Loc. cit.*

[8] Elsey, THIS JOURNAL, **42**, 2080 (1920).

formed, and though, on allowing the tube to stand, the bulky precipitate first formed became crystalline and showed evidences of being somewhat soluble only a few even fairly soluble salts were found. Many salts which are quite soluble at room temperature are only very slightly soluble at —33.5°, the temperature of the conductivity measurements. The tendency to form addition compounds seemed to be almost wholly lacking in the tertiary amines.

Of the 80 salts which were tested, the following were the only ones which seemed to be sufficiently soluble and which could be obtained sufficiently pure to warrant further investigation: silver nitrate, silver iodide, lithium chloride, hydrogen chloride (that is, the amine addition compound, as ethylamine hydrochloride) and barium thiocyanate.

Preparation of Substances.

Solutes.—The silver nitrate was prepared by twice recrystallizing a commercial sample of the salt and drying over sulfuric acid.

Silver Iodide.—A solution of silver nitrate was treated with a slight excess of potassium iodide solution and the resulting precipitate washed free from potassium nitrate and potassium iodide, then dried over sulfuric acid.

Lithium Chloride.—A recrystallized sample of lithium chloride was carefully dried over sulfuric acid in a vacuum desiccator.

Barium Thiocyanate.—A pure commercial sample of this salt was dried in a vacuum desiccator over sulfuric acid.

Amine Hydrochlorides.—These salts were all pure commercial preparations and were simply dried in a vacuum desiccator over sulfuric acid.

The slightest trace of moisture in an amine solution of either silver nitrate or silver iodide causes the salt to blacken and deposit metallic silver. Also, the amine hydrochlorides and lithium chloride are so deliquescent that it is almost impossible to weigh out these salts in the open air or even transfer from one container to another without their suffering contamination from the water vapor in the atmosphere. For this reason, the bottling arrangement described later was devised and proved very satisfactory.

Solvents.

The amines were pure commercial samples which had been stored in sealed glass containers over metallic sodium for several years and were thus thoroughly dry. To decrease the risk in working with the limited amount of solvent available, at the beginning of work with a given amine it was distilled over into an evacuated steel cylinder which was fitted with a good fitting steel needle-valve. The nipple of this valve was silver-soldered to a platinum tube and this in turn was sealed to the glass measuring apparatus by means of sealing-in glass.

Apparatus.

Conductivity Measuring Set.—The source of current was a small Vreeland oscillator, built to give frequencies of either 500 or 1000 cycles per second. The measurements were all made using the higher frequency as the tone obtained is much easier to hear in the telephone, which was tuned to this frequency. The resistance box was a 5-dial 100,000-ohm Curtis coil box. In working with dilute solutions, the capacity in the bridge arms was balanced by means of small variable rotary condensers, but with concentrated solutions these proved insufficient and a subdivided mica condenser, having a total capacity of 0.9 microfarad, was built and used. All precautions suggested by Washburn[1] were taken as to the shielding of cables and the individual parts of the apparatus from each other, the shields being carefully grounded.

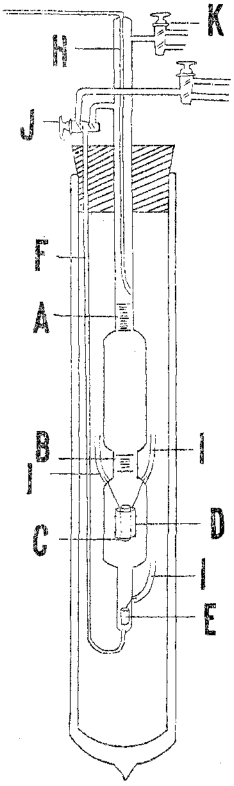

Fig. 1.

Conductivity Cell.—At the boiling point of liquid ammonia (—33.5°),[2] which was the temperature at which the measurements were made, the alkyl amines have too low a vapor pressure to be conveniently adjusted to a given volume by the method used by Franklin and his students[3] in working with liquid ammonia and methylamine.[4] For this reason the conductivity cell used was designed as shown in Fig. 1.

Two scales, A and B, graduated in millimeters, were etched on the cell as shown. The volume of the solution was found by reading the position of the meniscus with respect to these scales by means of a telemicroscope having an eyepiece graduated in tenths of a millimeter. The capillary F, through which the solution was removed, was large, to avoid risk of stoppage, and it was necessary, either always to make a volume reading with the liquid in the capillary at the same point, which was difficult, or else to apply a correction which varied with the position of the meniscus in the capillary. This second method was the one used, the correction applied to

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[1] Washburn and Bell, This Journal, 35, 177 (1913). Also see Catalog 48 of Leeds and Northrup Company.

[2] Franklin, *Ann. Phys.*, 24, 367 (1907). From the recent work of Cragoe, Meyers and Taylor, This Journal, 42, 206 (1920), it appears that the most probable value for the boiling point of ammonia is —33.35°, but the measurements here described were all carried out at a temperature of —33.5°.

[3] *Ibid.*, 27, 191 (1905).

[4] Gibbs, *ibid.*, 29, 1389 (1907); Fitzgerald, *J. Phys. Chem.*, 7, 254 (1903).

a given volume reading never being greater than 0.3 scale divisions, corresponding to a volume of 0.02 cc.

The volume of the cell was found by filling it to various points on the scale with water from a weighing pipet, the temperature being adjusted to 20°. In this way, the volume of the cell was found over the whole range of the 2 scales with an error of less than 0.1%. The volume of liquid required to fill the cell at room temperature to the first graduation of the lower scale was 6.093 cc. and to the top line of this scale 6.336 cc., while the volumes required to fill the cell to the top and bottom graduations of the upper scales were 11.96 cc. and 12.75 cc., respectively.

If the coefficient of expansion of soft glass is 8.5×10^{-6} then the cell would decrease in volume by 0.14% in changing from 20° to —33.5°, the temperature of the measurements. Moreover the decrease in the area of the platinum electrodes on changing to —33.5° would be 0.10% and would tend to increase the cell constant, K, by that amount. Also, the decrease in length of the glass rivets holding the electrodes apart would be 0.04% and would decrease K, leaving the probable increase in K about 0.06%. This uncorrected increase in K will partially balance an uncorrected decrease in the cell volume leaving a probable error in the results of about 0.08%. Since the error is undoubtedly small and cannot easily be experimentally determined, no attempt has been made to apply any of the above corrections to the conductivity results.

