[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Conductance of Dilute Solutions of Alkali Iodides in Dimethylamine[1]

BY ELIJAH SWIFT, JR.

While solutions of electrolytes in solvents of low dielectric constant exhibit many of the properties of aqueous solutions, there are differences in these properties which have not been investigated fully because of the experimental difficulties involved. Kraus and Fuoss[1a] have shown that for mixtures of dioxane and water, as well as for other systems, as the dielectric constant of the mixture is lowered, the shape of the conductance–concentration curve for any salt changes continuously. These curves can be accounted for quantitatively on the basis of a combination of ion association and interionic attraction.

It was the purpose of this investigation to extend the generality of this theory by using salts with ions which are comparatively small. Since the particular salts chosen have small ions, they should be only very feebly dissociated in dimethylamine ($D = 3.3$). By comparing the members of a series of salts, such as the alkali iodides, it should be possible to decide whether there may be any solvation of these small ions by a solvent of low dielectric constant with an "unshared electron-pair."

The solvent used, dimethylamine, has been shown to be extremely useful in precise thermodynamic studies of alkali metal amalgams by means of concentration cells.[2,3] In the course of this investigation it was found that while sodium and lithium iodides are extremely soluble and form low-conducting solutions, potassium and cesium iodides (and probably rubidium iodide by inference) are too insoluble to be of use without highly refined methods of potential measurement, or concentration cells of extremely low cell constant. The specific resistance of a saturated solution of potassium iodide at 25° is approximately 7×10^6 ohms, and that of cesium iodide about 4×10^7 ohms,[4] while a specific resistance of 10^4 is readily obtained with either sodium or lithium iodide. This latter is a convenient value for these thermodynamic studies.

Experimental

Dimethylamine was prepared from dimethylamine hydrochloride obtained from the Eastman Kodak Company, dried over activated alumina and desiccated by dissolving sodium fluorenone in it.[5] It was then twice distilled in vacuum to remove the last traces of dissolved gases and high boiling impurities, and was thereafter kept in sealed Pyrex containers out of contact with air at all times.

The salts were Mallinckrodt Reagent grade chemicals, fused in a platinum boat at a pressure of less than 10^{-4} mm. The solutions were made up in a closed system without exposing the fused salts to the atmosphere.[3] The concentrations of the original solutions were found by measuring the volume of solution in a special sealed pycnometer before running it into the conductance cell. The amount of dissolved salt was measured after the completion of each series of measurements. The cells used have been described by Bent and Keevil,[6] and were designed so that a series of successive quantitative dilutions could be made on the original solution in the cell without opening the sealed system.

When calculating the equivalent conductances of the solutions which were measured at 0°, it was assumed that the molar concentration was the same as at 25°. This is, of course, not strictly true, due to a change in the density of the solution, but makes too small a difference to be of importance here. No correction was made for the change in cell constant with temperature.

The resistances were measured with a Leeds and Northrup student type bridge with parallel capacitances, using a Shallcross variable resistance box, reading up to 1 megohm, as an auxiliary resistance. The resistances and the slide wire were calibrated carefully, and no error as great as 0.1% was found. However, vaporization of the solvent out of the conductance cell during measurements, cumulative errors in concentration, and the large temperature coefficient of conductance contributed to cut down the accuracy of the measurements to 2–5%, a somewhat greater error being made in the most dilute solutions. The resistances measured ranged from 7.0 ohms to 1 megohm.

To see whether the precision of the resistance measurements in cells of as low cell constant as this could be bettered, which would be worth while in other solvents where errors could be better controlled, the measurements on lithium iodide were made with a bridge of the type described by Jones and Josephs.[7] Readings were usually made at 1000 and 2000 cycles, and a frequency correction applied to obtain the true resistances.

In order to apply the frequency correction, it was necessary to know whether the difference in the reactance at the two frequencies was due to a capacitance in the cell or

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[1] Presented before the 96th meeting of the American Chemical Society, Milwaukee, Wisconsin, Sept. 5–9, 1938.

[1a] C. A. Kraus and R. M. Fuoss, THIS JOURNAL, **55**, 21 (1933).

[2] H. E. Bent and E. Swift, Jr., *ibid.*, **58**, 2016 (1936).

[3] H. E. Bent and A. F. Forziati, *ibid.*, **58**, 2020 (1936).

[4] Private communication from A. F. Forziati.

[5] H. E. Bent and H. M. Irwin, THIS JOURNAL, **58**, 2072 (1936).

