ΔH_3 only. Then the following two possibilities may be distinguished

$$\text{(a)}\quad \Delta H^0 > 0 \text{ or } \Delta H_2 + \Delta H_3 > 0$$
$$\text{(b)}\quad \Delta H^0 < 0 \text{ or } \Delta HH_2 + \Delta H_3 < 0$$

Therefore, in (a) $\Delta H_2 > \Delta H_3$ but ΔH_3 may be positive or negative. However, in (b) $\Delta H_2 + \Delta H_3 < 0$ and hence ΔH_3 must be negative. This implies that energy is released by ion solvation.

If these concepts are applied to the results of this study, they are found to be fairly consistent with the facts. The results for the series of tetraalkyl ammonium picrates will be considered first. ΔH^0 is most highly negative for tetramethylammonium picrate. Since ΔH_2 for this salt would be expected to be most highly positive it follows that ΔH_3 is most highly negative. This is reasonable since the smallest ions are the most highly solvated.

Data for tetrabutylammonium picrate in the three solvents studied show that ΔH^0 is most highly negative in ethylene chloride and least so for propylene chloride. Since ΔH_2 is independent of solvent it follows that ΔH_3 becomes increasingly negative in the order propylene chloride < ethylene chloride < ethylidene chloride. This implies that ethylidene chloride is the strongest "solvator" of tetrabutylammonium picrate, and propylene chloride the weakest.

The case of anisole is somewhat different. For tetrabutylammonium picrate in that solvent ΔH^0 is positive. Since ΔH_2 should be the same as for the three alkyl halides it follows that ΔH_3 may be either positive or negative. Now, ΔH^0 for tetrabutylammonium nitrate in anisole is much more highly positive than for tetrabutylammonium picrate. It would be expected that ΔH_2 would be more positive for tetrabutylammonium nitrate since the nitrate ion is smaller than the picrate ion and hence more tightly bound to the cation. However, no relation can be derived on this basis for the relative magnitudes of ΔH_3 for the two salts, and hence no statement can be made as to the relative solvation of the nitrate and picrate ions in anisole. Indeed, it follows from the mathematical considerations involved that the relative ion solvation can be determined by this method only in those cases in which $\Delta H^0 < 0$.

It thus appears that in those solvents having the same value of $d/dT(1/D)$ the extent of dissociation for a given salt depends only on the value of ΔH^0. Since for most solvents the temperature coefficient of dielectric constant is negative it follows that the entropy contribution to ΔF^0 is unfavorable to dissociation. Hence the extent of dissociation will be largely determined by ΔH^0. When ΔH^0 is negative it may be concluded that the solvated ions represent a more stable arrangement than the solvated ion pair, *i.e.*, the ion–solvent bond is stronger than the ion pair–solvent bond. When ΔH^0 is positive the reverse is true.

At present we do not have sufficient information to calculate such solute–solvent interactions from the fundamental properties of solute and solvent and to compare these values with experiment. Such a study, using simpler solvents, is now in progress.

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WORCESTER, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KENTUCKY]

Solvents Having High Dielectric Constants. II. Solutions of Alkali Halides in N-Methylacetamide from 30 to 60°[1a,b]

BY LYLE R. DAWSON, PAUL G. SEARS AND RICHARD H. GRAVES

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Conductances, densities and viscosities of solutions of lithium chloride and of potassium and sodium chlorides, bromides and iodides in N-methylacetamide have been measured within the temperature range from 30 to 60° for concentrations which ranged from 5×10^{-4} to 1.0 or 2.0 molar. Kohlrausch plots for all of the systems exhibit relatively good agreement with the Onsager limiting equation to concentrations of 0.01 molar or more. Plots of the product of the equivalent conductance and the square root of the relative viscosity of the solution *versus* the square root of the concentration yield straight lines to 0.3 molar or above. The Kohlrausch law of independent ion mobilities is shown to be valid in these solutions.