The 3 platinum electrodes C, D, and E, which were lightly coated with platinum black, each have an area of about 3 sq. cm. Electrodes C and D are concentric cylinders, held in position with relation to one another by glass rivets. The platinum leading-in wires ended in glass mercury wells I, I, I. Assuming the specific conductivity of a 0.02 N potassium chloride solution to be 0.002501 at 20°,[1] the cell constant K_1, for the pair of electrodes C and D, was 0.05374 Kohlrausch unit. The constant K_2, for the pair of electrodes C and E, was 10.95 units. These values were checked frequently and found to be constant. Electrodes C and E were used for measuring good conducting solutions. Electrodes C and D were used for solutions where the resistance between these electrodes was greater than 100 ohms. With solutions having a lower resistance between them the heating effect of the current was very noticeable, and where the resistance fell below 75 ohms there was a marked discrepancy between molecular conductivities calculated from these electrodes and Electrodes C and E.

Viscometer.—The viscometer used is shown in Fig. 2 and was an adaptation of a 2-capillary instrument suggested by Bingham,[2] the chief modification being in the method used in introducing the liquid to be

[1] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," 1898.

[2] *J. Ind. Eng. Chem.*, **6**, 233 (1914).

measured. This was forced in through Stopcock F and Capillary H, until the viscometer was filled to Mark A in Arm L, and Mark C in Arm R. Bingham used an automatic pipet method which filled the cell with exactly the same quantity of liquid each time, but this method was not applicable here, because of the difficulty of manipulation. In using the cell, after the proper amount of liquid had been introduced, Arm L was opened to atmospheric pressure by turning Stopcock E, and the liquid was forced to rise in Arm L, by means of hydrogen pressure applied through the 2-way stopcock D, until Bulb K was almost empty. The stopcocks D and E were now reversed, causing Arm R to be open to atmospheric pressure and the liquid in Arm L to be under a known hydrogen pressure. The time required for the meniscus to fall from Mark A to Mark B was then noted. The pressure was measured by means of a water manometer which was connected to the apparatus through a drying tube, both the drying tube and the hydrogen reservoir being protected against sudden changes in temperature by wrapping with hair felt.

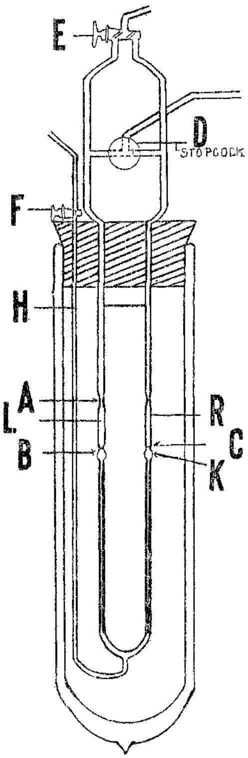

Fig. 2.

If the 2 arms of the instrument had been identical as to size and shape, the time taken to reverse the above process, the pressure remaining constant, should have been the same as the first time of flow from left to right. If the volume of liquid used each time is the same, then it is possible, according to Bingham, to apply a correction factor so that the viscosity may be determined from a single reading in either direction. As it was impossible in our case to control the filling of the cell within better than ±0.05 cc. in a total volume of less than 2 cc. a reading was taken in each direction and the mean of the 2 calculated results taken as the viscosity of the solution.

The equation given by Bingham for the use of the above viscometer is

$$\eta = Ctp - (mn\rho v/8\pi tl) \qquad (1)$$

where η is the viscosity in absolute units, C a constant for the given instrument, p the pressure in grams per sq. cm., m a constant, n the number of capillaries, v the volume of flow, ρ the density, and l the length of the capillaries. Substituting for the constants the values $m = 1.12$, $n = 2$, $v = 1.24$, $\pi = 3.1416$, $l = 20$, the above equation reduces to

$$\eta = Ctp - (0.0054\rho/t) \qquad (2)$$

Assuming the viscosity of water at 25° to be 0.01006[1] and the density to be 0.997 and substituting these values in Equation 2 together with the experimentally determined times of outflow with the corresponding pressures, the value of C was found to be 5.66×10^{-7}.

Density Apparatus.—In order to determine ρ for use in correcting the viscosity equation, a modification of Hare's method[2] of balancing columns was used. A diagram of the apparatus is shown in Fig. 3. The solution whose density was to be determined was forced into the U-tube which was surrounded by an ammonia bath at —33.5° through the stopcock and capillary Tube A. The stopcock B, which had been set to connect the 2 arms of the U-tube, was then turned to open the left arm to atmospheric pressure. By means of a third stopcock, C, the right arm was opened momentarily to a hydrogen reservoir which was fitted with a water manometer. Then the stopcocks were all closed and the heights of the solution column and of the water column measured with a cathetometer and compared. The results obtained were very inaccurate as the small quantity of solution available for each measurement made it necessary to make the U-tube of rather small-bore glass tubing and the difference in level in the 2 arms of the tube was usually less than 10 cm. In addition to this, trouble was had from an improper cathetometer mounting. However, the measurements were sufficiently accurate for the correction of the viscosity, as the value of the expression $0.0054\ \rho/t$ rarely exceeded 0.4% of the total value for the viscosity. Indeed it was found that for any but the most concentrated solutions it was sufficient to calculate the density of a solution from the normality, assuming no volume change in the solvent on the solution of the salt.

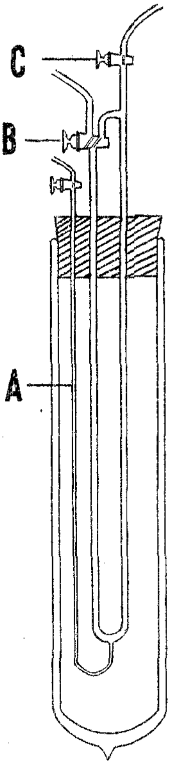

Fig. 3.

Recovery of the Solvents.—As the amines are expensive, their recovery from the solutions was essential and all the discarded solutions were run into a waste jar which was placed in a liquid ammonia bath. The hydrogen gas used for stirring and transferring the solutions was necessarily saturated with the solvent vapor, therefore it also was passed into the waste jar, whence it escaped through a gas wash-bottle containing dil. sulfuric acid. To recover the amine, the hydrogen was removed from the waste jar and the ammonia in the Dewar tube bath replaced

[1] Bingham and White, *Z. physik. Chem.*, 80, 670 (1912).

[2] The use of this method is a suggestion of Professor H. P. Cady, of the University of Kansas.

by warm water. By adjusting the proper stopcocks, the amine was then distilled directly back into its steel container.

