[Contribution from the Department of Chemistry, University of Kentucky]

Solvents Having High Dielectric Constants. V. Limiting Ionic Equivalent Conductances in N-Methylacetamide at 40°[1,2]

By Lyle R. Dawson, Eugene D. Wilhoit, Richard R. Holmes and Paul G. Sears

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Studies have been made concerning the conductance behavior at 40° of twenty uni-univalent electrolytes in N-methylacetamide at concentrations in the range $1–165 \times 10^{-4}$ *N*. The limiting equivalent conductance for each electrolyte has been evaluated using a Shedlovsky plot of Λ'_0 *versus* C. Consistency within the results and with previous work is evidenced by numerous checks concerning independent conductances of ions. The results indicate that 2,4,6-trinitrophenol, hydrogen chloride and all of the salts are completely dissociated in dilute N-methylacetamide solutions. In contrast to the differentiating action of isomeric dimethylformamide, N-methylacetamide acts as a leveling solvent toward acids and partially substituted ammonium salts. Values of the limiting ionic equivalent conductances which are based upon the octadecyltrimethylammonium octadecylsulfate and the trimethylphenylammonium benzenesulfonate methods show good agreement.

Introduction

The second and the fourth papers in this series[3,4] have described the conductance behavior of thirty-one uni-univalent electrolytes in N-methylacetamide (NMA), an unusual organic solvent which is characterized by an extremely high dielectric constant (165.5 at 40°) and extensive dissolving and dissociating power. The results which have been reported heretofore indicate that most soluble salts are completely dissociated in dilute NMA solutions and that analyses of conductance data for solutions having concentrations greater than 1×10^{-2} *N* are complex owing to a very pronounced increase in viscosity with increasing concentration. NMA acts as a leveling solvent in its dissociating action toward partially substituted ammonium halides, and series of relative cationic and anionic limiting conductances provide considerable evidence that unusual relative solute–solvent interactions are operative in NMA solutions.

The objectives of the research which is reported herein were to determine the conductance behavior of some typical acidic electrolytes, to evaluate limiting ionic equivalent conductances by approximation methods and to extend generally the previous studies using NMA as an electrolytic solvent.

Experimental

Apparatus.—Resistances were measured with a Jones bridge assembly at frequencies of 500, 1000 and 2000 cycles per second. No significant dependence of resistance upon the frequency of the impressed signal was observed. Three flask cells, which have been described previously,[5] were used throughout this work. The cell constants were determined by the intercomparison method using Jones cells having constants which had been evaluated by the method of Jones and Bradshaw.[6] The cells and their contents were maintained at 40.00 ± 0.02° in a constant temperature bath filled with light mineral oil.

Salts.—Octadecyltrimethylammonium octadecylsulfate, octadecyltrimethylammonium nitrate, octadecyltrimethylammonium iodide and potassium octadecylsulfate were prepared by the methods described by Thompson and Kraus.[7] The observed melting points of the final products were 153–156°, 200–202°, 235–238° and 181–183°, respectively. These four salts and the two benzenesulfonates were considered suitable for use only when their equivalent conductances changed less than 0.15% after successive recrystallizations.

Reagent grade potassium and sodium bromates, ammonium perchlorate and ammonium nitrate were recrystallized twice from distilled water prior to drying under suitable conditions.

The preparation and/or purification of the remaining electrolytes have been described in previous papers.[5,8–10]

Solvent.—NMA was prepared and purified as described previously.[4] The solvent which was used in this work froze above 29.5° and had the following physical properties at 40°: conductivity, $1–3 \times 10^{-7}$ ohm^{-1} cm.$^{-1}$; density, 0.9420 g./ml.; viscosity, 0.0302 poise; dielectric constant, 165.5 (at 10 megacycles).

Solutions.—All solutions were prepared on a weight basis and transfers were made in a dry box under a positive pressure of nitrogen. Friedman–La Mer weighing pipets were used for making successive additions of approximately 0.02 *N* stock solution to the solvent contained in a conductance cell. All weights were corrected to vacuum. The densities of the dilute solutions were assumed to be equal to that of the solvent. The conductivity of the electrolyte was obtained by subtracting the conductivity of the solvent from that of the solution. The maximum solvent correction usually did not exceed 3% of the total conductance.

Results

Owing to its extensive nature, a tabulation of corresponding values of the equivalent conductance and the concentration for each of the twenty electrolytes is not presented here.[11] The results are compactly summarized in Tables I, II and III. Similar trends in the data have been illustrated graphically in previous papers in this series.