The first paper of this series[2] described the electrical conductance of potassium chloride in formamide, which has a dielectric constant ranging from 118 to 103 within the temperature interval 3 to 40°.[3] Agreement with the limiting Onsager equation was shown to about 0.01 N where the slope of the Λ *vs.* $\sqrt{C}$ curve became less negative than the theoretical value. This was interpreted as evidence of the practically complete absence of ion association. However, as the concentration increased the plots became nearly linear, apparently as a consequence of an increase in viscosity which tended to counteract the concave-upward pattern observed with strong electrolytes in water.

The study reported herein is the primary phase of an investigation of the application of modern theories of solutions in areas hitherto unexplored in which the solvents have very high dielectric constants.[4] The present paper describes the behavior of several alkali halides in N-methylacetamide.

Experimental

Apparatus.—Conductances were measured at 1000 cycles with a shielded Jones bridge. Numerous additional measurements throughout the investigation at frequencies

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[1] (a) Presented at the 126th Meeting of the American Chemical Society in New York, September, 1954; (b) this work was supported in part by a contract with the Office of Ordnance Research.

[2] L. R. Dawson, T. M. Newell and W. J. McCreary, THIS JOURNAL, **76**, 6024 (1954).

[3] G. R. Leader, *ibid.*, **73**, 856 (1951).

[4] G. R. Leader and J. F. Gormley, *ibid.*, **73**, 5731 (1951).

ranging from 200 to 4000 cycles revealed no appreciable dependence of the conductance upon the frequency of the impressed voltage.

Five Jones and Bollinger[5] cells, with lightly platinized electrodes, which were used had cell constants ranging from 0.4204 to 31.99. The constants were determined by the method of Jones and Bradshaw.[6] All measurements were made with cells held in oil-baths the temperature of which did not vary more than 0.01° at 30 and 40°, or 0.1° at 50 and 60°.

For a part of the work, flask cells similar to those designed by Daggett, Bair and Kraus[7] were used and solutions were prepared by the method described by Hartley and Barrett.[8] The precision of the results was increased considerably by using the flask cells.

Viscosity measurements were made with size-100 Ostwald-Fenske viscometers which were calibrated with water (viscosity = 0.01005 poise at 20°), and two Bureau of Standards viscosity oils, H-8 and J-7. Changes in the viscometer constant with temperature were computed by the method recommended by Cannon and Fenske.[9]

Salts.—Lithium chloride was dehydrated at 350° under a stream of dry hydrogen chloride gas. Reagent grade potassium and sodium iodides were dried for one week ove anhydrous magnesium perchlorate in a vacuum desiccator. Reagent grade potassium and sodium chlorides were recrystallized from redistilled water and fused. Even after several recrystallizations, the bromides apparently contained a small amount of chloride; however, the other salts were 99.8% pure or better.

Solvent.-N-Methylacetamide was prepared by reaction of monomethylamine with glacial acetic acid and subsequent heating to crack out and distil off water. The product was purified by fractional distillation followed by five or more fractional freezing cycles using the procedure described by Berger and Dawson.[10] The N-methylacetamide used in this investigation froze above 29° and had a specific conductance lower than 2×10^{-6} ohm^{-1} cm.$^{-1}$ at 40°.

Solutions.—All solutions were prepared on a weight basis with transfers being made in a dry-box. Sufficient quantities of the solutions were prepared so that separate portions of each could be used for conductance, viscosity and density measurements.

Results

Properties of the solvent are listed in Table I. Results derived from the conductance data for the various systems are summarized in Table II. The conductance of each solution was corrected by subtracting the conductance of the solvent, and the data represent averages of duplicate or triplicate determinations. The precision throughout a duplicate or triplicate series of determinations was of the order of 0.2 to 0.4%.