Temperature Control.—All the measurements were made at the boiling point of ammonia, —33.5°, the different units of the apparatus being fitted with rubber stoppers and placed in Dewar tubes containing liquid ammonia. The temperature was maintained constant within ±0.05° by means of a toluene regulator opening or closing an electric circuit which actuated a telegraph sounder to whose arm was fastened the stem of a small steel needle-valve. The opening of this valve allowed a suction pump to increase the rate of boiling of the ammonia, causing the temperature to fall until the regulator functionated and closed the needle-valve again. The device is similar to that used by Franklin and Cady[1] excepting that the sounder arm controls a valve stem rather than pinching down on a rubber tube. The temperature was read on mercury thermometers which had been carefully checked against a certified thermometer. In the figures, for simplicity, the thermometers, toluene bulbs, and bath control tubes are omitted. The hydrogen used in transferring the solution from one part of the apparatus to another was generated by the electrolysis of 10% sulfuric acid. The hydrogen was then passed through an alkaline pyrogallic acid solution, traces of oxygen were burned out in a hot-wire tube, the gas was then dried by means of a chain of calcium chloride and phosphorus pentoxide drying tubes and was then stored under pressure in a glass reservoir.

Bottling Device.—This was devised to transfer the deliquescent amine hydrochlorides and lithium chloride from the large glass-stoppered stock-weighing bottles to the small tube for the sample to be used in a given measurement. This last tube was made from the neck and stopper of a small graduated flask and was of such a size that it would slip conveniently into the mouth of the accessory cell of the apparatus. An old balance case was fitted with a movable platform which carried spring-brass 2-fingered clamps for the two bottles, the movement of the platform being controlled by a rod fitted into the hole which ordinarily carries the balance-beam raising and lowering device. Into the left side of the case, opposite this central platform, were fitted 3 short brass sleeves, and, through these, 3 steel rods. The 2 outer rods each ended in 2 fingers of sheet spring-brass while the center rod ended in a platinum spoon. The door of the case was lined around the edge with felt and the joints between the iron rods and the brass sleeves were made tight with rubber tubing. To use the apparatus, the stock bottle and weighing tube were placed in their proper clamps, the door was tightly closed and a stream of dry air passed through the apparatus for some time. Then by pushing the platform back so that the back weighing tube was opposite the rear

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[1] Franklin and Cady, This Journal, 26, 499 (1904).

rod, its stopper could be removed by manipulation of the rod. The platform was then pulled to the front and the stopper removed from the second weighing bottle. The first tube was now in a position so that a spoonful of salt could be removed from it by the platinum spoon on the second rod and transferred to the smaller tube on pushing the platform again to the rear. The stoppers could now be replaced in the bottles, as, by the proper twisting of the rods the stoppers would "set" in the tubes and allow the clamps to be pulled off. This device proved to be very convenient.

Method of Making Measurements.

A weighed quantity of the solute was introduced into a small accessory cell adjacent to the conductivity cell. This cell was then closed with a ground-glass stopper, which was held in place by a brass cap, and the whole apparatus was swept free of air with a stream of pure dry hydrogen. The Dewar-tube thermostats were then filled with liquid ammonia and solvent was distilled into the accessory cell by opening the proper stopcocks. To hasten distillation a bath of warm water was usually held around the steel storage cylinder in order to overcome the cooling effect due to the rapid evaporation. On leaving the cylinder, the amine vapors were filtered through glass wool to remove solid impurities. After 2 or 3 cc. of solvent had distilled over, the stopcocks were reversed and a stream of hydrogen gas was bubbled through the mixture of salt and solvent in the accessory cell until solution was complete. Hydrogen pressure was then applied to the surface of the solution, the 3-way stirring stopcock was reversed and the solution forced over into the conductivity cell, entering through Tube H, Fig. 1. The accessory cell was washed with successive small portions of fresh solvent in the conductivity cell. Gaseous solvent could be introduced into the accessory cell either through a capillary tube reaching to the bottom, when it would condense at the bottom of the cell, or through a tube at the top, when it would condense all over the inner surface of the cell and thus the walls could be easily washed free of solute. The accessory cell was washed until the washings plus the original solution filled the conductivity cell to some point on the lower scale B, Fig. 1. The solution in the conductivity cell was then stirred until homogeneous by means of hydrogen forced in through the capillary F. The temperature of the bath was checked and the resistance of the solution measured. The volume of the solution was then determined by reading, by means of the telemicroscope, the position of the meniscus with respect to the glass scale B, and noting the height of the liquid in the capillary F. After again reading the resistance, the solution was diluted by the addition of fresh solvent until the cell was filled to a point on the upper glass Scale A. If the boiling point of the solvent was below room temperature, this fresh portion was added by distilling it in through the capillary F. The introduction of this layer of solvent under a denser solution very greatly decreased the time required for stirring the new solution. In this first dilution, advantage was usually taken of the opportunity for rinsing the accessory cell again as in the case of the more concentrated solutions very little washing could be done without filling the conductivity cell above Scale B. Also in the case of solvents boiling above room temperature, the fresh additions of solvent were made from the accessory cell. These solvents were forced into this cell from the glass storage vessel into which they had been distilled in vacuum from the original glass containers where they had been stored over metallic sodium. All connections were made of glass to avoid contamination.

After the solution had been made up to the scale A and thoroughly stirred, the scale and capillary were read and the resistance measured. Hydrogen pressure was turned on and the solution forced out through the capillary F until the meniscus had fallen to Scale B, when the stopcocks were closed, the pressure released, and the scale and capillary meniscus read. This remaining portion of the solution was then diluted with fresh solvent and measured as before.

The first portion of the "discarded" solution was, by proper adjustment of the stopcocks, led into the viscometer and density meter and used to rinse these cells after which it was run into the waste jar. The viscometer and density tube were filled with the remainder of the "discarded" solution. The viscosity and density of this solution were then determined as previously described, after which it also was forced into the waste jar.

The measurements were carried from the most concentrated solutions, which could be handled without risking the stoppage of the capillary tubes, to dilutions where the error in setting the bridge was greater than one part in 500. Due to the high resistance of even the most concentrated solutions, the measurements could not be carried out to very low concentrations. In most cases, the upper limit to the concentration of the solution measured was the limit of solubility of the salt.

Experimental Data.

Conductance Data.—In the following tables, c is the concentration in gram moles per liter. Λ is the molecular conductance, which is equal to 1000 χ/c, where χ is the specific conductance in reciprocal ohms, η is the absolute viscosity in c. g. s. units, and ρ is the density.

TABLE I.—SILVER NITRATE IN ETHYLAMINE.

c.	Λ.	η.	ρ.
	I.		
0.4917	5.310	......	.....
0.2508	3.820	......	.....
0.1220	2.283	......	.....

