[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

Solutions of Metals in Amine Solvents. I. The Conductance of Concentrated Solutions of Lithium in Methylamine[1,2]

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The conductance of lithium in methylamine has been measured from 5.26 to 0.03 g. atoms metal per liter of solvent. At saturation, the equivalent conductance is 5333; with decreasing concentration the conductance decreases exponentially, goes through a minimum of 48 at 0.1 *N* and increases with further dilution. Conductance in the metallic region is lower than in ammonia by a factor of one hundred. Below about 0.3 *N* the conductance is lower by a factor of ten, but the form of the conductance function is essentially the same as in ammonia.

It is well known that liquid ammonia will dissolve highly electropositive elements forming conducting solutions. The alkali metals are most soluble, forming blue solutions when dilute and lustrous bronze colored solutions when concentrated. Concentrated solutions resemble liquid metals in many respects. For example, a saturated solution of sodium at −33° has a specific conductance of about one-half that of mercury; but in terms of equivalent conductance the sodium solution is the better conductor. Conduction is essentially electronic and approaches a value of 1×10^6 Kohlrausch units at saturation. However, the temperature coefficient of conductance, though small, is positive.[3]

As the metal concentration is reduced the conductivity falls off exponentially, passes through a minimum of 500 units at approximately 0.05 *N*, then increases less rapidly with further dilution. The extrapolated value at infinite dilution is approximately 1030.[4] Solutions in the region of the minimum and more dilute exhibit quasi-electrolytic behavior. In extremely dilute solutions the positive carrier, identified as the metal ion, carries approximately one-eighth of the current[5]; the negative carrier is the so-called "solvated electron."[6] Evidently the minimum in the equivalent conductance curve represents a transition from quasi-electrolytic to electronic conduction.

Metals also dissolve in other amine solvents, but few investigations have been made in solvents other than ammonia. Only a single communication relates to conductivity studies.[7] In this study, Gibson and Phipps measured the conductance of solutions of potassium and cesium in methylamine from saturation down to dilutions of the order of 1×10^4 liters. However, these earlier results appear to be uncertain probably due to the presence of impurities. Moreover, the solubilities of the metals were too low to determine whether methylamine solutions might not exhibit metal-like behavior.

We are undertaking a rather comprehensive investigation of the properties of solutions of metals in amine solvents. In so doing we hope to obtain data which will tend to a better understanding of solutions of metals in ammonia as well. The present investigation is concerned with the conductivity of concentrated solutions of lithium in methylamine and provides us with information regarding the role of the solvent media in determining the magnitude and form of the conductance function. Apparently, only solutions of lithium in methylamine can be obtained at sufficiently high concentrations so that investigations may be extended into the semi-metallic region.

Experimental

Our present report covers the results of conductance measurements in methylamine at −22.8° over the concentration range from 0.03 to 5.26 g. atoms of lithium per liter of solvent. Both concentration and conductance have been expressed in these units since we have no density data for these metal solutions. Judging by the behavior of solutions of metals in ammonia, the more concentrated solutions in methylamine are probably less dense than the pure solvent; hence concentrations should be somewhat lower when expressed on a volume of solution basis. In ammonia, a solution containing 5.0 g. atoms of sodium per liter of solvent is only about 4.0 *N* in metal.

Three conductance cells were employed to cover the concentration range investigated. The constants were 6.364, 41.28 and 432.1, respectively. These values were determined as described previously.[8] Bright platinum electrodes sealed through Pyrex brand glass, using the tube seals described by Hnizda and Kraus,[9] proved the most effective electrode assembly. These could be heated to 300° and cooled to liquid air temperature repeatedly without failure. In order to minimize catalytic decomposition of the solutions, the electrode areas were kept to a minimum. In the case of the two cells with the larger constants the electrodes were placed in separate chambers which were connected at the bottoms by a length of small bore tubing; the length and diameter of this tubing largely determined the value of the cell constant.[10] The electrodes were carried by tubes sealed through glass caps attached to the top of each chamber; the electrodes were placed well toward the bottom of each chamber. The cell constants were insensitive to rotation of the ground glass caps or to the quantity of solution in the cell. The third cell was of more conventional design.[11] Each cell had a capacity of approximately 200 cc. Before metal and solvent were introduced the cells were cleaned thoroughly,[11] sealed to a system providing vacuum and solvent, heated to 300° and evacuated to less than 1×10^{-5} mm. for about 10 hours.