Table I

Properties of N-Methylacetamide

Temp., °C.	30	40	50	60
Density, g./ml.	0.9503	0.9421	0.9336	0.9254
Viscosity, poise	0.03885	0.03019	0.02411	0.01958
Dielectric constant	178.9	165.5	151.8	138.6

Discussion

Kohlrausch plots which are typical of the solutions studied in this investigation are shown in Figs. 1–3. Comparisons between the halides of a given alkali as well as between alkali salts having a common anion appear in Fig. 2. Close correspondence between the experimental results and the theoretical values for solutions of sodium chloride may be observed in Fig. 3 where the dotted lines represent the theoretical slopes.

Table II

Results Derived from Conductance Data for Solutions of Salts in N-Methylacetamide

Salt	Temp., °C.	Λ_0	$\Lambda_0\eta$	Exptl. slope	Onsager slope	Dev., %
LiCl	30	14.1	0.550	10.6	10.0	5
	40	18.1	.548	14.1	13.3	6
	50	22.4	.543	17.2	17.1	1
	60	27.4	.536	22.1	21.9	1
NaCl	30	15.5	.601	10.9	10.1	7
	40	19.6	.594	13.4	13.4	1
	50	24.5	.590	18.1	17.3	5
	60	29.7	.581	22.6	22.1	3
NaBr	40	21.0	.636	14.0	13.5	4
NaI	30	17.8	.692	11.6	10.3	13
	40	22.8	.688	14.7	13.6	8
	50	28.0	.676	18.1	17.5	3
	60	34.0	.666	22.0	22.4	−2
KCl	30	15.8	.611	12.4	10.1	23
	40	20.1	.606	15.0	13.4	12
KBr	30	16.6	.645	10.8	10.1	6
	40	21.1	.637	13.8	13.5	2
	50	26.2	.632	17.1	17.4	−2
	60	32.1	.629	21.0	22.2	−5
KI	30	18.1	.705	11.4	10.3	11
	40	23.1	.698	15.3	13.7	12

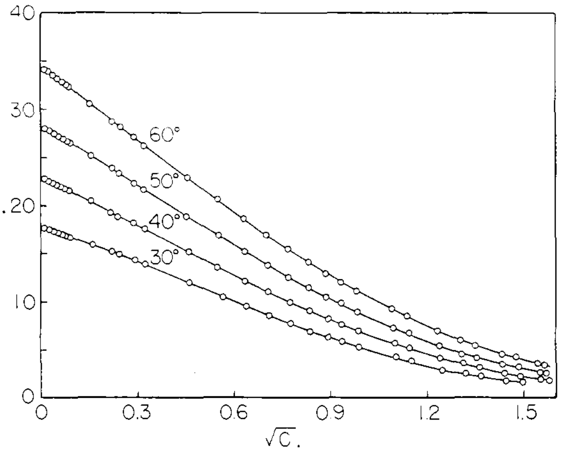

Fig. 1.—Kohlrausch plots for sodium iodide in N-methylacetamide.

From Table II it may be seen that some of the graphs have less than the theoretical limiting slopes indicating the practically complete absence of ion association; others exhibit slopes greater than the theoretical values, which behavior usually is taken as evidence of some degree of ion association. Accordingly, in the latter cases, the Shedlovsky[11] method of extrapolation was tried. A typical example is shown in Fig. 4. Throughout the systems studied, it was found that use of the Shedlovsky extrapolation method changed the Λ_0 value by no more than the experimental error, *i.e.*, by less than 0.5%.

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(5) G. Jones and G. M. Bollinger, This Journal, **53**, 411 (1931).

(6) G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

(7) H. M. Daggett, Jr., E. J. Bair and C. A. Kraus, *ibid.*, **73**, 799 (1951).

(8) H. Hartley and W. H. Barrett, *J. Chem. Soc.*, **103**, 786 (1913).

(9) M. R. Cannon and M. R. Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 297 (1938).

(10) C. Berger and L. R. Dawson, *Anal. Chem.*, **24**, 994 (1952).