TABLE I (*continued*).

c.	A.	η.	ρ.
	II.		
0.5184	5.204	......	.....
0.2731	3.982	......	.....
0.1358	2.517	......	.....
0.06791	1.522	......	.....
0.03311	1.102	......	.....
0.01673	0.8937	......	.....
0.008196	0.9528	......	.....
0.004140	1.090	......	.....
	III.		
0.7411	5.762	0.01374	0.888
	IV.		
0.02559	1.107	......	.....
0.01260	0.9945	......	.....
0.006240	1.052	......	.....
0.003117	1.254	......	.....
0.001485	1.651	......	.....
0.0007315	2.208	......	.....
0.0003533	2.864	......	.....
0.0001771	3.960	......	.....
	V.		
0.1797	3.263	......	.....
0.08535	1.951	......	.....
0.04400	1.280	......	.....
0.02201	0.9874	......	.....
0.01086	0.9284	......	.....
0.005428	1.007	......	.....
	VI.		
1.004	5.633	......	.....
0.5420	5.587	0.009700	.....
0.2785	4.231	0.008069	.....
0.1402	2.715	0.007101	.....
0.07045	1.690	0.006271	.....
	VII.		
1.999	3.180	0.07098	.....
	VIII.		
0.06665	1.700	......	.....
0.03436	1.191	0.005948	.....
0.01719	0.9944	0.005849	.....
0.008500	0.9814	0.005764	.....
0.004277	1.008	0.005757	.....
0.002170	1.336	0.005757	.....
	IX.		
0.0009003	2.196	......	.....
0.0004566	3.003	0.005823	.....
0.0002293	4.132	0.005752	.....
0.0001016	5.618	0.005737	.....
0.00006145	7.621	0.005754	.....

TABLE I (*continued*).

Silver Iodide in Ethylamine.

c.	Λ.	η.	ρ
	I.		
0.2253	0.00739	......	.....
0.1012	0.01002	0.006046	.....
0.05629	0.01349	0.005951	.....
0.02888	0.01820	0.005894	.....
0.01460	0.02562	0.005856	.....
	II.		
0.6641	0.004841	......	.....
0.3494	0.006337	0.006922	.....
0.1728	0.008318	0.006373	.....
0.08780	0.01093	0.005977	.....
	III.		
1.023	0.003331	......	.....
0.6339	0.004707	0.007994	.....
0.3246	0.006216	......	.....
	IV.		
2.156	0.001913	......	.....
1.116	0.003600	0.009965	.....
1.068	0.003721	......	.....
0.5514	0.005085	......	.....

Barium Thiocyanate in Ethylamine.

c.	Λ.	η.	ρ
	I.		
0.09393	0.4023	......	.....
0.08937	0.3882–0.3899	0.006747	.....
0.04576	0.2518	0.006244	.....
0.02364	0.2035	0.006067	.....
0.01234	0.2017	......	.....
0.01234	0.2063	......	.....
0.006275	0.2086	......	.....
	II.		
0.4099	1.251	......	.....
0.2120	0.8549	......	.....
0.1121	0.4747	......	.....
0.1121	0.4802	......	.....
	III.		
0.5550	1.284	......	.....
0.2809	0.9333	0.009230	.....
0.1393	0.5180	......	.....
0.1392	0.5557	0.007192	.....
0.07076	0.3159	......	.....
0.07088	0.3298	0.006475	.....
0.03618	0.2386	0.006154	.....
0.01893	0.2052	0.006067	.....

TABLE I (*continued*).

Ethylamine Hydrochloride in Ethylamine.

c.	Λ.	η.	ρ.
	I.		
2.872	2.557	......	.....
1.489	3.755	0.01863	0.811
0.7518	2.854	0.009860	0.771
0.3817	1.461	0.007614	0.767
0.1898	0.6276	0.006634	.....
0.09458	0.3308	0.006165	.....
	II.		
0.2105	0.6787	......	.....
0.1071	0.3560	......	.....
0.05406	0.2383	......	.....
0.02711	0.1980	......	.....
0.01342	0.1980	......	.....
0.006492	0.2255	......	.....
0.003181	0.2815	......	.....
0.001575	0.3686	......	.....

The conductivities of solutions of silver nitrate and of ethylamine hydrochloride in ethylamine have been measured by Fitzgerald[1] at —33.5°, but he was unable to carry the measurements past a minimum of molecular conductivity. However, in the present experiments in both of these solutions, it has been possible to pass a minimum of molecular conductivity. In Fig. 4 one may see the general form of the conductivity curves in ethylamine, the molecular conductivities being plotted against the logarithms of the concentrations. The curve for silver nitrate shows the

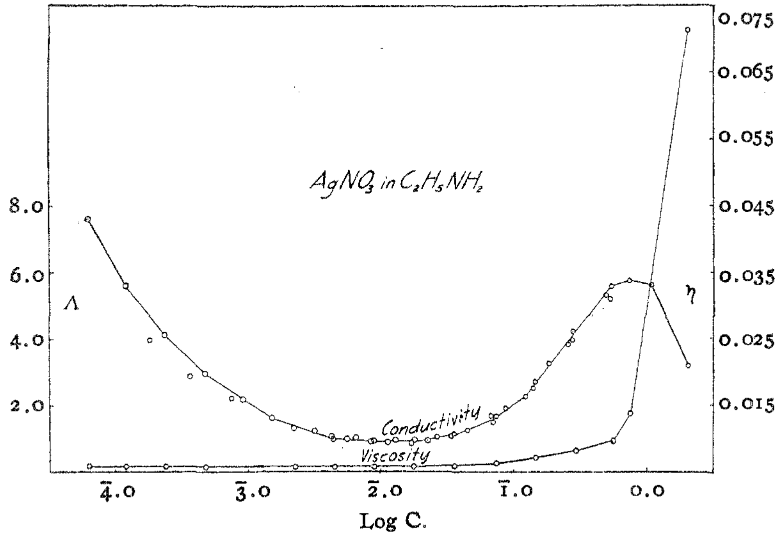

Fig. 4.