Lithium metal of highest purity[12] was cut under mineral

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[2] Presented before the Division of Physical and Inorganic Chemistry, American Chemical Society, at Miami, Florida, April, 1957. Taken in part from a thesis by Archie E. Young, II, presented in partial fulfillment of the requirements for the Ph.D. degree, June, 1955.

[3] C. A. Kraus and W. W. Lucasse, THIS JOURNAL, **43**, 2529 (1921).

[4] C. A. Kraus, *ibid.*, **43**, 750 (1921).

[5] C. A. Kraus, *ibid.*, **36**, 864 (1914).

[6] C. A. Kraus, *ibid.*, **30**, 1323 (1908).

[7] G. E. Gibson and J. Phipps, *ibid.*, **48**, 318 (1926).

[8] E. C. Evers and A. G. Knox, Jr., *ibid.*, **73**, 1739 (1951).

[9] V. F. Hnizda and C. A. Kraus, *ibid.*, **71**, 1565 (1949).

[10] P. L. Mercier and C. A. Kraus, *Proc. Nat. Acad. Sci. U. S.*, **42**, 487 (1956).

[11] A. R. Young, II, Thesis, University of Pennsylvania, June, 1955.

[12] The lithium metal was obtained from The Lithium Corporation of America.

oil, washed free of oil using dry benzene saturated with helium, and transferred to the cell through a side tube; entry was effected through a ground glass joint. All these operations were carried out under an atmosphere of helium. The cell was again evacuated to less than 1×10^{-5} mm. and was exhausted for several hours. Methylamine was then distilled from a small weighed storage cylinder into the cell cooled to −78°. The quantity of amine employed as solvent was determined by removing and reweighing the cylinder. Appropriate corrections were made for the weight of amine remaining in connecting tubes and in the vapor phase above the metal solutions. To compute the latter, rough measurements were made of the vapor pressures of the solutions at −23°.[11]

The methylamine was a Rohm and Haas product obtained from the Matheson Chemical Company.[13] The solvent was first distilled from the commercial cylinder into a smaller iron cylinder (4-liter capacity) containing lithium metal. After standing several days, the hydrogen together with about 10% of the solvent was discharged to the hood. About 500 cc. of amine was distilled into an all glass system where it was refluxed for several hours with fresh lithium metal; then it was stored for about 24 hours at Dry Ice temperature. This treatment was designed to remove water and other reducible impurities. Also by discharging solvent from the storage cylinder, we felt we had removed a considerable fraction of the ammonia; and the higher amines should have remained largely behind in the commercial cylinder and in the storage cylinder. In order to insure further fractionation, only the middle one-half of the solvent stored over lithium in the glass system was finally collected in a small stainless steel cylinder (capacity 500 cc.) for use as described above. Entry to the cylinder was effected by means of a small packless diaphragm valve. The cylinder was attached to the vacuum system by means of deKhotinsky cement, after having first wrapped the glass to metal joint with aluminum foil to minimize contact between solvent and the cement.

By successive additions of solvent it was possible to obtain conductivity measurements for several concentrations using the same sample of metal. We judged the reliability of our data by their reproducibility and by noting the time rate of change of resistance at any one concentration, after temperature equilibrium had been established. Usually, when the resistance change exceeded 0.2% per hour, we discarded the data. Sometimes it was not possible to measure the conductance at more than one concentration. On one occasion it was possible to carry out as many as seven successive dilutions without noticeable decomposition. After completion of an experiment, the solvent was distilled back into the small weighed container for further use. The lithium content of the cell was determined by titration with standard acid.

Temperature control was achieved by employing a bath consisting of a solid–liquid equilibrium mixture of reagent grade carbon tetrachloride. This was maintained as a viscous slurry during the course of the conductivity measurements by the periodic addition of liquid air. The freezing point of the mixture was checked by means of a copper–constantan thermocouple in combination with a Leeds and Northrup precision potentiometer. The temperature was maintained well within the range of −28.2 ± 0.10°. We feel that variations due to temperature are within the limits of our other experimental errors; a plot of specific conductances *vs.* concentration fell on a smooth curve within ±0.3%.