Discussion

The plot of Λ *versus* $\sqrt{C}$ for each electrolyte is linear over the entire experimental concentration range which, as a result of limited solubilities in some cases, varied from $1–14 \times 10^{-4}$ *N* for OctdMe$_3$NOctdSO$_4$ to $1–165 \times 10^{-4}$ for KSCN. Ac-

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[2] Taken from a thesis submitted by Richard R. Holmes and from a part of a dissertation submitted by Eugene D. Wilhoit in partial fulfillment of the requirements for advanced degrees.

[3] L. R. Dawson, E. D. Wilhoit and P. G. Sears, This Journal, **78**, 1569 (1956).

[4] L. R. Dawson, P. G. Sears and R. H. Graves, *ibid.*, **77**, 1986 (1955).

[5] D. P. Ames and P. G. Sears, *J. Phys. Chem.*, **59**, 16 (1955).

[6] G. Jones and B. C. Bradshaw, This Journal, **55**, 1780 (1933).

[7] W. E. Thompson and C. A. Kraus, *ibid.*, **69**, 1016 (1947).

[8] P. G. Sears, R. K. Wolford and L. R. Dawson, *J. Electrochem. Soc.*, **103**, 633 (1956).

[9] P. G. Sears, G. R. Lester and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956).

[10] G. R. Lester, T. A. Gover and P. G. Sears, *ibid.*, **60**, 1076 (1956).

[11] Tables of corresponding equivalent conductance and concentration data have been deposited as Document number 5147 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

TABLE I

TEST OF ONSAGER'S EQUATION FOR SOLUTIONS OF SALTS IN N-METHYLACETAMIDE AT 40°

Electrolyte	Λ_0	Exptl. slope (S_E)	Theor. slope (S_T)	$\frac{(S_E - S_T)100}{S_T}$
HCl	20.65	13.4	13.4	0
HPi[a]	20.85	14.0	13.4	5
NaO_3SPh	18.41	15.0	13.3	13
Me_3PhNO_3SPh	20.47	14.4	13.4	8
$OctdMe_3Ni$[b]	21.76	16.2	13.5	20
$OctdMe_3NNO_3$	21.64	15.5	13.5	15
$KOctdSO_4$	15.47	14.0	13.1	7
$OctdMe_3NOctdSO_4$	14.27	14.5	13.0	11
NH_4ClO_4	26.45	14.2	13.8	3
NH_4NO_3	24.23	15.0	13.7	10
$KClO_4$	25.22	14.8	13.7	8
KSCN	24.48	14.7	13.7	7
KNO_3	22.94	15.8	13.6	16
$KBrO_3$	21.96	15.0	13.5	11
KPi	20.19	15.0	13.4	12
$NaClO_4$	24.96	14.2	13.7	4
NaSCN	24.24	14.7	13.7	8
$NaNO_3$	22.67	15.8	13.6	17
$NaBrO_3$	21.82	14.8	13.5	10
NaPi	20.17	13.8	13.4	3

[a] Pi represents picrate. [b] Octd represents octadecyl.

TABLE II

DATA DERIVED FROM PLOTS OF THE SHEDLOVSKY MODIFICATION OF THE ONSAGER EQUATION

Electrolyte	Λ_0	B	Electrolyte	Λ_0	B
HCl	20.68	0	$KClO_4$	25.22	−11
HPi	20.87	−11	KSCN	24.47	− 7
NaO_3SPh	18.37	−18	KNO_3	22.92	−28
Me_3PhNO_3SPh	20.46	−20	$KBrO_3$	21.95	−18
$OctdMe_3NI$	21.72	−32	KPi	20.18	−17
$OctdMe_3NNO_3$	21.60	−20	$NaClO_4$	24.95	− 2
$KOctdSO_4$	15.45	−10	NaSCN	24.14	− 6
$OctdMe_3NOctdSO_4$	14.26	−40	$NaNO_3$	22.65	−23
NH_4ClO_4	26.45	− 3	$NaBrO_3$	21.82	−15
NH_4NO_3	24.24	−13	NaPi	20.17	− 3