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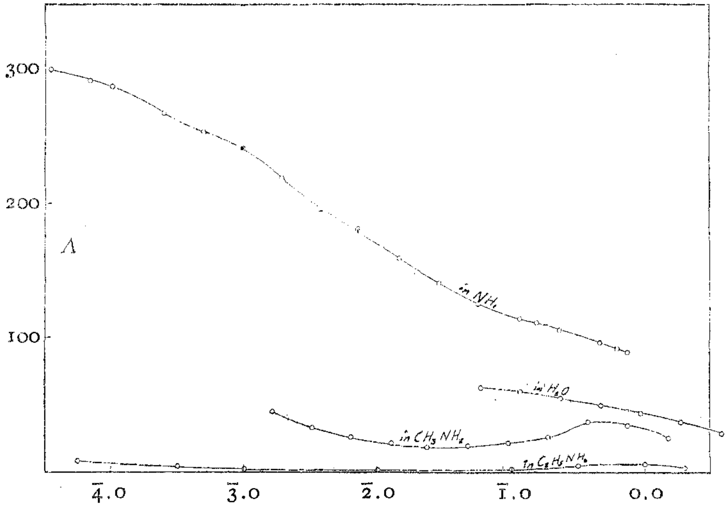
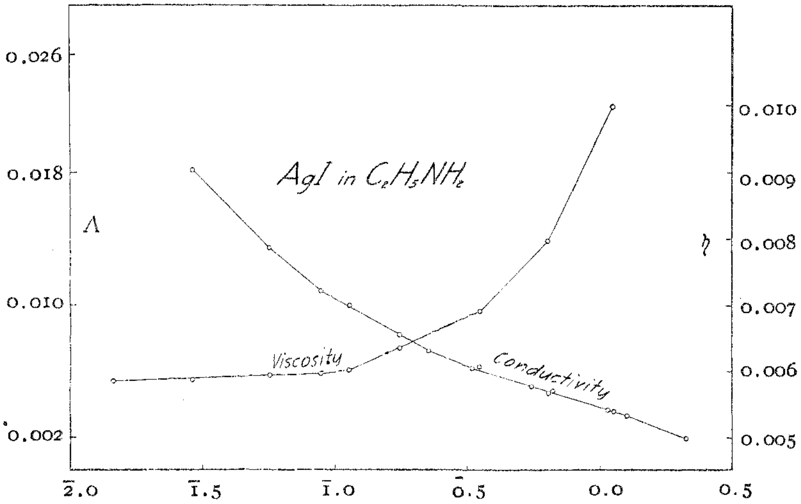
[1] *Loc. cit.*

form first noted by Gibbs[1] in methylamine solutions. With decreasing concentration the molecular conductivity rises to a maximum, then falls to a minimum, and rises to a final maximum in very dilute solutions.



Log C.
Fig. 5.—Conductivity of silver nitrate.

Only the final rise to a maximum of molecular conductivity at infinite dilution does not appear on account of our inability to work with the higher resistances met with in dilute solutions. In Fig. 5 are plotted the



Log C.
Fig. 6.

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[1] *Loc. cit.*

conductivity curves for silver nitrate in water, ammonia, methylamine and ethylamine. Data for the conductivity of silver nitrate in concentrated water solutions is plotted from data given by Sloan.[1]

Silver iodide (Fig. 6), which is extremely soluble in both ethyl and dimethylamine, melting down in the vapors of ethylamine at room temperature, apparently is dissociated to a very much less extent even than the other salts, as one is forced to use units only $^1/_{1000}$ as great in order to plot the curve for silver iodide on the same sheet as silver nitrate. It will also be noticed that for this salt there is no indication of a maximum in concentrated solutions, the equivalent conductivity rising regularly from the most concentrated to the most dilute solutions. In solutions of silver nitrate and ethylamine hydrochloride (Fig. 7) in ethylamine, the maximum of equivalent conductivity for each salt is in a solution of about normal strength while in the case of silver iodide solutions the equivalent conductivity was still decreasing at much higher concentrations. It is interesting to note that the 2 former solutions begin to increase rapidly in viscosity at about the same point while the rapid rise for silver iodide solutions does not come until greater concentrations are reached, and the marked increase in viscosity apparently does not alter the rate of decrease of the equivalent conductivity.

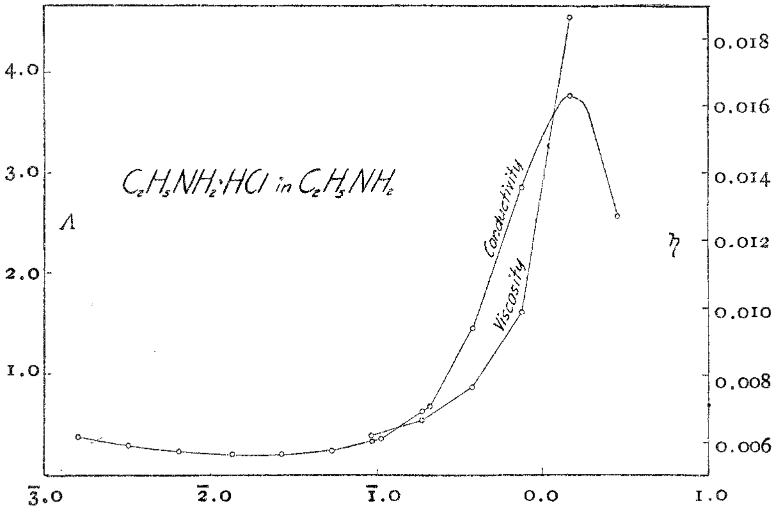

Fig. 7.

The above action in the case of "normal" electrolytes is further evidence, tending to show the close connection between the maximum in molecular conductivity which occurs in concentrated solutions and the viscosity. No attempt has been made to correct the conductivities of

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[1] Sloan, THIS JOURNAL, 32, 946 (1910).

the concentrated solutions for the viscosity according to the method of Sakhanov,[1] for, while the relation between viscosity and conductivity is recognized, we believe it futile, arbitrarily to apply a correction which considers only one of the several factors which determine the course of the conductivity curve in concentrated solutions.

An attempt was made to measure the conductivity of a solution of cadmium iodide in ethylamine, but it was found that the bulky aminate formed on contact of solute and solvent is only slightly soluble in ethylamine at liquid ammonia temperatures. This is interesting as Kahlenberg and Ruhoff[2] were able to prepare and measure the conductivity of a 1.3 N solution of this salt in amylamine. Their measurements, it is true, were made at 0°, but the cadmium iodide showed no signs of possessing any such solubility in ethylamine at room temperatures as they found it to possess in amylamine at 0°.

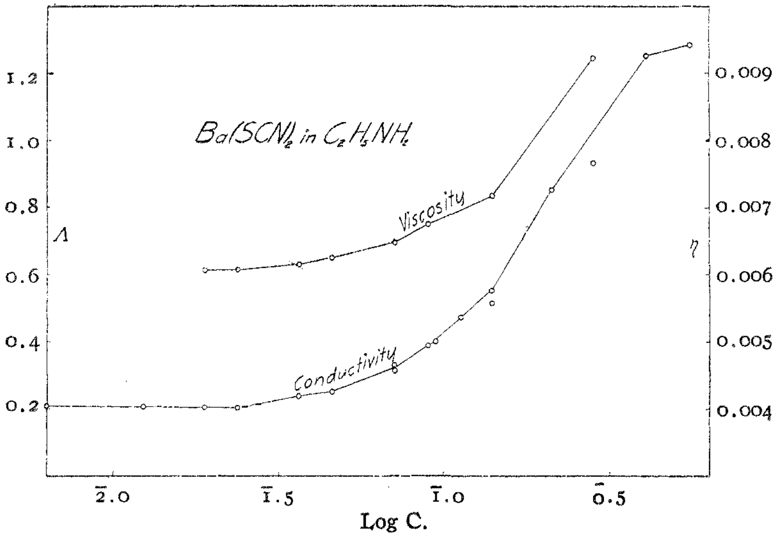

Fig. 8.