(11) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

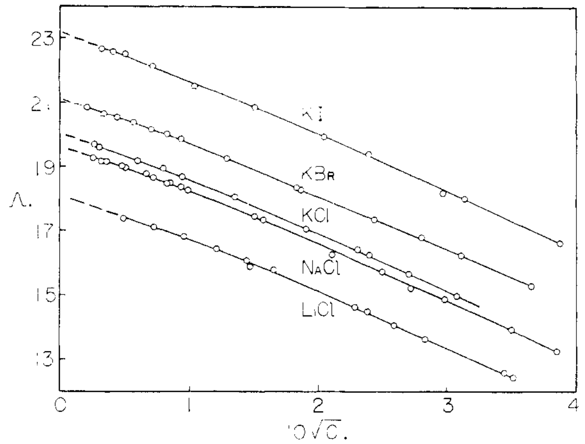

Fig. 2.—Kohlrausch plots for some alkali halides in N-methylacetamide at 40°.

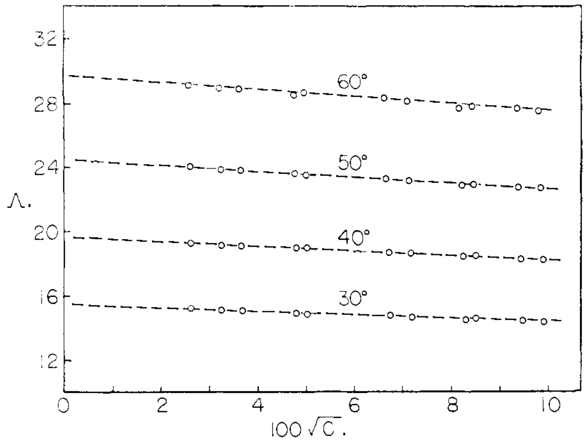

Fig. 3.—Kohlrausch plots for dilute solutions of sodium chloride in N-methylacetamide. Dashed lines represent theoretical behavior.

It is of interest to determine whether Kohlrausch's law of independent ion migration is valid for these solutions. Transference data are not available; however, if the limiting equivalent conductance of an ion is independent of the corresponding ion having an opposite charge, differences in the limiting conductances of two salts having an ion in common should be constant. Table III shows that this relation holds within the limits of experimental and extrapolation precision. The validity of the Kohlrausch law is strong evidence of the general reliability of the data.

Table III

Limiting Equivalent Conductances Used to Test the Kohlrausch Law of Independent Ion Mobilities

Temp., °C.	30	40
KCl	15.8	20.1
NaCl	15.5	19.7
	0.3	0.4
KBr		21.1
NaBr		21.0
		0.1
KI	18.1	23.1
NaI	17.8	22.8
	0.3	0.3

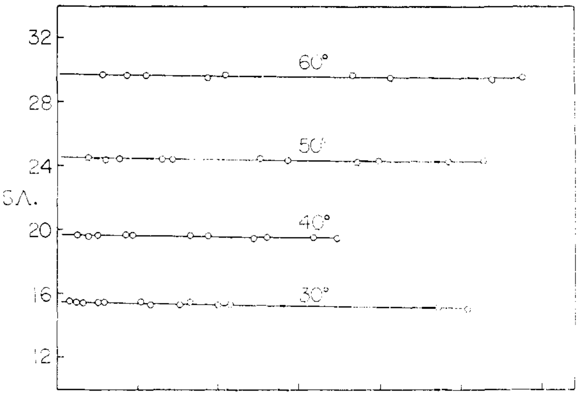

Fig. 4.—Plots of the Shedlovsky equation for sodium chloride in N-methylacetamide.