[6] H. E. Bent and N. B. Keevil, *ibid.*, **60**, 193 (1938).

[7] Grinnell Jones and R. C. Josephs, *ibid.*, **50**, 1049 (1928).

in the resistance, or a combination of the two. Measurements were made at one particular concentration, using four different frequencies. Applying the equation suggested by Jones and Josephs[8] and neglecting the higher terms, good agreement was found among the calculated resistances.

TABLE I

$$R_{\text{true}} = R_{\text{meas.}}(1 - R^2_{\text{measd.}}W^2C^2 + \ldots)$$

Frequency	$R_{\text{measd.}}$	$R_{\text{calcd.}}$
800	78485	78345
1000	78545	78325
1600	78920	78348
2000	79250	78344

It seems probable that if the other factors besides the electrical measurements can be controlled, measurements can be made in cells of this type which will be nearly as precise as those made in aqueous solutions with the best equipment.[9]

TABLE II

CONDUCTANCE OF SODIUM IODIDE IN DIMETHYLAMINE

Concn., moles/liter	Equiv. cond.	Concn., moles/liter	Equiv. cond.
Run I, 25°		Run II, 25°	
3.54×10^{-1}	1.56	1.82×10^{-2}	0.0943
7.17×10^{-2}	0.186	3.84×10^{-3}	.0647
1.46×10^{-2}	.0632	8.12×10^{-4}	.0854
2.95×10^{-3}	.0488	1.50×10^{-4}	.164
5.99×10^{-4}	.0778	3.63×10^{-5}	.361
1.21×10^{-4}	.160	7.68×10^{-6}	.865
2.46×10^{-5}	.450	1.62×10^{-6}	2.15
4.99×10^{-6}	1.40		
Run I, 0°			
1.46×10^{-2}	0.110		

TABLE III

CONDUCTANCE OF LITHIUM IODIDE IN DIMETHYLAMINE

Concn., moles/liter	Equiv. cond., 25°	Equiv. cond., 0°
6.58×10^{-2}	1.13	1.75
1.21×10^{-2}	0.199	0.452
2.22×10^{-3}	.171	.438
4.07×10^{-4}	.301	.789
7.47×10^{-5}	.652	1.70
1.37×10^{-5}	1.791	4.63
2.52×10^{-6}	5.248	13.53

TABLE IV

CONDUCTANCE OF POTASSIUM IODIDE IN DIMETHYLAMINE

Concn., moles/liter	Equiv. cond., 25°	Equiv. cond., 0°
	Run I	
3.69×10^{-4}	0.280	....
5.57×10^{-4}	.640	....
	Run II	
8.77×10^{-4}	0.164	....
1.63×10^{-4}	.352	0.731
3.03×10^{-5}	.737	1.58
5.64×10^{-6}	2.31	4.91
1.05×10^{-6}	5.63	18.32

An attempt was made to use d. c. in order to carry the measurements to lower concentrations, but this was not successful due to a small variable potential in the cell which could not be balanced out or removed by short circuiting.

It was unnecessary to correct for the conductance of the solvent, which has been found[2] to be about 3×10^{-12}, far too low to affect these measurements.

Results and Discussions

It is evident from examination of the figure that these systems are in accord with the Kraus and Fuoss theory, qualitatively at least. Both lithium iodide and sodium iodide exhibit minima in their conductance–concentration curves in the neighborhood of 0.005 *M*, and it is probable that potassium iodide would also if it were more soluble. Kraus and Fuoss[1a] state that, except for viscosity effects, the forms of conductance–concentration curves are dependent almost exclusively on the dielectric constant. If we compare the results of these measurements in dimethylamine ($D = 3.3$) with theirs in a dioxane–water mixture of $D = 3.5$, it is seen that for tetraisoamylammonium nitrate the minimum falls at almost exactly the same concentration. The minimum is also at this concentration for the same salt in a mixture of dioxane and ethylene dichloride ($D = 3.1$). It might be expected that the alkali iodides, having so much smaller ionic radii than tetraisoamylammonium nitrate, would show a stronger tendency to form triple ions, and that the minimum would occur at a lower concentration. It is evident, however, that the ionic size has little effect on the position of the minimum even in the extreme case of these small ions. This fact has been discussed by Kraus and Fuoss,[10] who have shown that, from a theoretical standpoint, the dielectric constant is the controlling factor in the position of the minimum, and that the ionic radius has little effect.