In measuring the conductivity of solutions of barium thiocyanate in ethylamine, it was noticed that the resistance seemed to vary with the time, and in order to check this observation a dilute solution of the salt was prepared and the molecular conductivities observed with the time of measurement are given.

If the conductivity is plotted against the time the form of the curve seems to indicate that perhaps we are dealing with an example of aminolysis (solvolysis) which proceeds slowly enough to be followed with ease by this conductivity method.

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[1] Sakhanov, *J. Phys. Chem.*, 21, 169 (1917).

[2] Kahlenberg and Ruhoff, *ibid.*, 7, 254 (1903).

TABLE II.
Aminolysis of Barium Thiocyanate in Ethylamine.
(c = 0.0651).

Time (hours).	Λ.
0.767	0.3754
1.067	0.3754
1.158	0.3772
1.384	0.3778
1.650	0.3783
1.966	0.3789
2.684	0.3799
3.516	0.3812
4.384	0.3822
5.267	0.3841
6.200	0.3853
8.117	0.3878
10.267	0.3912
11.500	0.3922
12.017	0.3929
23.70	0.4036
83.45	0.4057
95.45	0.4061

In water solutions such examples are rare as the rate of reaction of electrolytes brings almost instant equilibrium between solute and solvent, but in a few instances[1] it has been possible to follow the rate of hydrolysis by the conductivity method as above.

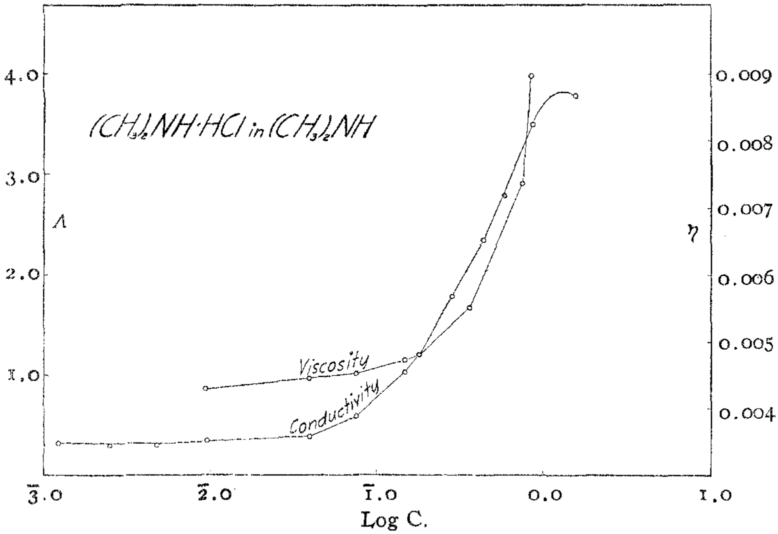

Fig. 9.

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[1] Furman, "Hydrolysis of Stannic Fluoride," THIS JOURNAL, 40, 906 (1918). For other examples see Foster, *Phys. Rev.*, 9, 41 (1899), and Kohlrausch, *Z. physik. Chem.*, 33, 257 (1900).

TABLE III.

Dimethylamine Hydrochloride in Dimethylamine.

c.	Λ.	η.	ρ.
I.			
0.009399	0.3417	0.004290	.....
0.004713	0.3061	......	.....
0.002437	0.3003	......	.....
0.001201	0.3206	......	.....
II.			
0.5697	2.775	......	.....
0.2843	1.786	0.005284	.....
0.1459	1.030	0.004720	.....
0.07458	0.5909	0.004523	.....
0.03855	0.3851	0.004451	.....
III.			
1.557	3.774	......	.....
0.8535	3.487	0.008947	.....
0.4346	2.342	......	.....
IV.			
0.7847	.....	0.007360	0.740
0.3585	.....	0.005496	0.734
0.1788	.....	0.004802	0.728

Silver Iodide in Dimethylamine.

c.	Λ.	η.	ρ.
I.			
1.259	0.002431	......	.....
0.6375	0.0004819	0.005558	.....
0.3195	0.0007660	0.005023	.....
0.1592	0.001110	0.004612	.....
II.			
2.695	0.000059	......	.....
1.366	0.0002217	0.007992	.....
0.7011	0.0004584	......	.....
III.			
2.03	......	......	1.17
IV.			
0.1285	0.006503	......	.....
0.06389	0.008974	0.004415	.....
0.03197	0.01109	0.004394	.....
0.01629	0.01438	0.004368	.....
0.008316	0.01919	0.004360	.....

In Table III are shown the results obtained in dimethylamine solutions. The curve for dimethylamine hydrochloride shows the typical form obtained in ethylamine curves. A maximum in concentrated solutions is indicated and apparently the minimum had been passed in a 0.005 *N* solution. Silver iodide, although quite soluble, gave a very poorly conducting solution, the slight molecular conductivity falling off rapidly with increasing concentration, in every way behaving as the solution in ethylamine. Franklin[1] has previously noted the fact that silver

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[1] *Loc. cit.*

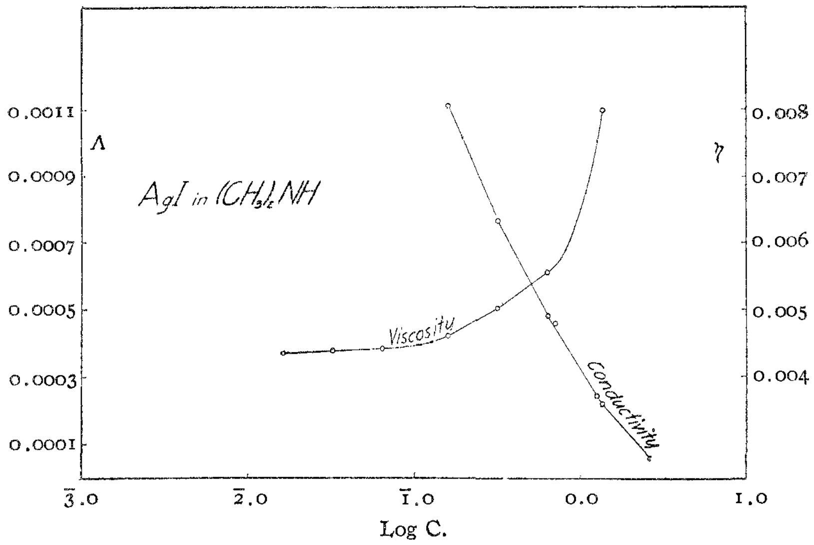

Fig. 10.

iodide has an abnormally low conductivity in ammonia solutions. This abnormality is apparently merely accentuated in the amine solutions.