Onsager's treatment predicts that Kohlrausch plots, Λ *versus* $\sqrt{C}$, for strong electrolytes should become convex to the concentration axis as the concentration is increased, and this is actually the case in aqueous media. In N-methylacetamide solutions of the alkali halides this behavior does not appear until 0.8 molar or above. It is believed that the persistent downward trend of the plot may be attributed to the large increase in viscosity of the solution as the concentration becomes greater. For example, the viscosity of a 0.5 molar solution of potassium iodide in N-methylacetamide is 1.5 times the viscosity of the pure solvent at 30°. In these systems, the logarithm of the viscosity is a linear function of the concentration over the range investigated (typical graph shown in Fig. 7). Likewise the density was found to be a linear function of the molality.

Examination of numerous relationships among the data revealed that the product of the equivalent conductance and the square root of the relative viscosity is a linear function of the square root of the concentration. If it is assumed that

$$\Lambda = \frac{\Lambda'}{\sqrt{\eta_r}} = \frac{\Lambda_0 - (\alpha + \beta\Lambda_0)\sqrt{C}}{\sqrt{\eta_r}}$$

or

$$\Lambda\sqrt{\eta_r} = \Lambda_0 - (\alpha + \beta\Lambda_0)\sqrt{C} \qquad (1)$$

where

$$\alpha = \frac{82.42}{(DT)^{1/2}\eta},\ \beta = \frac{8.204 \times 10^5}{(DT)^{3/2}}$$

Λ and η_r are the experimentally determined equivalent conductance and relative viscosity, respectively, then a graph of $\Lambda\sqrt{\eta_r}$ *versus* $\sqrt{C}$ should yield a straight line having the theoretical Onsager slope. Such plots for the alkali halides in N-methylacetamide give straight lines to approximately 0.4 molar (Fig. 5). Furthermore, agreement with the theoretical slopes is surprisingly good.

An extension of the Onsager[12] equation may be written

$$\Lambda = \Lambda_0 - (\alpha + \beta\Lambda_0)\sqrt{C} + BC\theta_r$$

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(12) L. Onsager, *Physik. Z.*, **28**, 227 (1927).

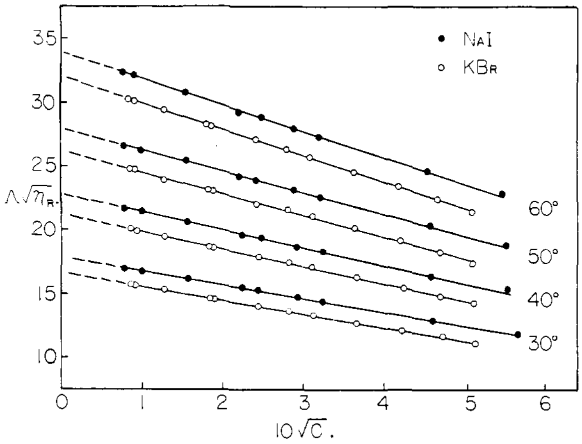

Fig. 5.—Plots of equation 1 for solutions of sodium iodide and potassium bromide in N-methylacetamide.

or

$$\Lambda + (\alpha + \beta\Lambda_0)\sqrt{C} = \Lambda_0 + BC\theta_r \qquad (2)$$

where θ_r is the relative fluidity. Typical plots of equation 2 for some of the alkali halides are shown in Fig. 6. This equation describes satisfactorily

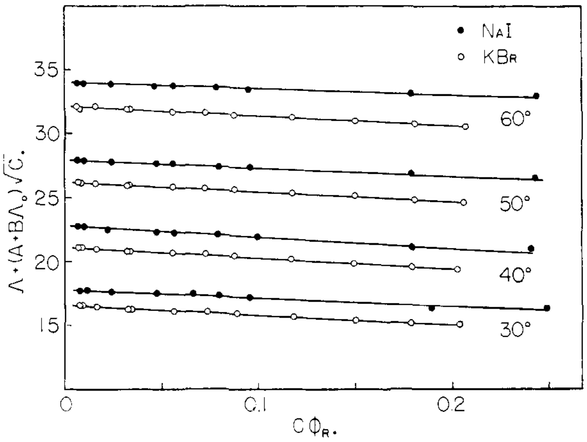

Fig. 6.—Plots of equation 2 for solutions of sodium iodide and potassium bromide in N-methylacetamide.

the conductances of the systems studied up to concentrations of 0.2 to 0.3 molar. Slopes and intercepts of the plots of equations 1 and 2 are listed in Table IV.