We should like to defer further discussion of our experimental methods to a later paper, where we shall discuss factors affecting stability of metal–amine solutions and present some preliminary results on the kinetics of their decomposition; but it cannot be overemphasized that purity of materials, rigid exclusion of air and extreme cleanliness of equipment are essential, as has been pointed out previously[9,14] in investigations employing ammonia as solvent. It has been our experience that methylamine solutions are even more sensitive to catalytic decomposition than are ammonia solutions. These are metastable systems and a trace of a variety of substances including the metal electrodes themselves catalyze the reaction to produce amide and hydrogen. Evidently the instability of the solutions was the prime source of inaccuracies in the earlier results.[7] Also, we have found potassium to be very much less soluble in methylamine than was reported by Gibson and Phipps. For this and other reasons,[15] we believe their solvent must have been contaminated with ammonia.

The results of conductivity measurement in methylamine are recorded in Table I. Column 1 gives the concentration in g. atoms of lithium per liter of solvent, column 2, the specific conductivity and column 3, the equivalent conductance. Constants for the solvent at −22.8° are: density, 0.714 g./cc.[16]; dielectric constant, 12.3[17] and viscosity, 0.00353 poise.[18]

TABLE I

THE CONDUCTANCE OF SOLUTIONS OF LITHIUM IN METHYLAMINE AT −22.8°

$C \times 10^2$	$k \times 10^2$	Λ	$C \times 10^2$	$k \times 10^2$	Λ
3.48	0.1866	53.65	26.79	1.551	57.89
4.86	.2459	50.60	27.38	1.615	58.98
6.30	.3101	49.23	34.94	2.397	68.62
8.36	.3996	47.81	38.07	2.699	70.89
9.02	.4247	47.08	51.32	4.127	80.42
13.32	.6287	47.19	76.22	8.036	105.4
13.95	.6650	47.67	118.4	24.18	204.4
15.42	.7404	48.03	136.6	34.23	250.6
15.52	.7460	48.06	265.3	499.5	1865
17.78	.8662	48.73	353.0	1116	3160
19.68	1.000	50.83	404.2	1649	4079
22.72	1.213	53.37	(1169)[a]	2805	.....
23.63	1.271	53.81	(1669)[a]	2805	.....
25.27	1.414	55.94			

[a] Saturated solutions, see Fig. 1. These values are apparent concentrations, *i.e.*, they were calculated as if all the metal had dissolved.

Discussion

As shown by the last two data in Table I, identical values were obtained for the specific conductivity, namely, 28.05 ohm^{-1} cm.^{-1} at apparent concentrations of $C = 11.69$ and $C = 16.69$, respectively. In these experiments particles of metal were observed floating on top of the deep blue solutions; therefore the solutions were saturated with metal. Using these data together with those obtained at somewhat lower concentrations, it is possible to estimate the solubility of lithium. The most convenient method was to plot log k *vs.* $1/C$ as shown in Fig. 1. Intersection of the two curves gives a concentration of 5.26 g. atoms lithium per liter of solvent at saturation, and an equivalent conductance of 5333. By way of comparison, the atomic conductance of lithium metal at 0° is 1.5×10^6, a value approximately three hundred-fold greater than that of the saturated solution. Data are not available for a saturated solution of lithium in ammonia, but for sodium the conductivity is approximately 1×10^6 Kohlrausch units.[3]

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(13) The analysis provided us was: monomethylamine 98%, dimethylamine 0.5%, trimethylamine 0.5%, water, 0.5%, ammonia, less than 0.2%.

(14) J. F. Dewald and G. Lepoutre, THIS JOURNAL, **76**, 3369 (1954).

(15) Gibson and Phipps report the appearance of two phases in their solutions at higher potassium concentrations. This we have not observed with our solvent, but we have found that solutions of lithium in ethylamine are extremely sensitive to ammonia. The addition of traces of ammonia results in the formation of two phases and the ammonia appears to catalyze the reaction of metal with solvent. We shall discuss this phenomenon in some detail at a later date, M. Klein, unpublished results, this Laboratory.

(16) W. A. Felsing and A. R. Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929).