TABLE IV.

Lithium Chloride in Diethylamine.

c.	Λ.		
0.1998	0.0004988	......	.....
0.1021	0.0006138	......	.....
0.05199	0.0009478	......	.....
0.02544	0.001205	......	.....

TABLE V.

Silver Nitrate in Propylamine.

c.	Λ.	η.	ρ.
0.4588	3.270 (this value is at 20° C.).		.....
0.4588	1.660	......	.....
0.2802	1.230	0.01500	0.841
0.1387	0.6031	0.01218	.....
0.06789	0.2479	0.01112	.....
0.03376	0.1224	0.01066	.....
0.01657	0.07865	......	.....
0.008183	0.06476	0.01033	.....
0.003994	0.06434	0.01028	.....

Lithium chloride was the only one of the several salts used which was at all soluble in diethylamine at —33.5° and it was only moderately soluble. The solutions in dimethylamine were conductors of the same order as ethylamine solutions, but diethylamine proved to be an extremely poor electrolytic solvent, the conductivity of the lithium chloride solution in it being of the same order as the conductivity of the silver iodide solution in dimethylamine, a 0.1 N solution having a molecular conductivity of only 0.0006 Kohlrausch unit.

Only one series of measurements was made in propylamine. Silver nitrate is only fairly soluble, a 0.26 N solution being approximately saturated with the salt at —33.5°, the limited solubility thus preventing the appearance of a maximum of conductivity in concentrated solutions.

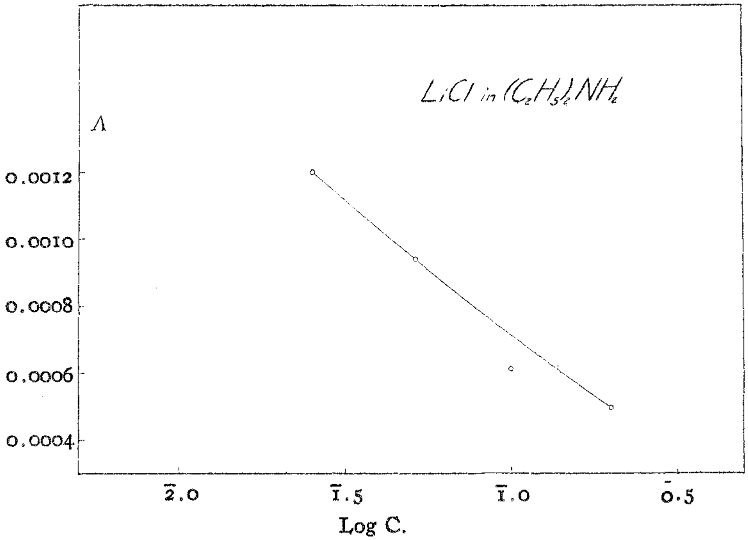

Fig. 11.

The molecular conductivity was about the same as for the corresponding solution in ethylamine, the lower values being doubtless due more to the greater viscosities encountered than to a difference in the dielectric constants.

None of the salts used in the preceding measurements would form a conducting solution in trimethylamine or triethylamine or diethylamine other than as noted. In Table VI, the specific conductivities of solutions saturated at —33.5° with these salts in the above solvents are given. In the table, a is one arm of the bridge where the total length is 1000 units, χ is the specific conductivity, f is the capacity in microfarads which must be introduced in parallel with the resistance box to get a good minimum in the telephone, and m is the fraction of the bridge over which a perfect minimum is secured.

TABLE VI.

Solute.	Solvent.	a.	χ.	f.	m. %.
$(CH_3)_3N.HCl$	$(CH_3)_3N$	999.4	3.2×10^{-10}	0.1288	0.02
$(C_2H_5)_2NH.HCl$	$(C_2H_5)_2NH$	988.1	6.5×10^{-9}	0.001	0.02
AgI	$(C_2H_5)_2NH$	995.2	2.6×10^{-9}	0.019	0.02
LiCl	$(C_2H_5)_3N$	997.4	1.4×10^{-8}	0.027	0.05

The above solutions were saturated at room temperature by stirring the solvent and solid salt together by the use of hydrogen. The solutions were then transferred to the conductivity cell at —33.5°. In no instance was solid salt observed to separate out on cooling to the lower temperature and apparently but very little, if any, salt had been dissolved in any case.

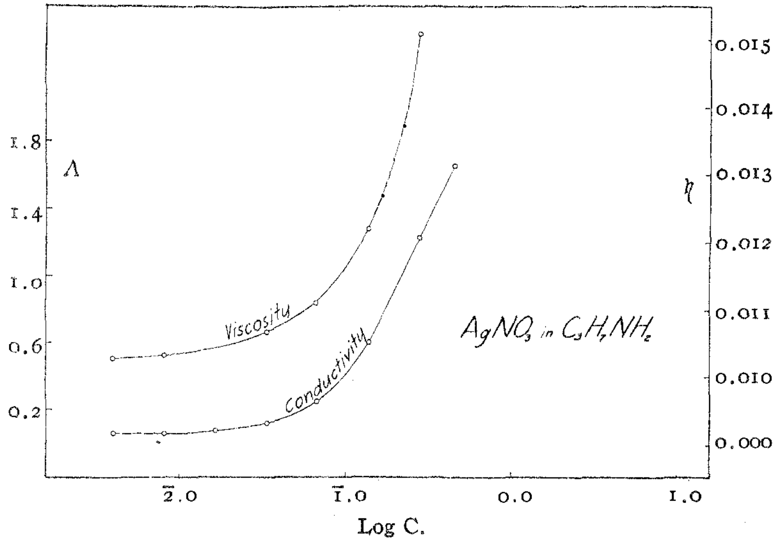

Fig. 12.

In Table VII are given the specific conductivities of the different solvents used, and it will be seen that the so-called solutions listed in Table VI are but little, if any, better conductors than the pure solvents.

TABLE VII.

Specific Conductivities of Amines.

	a.	*χ.*	*f.*	*m.*
$(CH_3)_3N$	999.6	2.2×10^{-10}	0.1378	0.02
$C_2H_5NH_2$	923.0	4.6×10^{-8}	0.001	0.05
$(C_2H_5)_2NH$	995.4	2.5×10^{-9}	0.019	0.05
$(C_2H_5)_2NH$	996.0	2.2×10^{-9}	0.024	0.05
$(C_2H_5)_2NH$	995.5	2.4×10^{-9}	0.024	0.05
$(C_2H_5)_2NH$	995.9	2.2×10^{-9}	0.025	0.05

Since the dissociation of the solute is far from complete even in the most dilute solution measured (0.00006 *N*), some more delicate type of detector than the simple telephone is essential to enable any further study of these high resistance solutions to be made. For this use, one of the thermionic detectors or oscillation valves used in wireless work (such as the "audion" or "pliotron"), should be readily adaptable. The audion valve circuit could replace the telephone across the bridge arms and the resulting unilateral oscillating current detected either by a telephone or by a galvanometer.[1]

In Table VIII are given the results of the measurements of the viscosities of the various solvents used. The viscosities of a number of samples

TABLE VIII.