TABLE IV

DATA FROM PLOTS DERIVED FROM MODIFIED EQUATIONS

Salt	Temp., °C.	Λ_0 Eq. 1	Λ_0 Eq. 2	Slope Eq. 1	Slope Eq. 2
NaI	30	17.8	17.8	10.5	6.76
	40	22.8	22.8	13.9	7.96
	50	28.0	27.9	16.8	5.74
	60	33.9	33.9	20.6	4.78
KBr	30	16.6	16.6	10.6	7.62
	40	21.1	21.1	13.4	7.69
	50	26.1	26.2	16.6	7.50
	60	32.0	32.1	20.7	7.40
KI	30	18.1	18.1	10.8	7.88
	40	23.1	23.1	13.6	7.88

Complete dissociation of uni-univalent salts would be expected in solvents having very high dielectric constants. All of the evidence which we

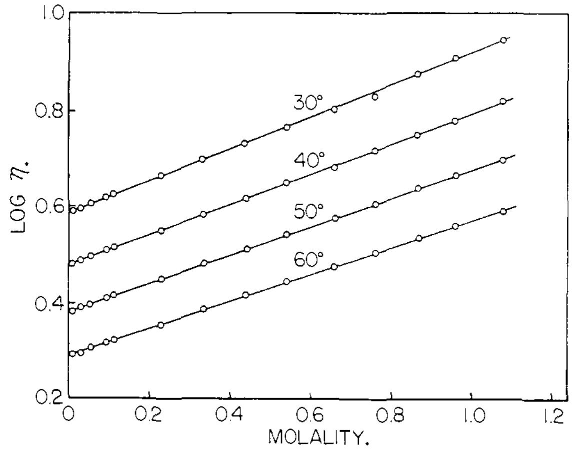

Fig. 7.—The logarithm of the viscosity of solutions of sodium iodide as a function of the molality.

have obtained leads to this conclusion for the systems investigated. Positive deviations (*i.e.*, greater slopes) of the Kohlrausch plots from the theoretical appear to result from viscosity effects. General agreement with the theoretical slopes exists for most of these systems to much higher concentrations than in water. Limiting equivalent conductances obtained from extrapolation of viscosity-corrected data (equation 1) agree quite well with those obtained by other methods.

There is strong evidence that N-methylacetamide exists as long-chain polymers.[2] Evidence that the introduction of most foreign substances disrupts the chains, with a resulting abrupt decrease in dielectric constant, will be presented in a subsequent paper. Thus the magnitude of the actual dielectric constant of the solvent in the solution is very uncertain. Whether either or both types of ions become solvated is unknown; however the fact that the salt is soluble and that the Walden product, $\Lambda_0\eta$, is lower than for similar solutions in water may be considered as evidence of solute–solvent interaction. Of course, Stokes' law of hydrodynamics could not be expected to apply accurately in a medium where the solvent particles are very large in comparison to the solute particles.

The Walden product, $\Lambda_0\eta$, decreases as the temperature increases, which means that the solvodynamic units encounter greater resistance to flow than would be expected if they remained the same size or became smaller. Their effective sizes may increase because greater thermal agitation promotes disruption of the chain-like molecular groups in the solvent thus permitting increased solvation.

Although there are uncertain factors involved, the approximate correspondence shown between experimental results and the theoretically predicted behavior extending to relatively large concentrations is unexpected. Suitable viscosity corrections permit extension of the theoretical equations even further. The conductance behavior of these solutions in comparison to aqueous systems would seem even more unusual if the concentrations were expressed as mole fractions or mole ratios rather than as molarity.

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