(17) H. Urich and W. Nespital, *Z. physik. Chem.*, **B16**, 221 (1932).

(18) D. M. Berns, unpublished observations, this Laboratory.

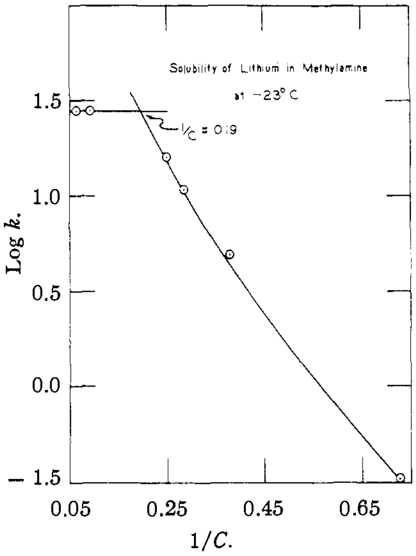

Fig. 1.—The solubility of lithium in methylamine at −22.8° log specific conductance *vs.* 1/*C*.

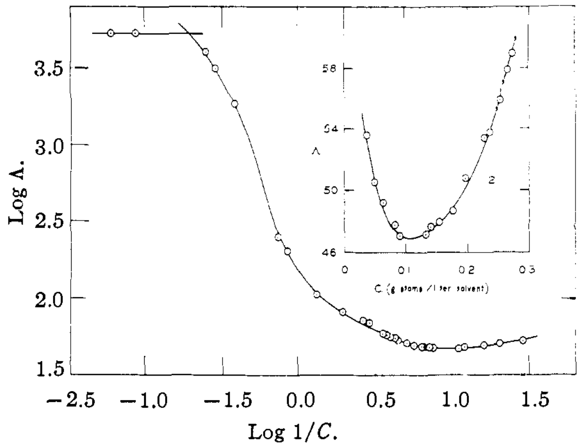

Fig. 2.—The conductance of lithium in methylamine at −22.8°: curve 1, log Λ *vs.* 1/*C*; curve 2, Λ *vs.* *C* in the region of the minimum.

This value is approximately two hundred-fold greater than for lithium in methylamine. But a saturated solution of sodium in ammonia contains about 7.5 g. atoms of metal per liter of solvent. Therefore it would probably be better to use the conductivity of a solution containing 5.26 g. atoms of sodium per liter of ammonia in making this comparison. According to Kraus' data,[3] such a solution has a conductivity of about 5 × 10^5 units. This value is higher than for lithium in methylamine by a factor of one hundred.

Our results clearly show that the electron is considerably less mobile in methylamine than in ammonia throughout the range of concentrations investigated. Curve 1 of Fig. 2 is a plot of log Λ *vs.* log 1/*C* for lithium in methylamine at −23° from saturation down to a concentration of about 0.03*C*. A comparison of these data with those for sodium in ammonia demonstrates that down to a concentration of about 1.0*C*, the sodium solution is a better conductor by a factor of about one hundred. At lower concentrations, the conductivities approach one another; below about 0.3*C* the sodium solution is a better conductor by a factor of about ten. At this time we do not wish to speculate regarding the conduction mechanism, but wish merely to place our data on record. However, there is no question regarding the metal-like nature of the more concentrated solutions. Above about 0.6*C* the electron carries substantially all the current, both in ammonia[5] and in methylamine.[19]

As is the case with metals in ammonia, solutions of lithium in methylamine show a minimum in the conductance function at lower concentrations. This is shown in the expanded plot, curve 2, Fig. 2. The minimum here occurs at about 0.1*C*; this value is to be compared with that for lithium in ammonia which occurs at about 0.04*C*.

At concentrations below the minimum, both in ammonia and in methylamine, the behavior of the conductance function indicates strong interaction between the electron and metal ion. No other explanation would seem to account for the decrease in equivalent conductance as the concentration is increased to the minimum. Evidently the magnitude of the conductivity is very greatly influenced by the structure of the solvent, whereas the appearance of a minimum may be attributable to a change in the mechanism from quasi-electrolytic to metallic conduction. Other features of the conductance function will be discussed in subsequent communications.

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Philadelphia, Pa.

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[19] Unpublished observations, H. M. Klein, this Laboratory.