Viscosity of Ammonia at —33.5°.

s.	*d.*	*p.*	*t.*	η'.	η.
1......	L to R	78.69	58.4	0.002542	
	R to L	78.44	58.9	0.002556	0.002549
	L to R	78.24	58.9	0.002549	
	R to L	77.74	59.0	0.002531	0.002540
	L to R	67.12	67.7	0.002520	
	R to L	66.77	68.9	0.002553	0.002537
	L to R	66.47	69.0	0.002545	
	R to L	66.22	69.5	0.002554	0.002550
2......	L to R	78.46	58.2	0.002526	
	R to L	78.26	59.2	0.002564	0.002545
	L to R	78.16	58.3	0.002520	
	R to L	78.04	59.2	0.002556	0.002538
3......	R to L	78.02	58.9	0.002542	
	L to R	77.87	59.3	0.002556	0.002549
	R to L	77.80	59.1	0.002545	
	L to R	77.65	59.1	0.002539	0.002542
4......	L to R	51.50	87.8	0.002518	
	L to R	51.50	88.8	0.002548	0.002553
	R to L	51.45	87.9	0.002519	
	L to R	51.42	89.0	0.002550	0.002535
	R to L	40.31	112.2	0.002528	
	L to R	40.32	113.5	0.002558	0.002543
	R to L	40.33	112.2	0.002529	
	L to R	40.40	113.7	0.002568	0.002549
				Mean..........	0.002543

Viscosity of Ethylamine at —33.5°.

1......	L to R	46.13	221.2	0.005757	
	R to L	46.07	221.7	0.005762	0.005760
2......	L to R	46.38	219.7	0.005747	
	R to L	46.15	220.2	0.005733	0.005740
3......	L to R	47.36	215.3	0.005751	
	R to L	47.21	216.0	0.005753	0.005752
4......	L to R	47.99	212.2	0.005746	
	R to L	47.71	212.8	0.005727	0.005737
5......	L to R	48.36	210.9	0.005754	
	R to L	48.26	211.3	0.005753	0.005754
				Mean.........	0.005749

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[1] Hall and Adams, THIS JOURNAL, 41, 1515 (1919).

TABLE VIII (*continued*).

s.	*d.*	*p.*	*t.*	*η'.*	*η.*
Viscosity of Dimethylamine at 33.5°.					
1......	L to R	40.5	191.1	0.004360	
	R to L	40.35	192.1	0.004365	0.004363
2......	L to R	40.56	191.9	0.004387	
	R to L	40.51	191.5	0.004370	0.004379
3......	L to R	43.64	177.5	0.004361	
	R to L	43.50	177.8	0.004358	0.004360
4......	L to R	43.48	178.8	0.004367	
	R to L	43.30	179.2	0.004368	0.004368
				Mean.........	0.004368
Viscosity of Trimethylamine at —33.5°.					
1......	L to R	40.42	140.3	0.003183	
	R to L	40.37	140.5	0.003184	0.003184
	L to R	35.37	160.3	0.003185	
	R to L	35.18	161.2	0.003187	0.003186
2......	L to R	37.04	155.6	0.003237	
	R to L	36.90	155.5	0.003222	0.003230
	L to R	38.92	148.5	0.003245	
	R to L	38.72	147.9	0.003215	0.003230
				Mean.........	0.003208
Viscosity of Diethylamine at —33.5°.					
1......	L to R	73.35	200.4	0.008301	
	R to L	73.25	201.2	0.008322	0.008312
	L to R	73.15	201.0	0.008302	
	R to L	72.98	201.1	0.008287	0.008295
2......	L to R	73.43	196.8	0.008160	
	R to L	73.25	198.4	0.008168	0.008164
	L to R	73.05	198.3	0.008179	
	R to L	72.91	199.7	0.008223	0.008201
3......	L to R	73.22	198.9	0.008166	
	R to L	73.08	200.0	0.008253	0.008209
				Mean.........	0.008236
Viscosity of Triethylamine at —33.5°.					
1......	L to R	52.26	262.9	0.007760	
	R to L	53.26	256.1	0.007703	0.007732
	L to R	53.21	257.4	0.007735	
	R to L	53.16	257.1	0.007719	0.007727
2......	L to R	53.51	255.6	0.007724	
	R to L	53.36	256.0	0.007713	0.007718
				Mean.........	0.007726

of each solvent were measured all at —33.5°. In the table s is the number of the sample; d, the direction of flow between the capillaries; p, the pressure in grams per sq. cm.; t, the time; and η', the calculated viscosity. The mean of the L to R and R to L values or η is the true viscosity.

The viscosity of liquid ammonia at —33.5° has also been measured by Fitzgerald,[1] who found the average value $\nu = 0.00266$, using a viscometer of the Ostwald type. The average value found in the present work was 0.00254. The only possible claims for consideration of this latter value over that of Fitzgerald are that it is the mean of a greater number of observations and that the type of viscometer used gave a much longer time of flow, very greatly reducing the possibility of eddy currents.

TABLE IX.

Density of Amines at —33.5°.

Amine.	Density.
Dimethylamine	0.727
Trimethylamine	0.702
Ethylamine	0.742
Diethylamine	0.713
Triethylamine	0.778

In Table IX are given the mean values of measurements of the densities of the amines. These results were obtained by use of the densitimeter in the manner described for solutions. The experimental values are not given as the results are very inaccurate indeed.

Summary.

Viscosity and conductivity measurements have been made on a number of solutions in ethyl, dimethyl, trimethyl, diethyl, triethyl and propyl amines.

Dimethylamine proved to be a poorer solvent than ethylamine, though the salts which did dissolve formed solutions having about the same molecular conductivity.

Diethylamine is a still poorer solvent and a distinctly poorer ionizing agent, a lithium chloride solution in it being no better conductor than a solution of silver iodide in ethylamine.

The tertiary amines are distinctly not electrolytic solvents, no evidence of salt solution being found in any case and solvent in equilibrium with solid solute did not appreciably gain in conductivity.

In conclusion, the writer wishes to thank Dr. E. C. Franklin for his kindly guidance and to express his appreciation of him, both as a friend and a teacher.

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[1] *Loc. cit.*