Below the minima the curves for all three salts show a slope of $-1/2$ within the limits of experimental error, corresponding to the association of two ions to form an ion-pair. It was not found possible to calculate Λ_0 and the dissociation constants of these equilibria, since the curves show no downward deviations from linearity in the low concentration region. However, we may estimate these constants by means of Walden's rule, using data obtained for aqueous solutions, but due to lack of necessary data on viscosities, it is

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(8) Grinnell Jones and R. C. Josephs, THIS JOURNAL, **50**, 1076 (1928).

(9) See, for example, Grinnell Jones and collaborators, *ibid.*, **56**, 602 (1934); **58**, 2561 (1936); **59**, 731 (1937).

(10) R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 2387 (1933).

somewhat difficult to apply it in this case. If we assume the value of the viscosity of dimethylamine at 25° to be 0.002, as compared with water at 18° = 0.01, the three values of Λ_0 are as follows: LiI = 500, NaI = 550, KI = 650. Rough calculations of the dissociation constants from the data of this paper give for LiI, $K = 2.5 \times 10^{-10}$, for KI, $K = 1 \times 10^{-10}$ and for NaI, $K = 4 \times 10^{-11}$. These values are of course only approximate, but are probably correct within a factor of ten and, relative to each other, this discrepancy is doubtless even smaller. The degree of dissociation at the minimum is only about 10^{-4}, and the single ion concentration must be at least as low as 5×10^{-7}, which is an upper limit because of a considerable formation of triple ions.

Although the ionic diameters of the three positive ions in the crystalline state increase from lithium to potassium, the conductances at any given concentration do not occur in that order. We would expect that since the potassium ion is larger than the sodium ion, the conductance curve of its iodide would be lower than that of the sodium iodide because of its lower mobility. That this is not the case is probably because of the greater dissociation of the potassium salt due to its greater diameter. It is evident that the increase in dissociation is of more importance than the decrease in mobility, a fact that might be anticipated since the relationship between the dissociation and the ionic diameter is exponential in nature[11] and the mobility decreases only as the square of the ionic diameter.

On the other hand, these facts might be interpreted as showing that the sodium ion is solvated and hence has a lower mobility, as is the case in liquid ammonia solutions. If the sodium ion is solvated and hence low-conducting, the lithium ion should be even more so. That this is not true may be seen by comparison of these curves with that for lithium iodide which lies above them. It is highly probable that the difference in conductivity between the sodium and the lithium salts is not due to a difference in mobility, which would hardly amount to a factor of 3–4. Therefore we are led to the conclusion that the lithium salt is more highly dissociated due to solvation, which increases the size of the lithium ion greatly. This is in accordance with the fact that this solvent is a strong base; that is, it solvates a proton very readily.

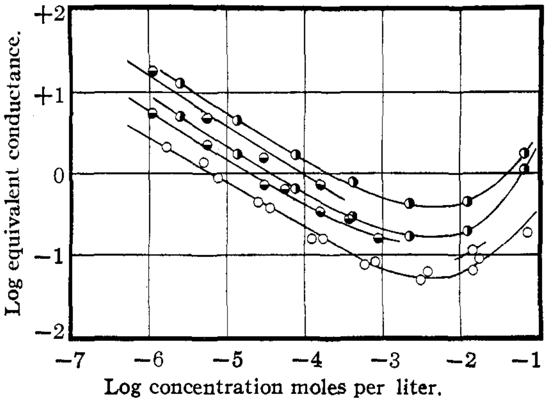

Fig. 1.—◑, LiI; ○, NaI; ◒, KI. The measurements at 0° lie *above* those at 25° in every case.

Additional evidence for an enhanced size of the lithium ion comes from consideration of the temperature coefficients of the resistance. These temperature coefficients are very large and positive; that is, the resistance is smaller at the lower temperature. This is the reverse of what is observed in aqueous solutions, but has often been observed in solutions of low dielectric constant. According to Coolidge and Bent,[12] since the process of separating two ions in solution requires work, the heat content of the system is increased thereby. During ionization, however, the molecules of the solvent are subjected to an electrostatic field which tends to orient them. This involves an entropy change which decreases the heat content of the system. ΔH (ionization) = ΔF (separation of ions, positive) + $T\Delta S$ (orientation, negative). Since the conductivity is greater at the lower temperature, it is evident that the dissociation is greater there and since $K_{\text{d.}}$ is larger at the lower temperature, ΔH must be negative. Therefore for these systems the energy involved in the orientation of the solvent is greater than the work of separation of the two ions. Unfortunately there are no viscosity data available for dimethylamine except at the temperature of boiling ammonia,[13] and so it is impossible to calculate the values of ΔH and ΔS for these solutions. However, we can compare the three salts without knowing the absolute values. In Table V below, r represents the temperature coefficient of the resistance, written as $(R_{25} \times R_0)/R_{25}$.

In this table it is seen that the temperature coefficients fall in the order sodium iodide,

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[11] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 1019 (1933).

[12] A. S. Coolidge and H. E. Bent, *ibid.*, **58**, 505 (1936).

[13] H. McK. Elsey, *ibid.*, **42**, 2454 (1920).

Table V

Concn. KI		Concn. NaI	r	Concn. LiI	r
......	..	......	..	6×10^{-2}	0.35
......	..	1×10^{-2}	0.43	1×10^{-2}	.56
......	..	......	..	2×10^{-3}	.61
1×10^{-4}	0.52	......	..	4×10^{-4}	.62
3×10^{-5}	.53	......	..	7×10^{-5}	.62
5×10^{-6}	.58	......	..	1×10^{-5}	.61
1×10^{-6}	.69	......	..	2×10^{-6}	.61

potassium iodide, lithium iodide, with lithium iodide having the largest coefficient. This in turn means that ΔH for lithium iodide has the largest negative value, indicating either that the entropy of orientation of the solvent is greater for this ion or that the free energy of ionization is smaller. Bent and Keevil[6] point out from their somewhat meager data on ether solutions that while ΔF varies somewhat with the distance of closest approach of the ions, the entropy change is relatively constant. If this is generally true, then the variation in ΔH is due to a difference in ΔF, rather than ΔS. Since the free energy of ionization decreases with increasing ion size, that is, larger salts are more easily ionized, it follows that the lithium ion has the largest ionic radius with the potassium ion next, as deduced previously. This again probably means that the lithium ion is solvated.

In a recent article,[14] Kelso and Felsing have reported finding negative partial molal volumes for lithium chloride in methylamine solutions. This probably indicates some solvation of this salt, while sodium nitrate has a positive partial molal volume, and probably is not solvated. These findings are in accord with the results of this research in a very similar solvent, and throw some light on the mechanism of the ionization process in solution. Since only an extremely small fraction of the lithium salt present is in the form of single ions in a solution of ordinary concentration such as those measured by Kelso and Felsing, the large negative partial molal volume observed must be caused by the ions in combination, rather than those existing as single ions. If these negative partial molal volumes are to be interpreted as indicating solvation, then the ions in the ion pairs are solvated and the greater dissociation of the lithium salt is due to the greater separation of the ions in the ion-pairs, resulting in a weakening of the coulombic force between them.

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Summary

1. The conductances of dilute solutions of sodium, potassium and lithium iodides in dimethylamine have been measured.

2. The results are qualitatively in accord with the Kraus and Fuoss theory.

3. It was found that the lithium ion is probably solvated by dimethylamine.

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[14] E. A. Kelso with W. A. Felsing, This Journal, **60**, 1949 (1938).

[Contribution from the Chemical Laboratories of the State University of Iowa]

Stable Sulfur Dithiocyanate

By P. A. Bond and G. A. Weaver, Jr.

In 1926, while investigating the solubilities of inorganic salts in sulfur monochloride, Baker[1] found that the thiocyanates of barium and potassium formed orange-red precipitates which were amorphous, insoluble in the strongest alkali, and stable in all except the most powerful oxidizing acids. Since the determination of the exact nature of this product did not come within the scope of the thesis, the reaction was not investigated further at that time. It seemed probable, however, that the orange-red powder belonged to the general class of "pseudo thiocyanates," upon which considerable research has been carried out.

In 1922, Lecher and Goebel[2] prepared the compound sulfur monothiocyanate, $S_2(SCN)_2$, by treating a mercuric thiocyanate in carbon disulfide with sulfur monochloride. The entire experiment was carried out at low temperatures in an apparatus described as being "practically completely protected from air."

Also, Lecher and Whittwer[3] prepared sulfur dithiocyanate, $S(SCN)_2$, by treating the free

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[1] Baker, "Solubilities of Inorganic Salts in S_2Cl_2," Thesis, State University of Iowa, 1926.

[2] Lecher and Goebel, *Ber.*, **55**, 1483–1495 (1922).

[3] Lecher and Whittwer, *ibid.*, **55**, 1481–1482 (1922).