TABLE III

DATA PERTINENT TO LIMITING IONIC EQUIVALENT CONDUCTANCES IN NMA AT 40° BASED ON THE $OctdMe_3NOctdSO_4$ METHOD

Cation	λ_0^+	Anion	λ_0^-
$Me_2NH_2^+$	13.6	ClO_4^-	16.8
Me_3NH^+	12.9	SCN^-	16.1
Me_4N^+	12.0	I^-	14.6
$Et_2NH_2^+$	11.9	NO_3^-	14.5
$MeNH_3^+$	11.9	BrO_3^-	13.6
Et_4N^+	11.6	Br^-	12.8
$EtNH_3^+$	10.9	Pi^-	11.8
Me_3PhN^+	10.2	Cl^-	11.5
$BuNH_3^+$	9.8	$PhSO_3^-$	10.3
NH_4^+	9.7	$OctdSO_4^-$	7.1
$Bu_2NH_2^+$	9.4		
Pr_4N^+	9.1		
H^+	9.1		
K^+	8.4		
Na^+	8.2		
Bu_4N^+	7.8		
$OctdMe_3N^+$	7.1		
Li^+	6.6		

cording to the Onsager equation[12]

$$\Lambda = \Lambda_0 - \left[\frac{8.204 \times 10^5}{(DT)^{3/2}}\Lambda_0 + \frac{82.42}{(DT)^{1/2}\eta}\right]\sqrt{C}$$

the theoretical limiting slope of a plot of Λ *versus* $\sqrt{C}$ for a uni-univalent electrolyte in NMA at 40° should be $-[0.0695\ \Lambda_0 + 11.99]$. With the single exception for hydrogen chloride, the data presented in Table I show that the experimental slope in every case is numerically greater than the Onsager slope; the differences range from 0 to 20% with a mean of 9%. Although the numerically greater experimental slopes perhaps suggest some extent of ionic association, it is believed that the nature of the slopes of the plots of Λ *versus* $\sqrt{C}$ for electrolytes in NMA is greatly influenced by the viscosities of the solutions rapidly increasing with increasing concentration (for example, the approximate relative viscosities of 0.01, 0.5 and 1.0 N solutions of a typical uni-univalent electrolyte in NMA are 1.01, 1.55 and 2.25, respectively[13]).

Values of the limiting equivalent conductances were calculated directly from the experimental equivalent conductance data using the Shedlovsky rearrangement of the Onsager equation.[14] Values of the limiting equivalent conductance calculated in this manner are designated as Λ'_0 and generally are found to deviate from the true value for the limiting equivalent conductance by a linear function of the concentration as

$$\Lambda'_0 \equiv \frac{\Lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}} = \Lambda_0 + BC$$

which for electrolytes in NMA at 40° becomes

$$\Lambda'_0 \equiv \frac{\Lambda + 11.99\sqrt{C}}{1 - 0.0695\sqrt{C}} = \Lambda_0 + BC$$

As in previous studies,[3,4] the plot of Λ'_0 *versus* C for each electrolyte is linear over the entire experimental concentration range and is characterized by a small negative slope probably resulting from viscosity effects. Data pertinent to plots of Λ'_0 *versus* C are summarized in Table II. Corresponding values of Λ_0 in Tables I and II in some cases differ by a few hundredths of a unit; however, it is believed that those in Table II are probably more accurate inasmuch as a preferable extrapolation procedure was used.

A survey of the values of Λ_0 in Table II together with those obtained in previous studies reveals numerous confirmations of the Kohlrausch law of independent ionic conductances therein indicating consistency within the results reported herein as well as with those published previously.

On the basis of experimental and theoretical structural considerations, Thompson and Kraus[7] have suggested that the limiting equivalent conductances of the $OctdMe_3N^+$ and the $OctdSO_4^-$ ions are approximately equal and can be evaluated by halving the limiting equivalent conductance of $OctdMe_3NOctdSO_4$. If the limiting equivalent conductances of these two large similarly-shaped ions are known, other limiting ionic equivalent

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(12) L. Onsager, *Physik. Z.*, **28**, 277 (1927).

(13) P. G. Sears, Dissertation, University of Kentucky, 1953.

(14) T. Shedlovsky, THIS JOURNAL, **54**, 1405 (1932).

conductances can be evaluated from properly related data for electrolytes containing either the $OctdMe_3N^+$ or the $OctdSO_4^-$ ion and for other electrolytes having common anions or cations. Table III contains values of limiting ionic conductances in NMA at 40° which are based upon this approximation method. Data from previous papers[3,4] were utilized also in order to provide an up-to-date comprehensive tabulation for NMA solutions.

The trimethylphenylammonium and the benzenesulfonate ions, like the $OctdMe_3N^+$ and the $OctdSO_4^-$ ions, are relatively large similarly-shaped species having comparable dimensions and are characterized by almost equal limiting conductances in aqueous solutions.[15,16] Consequently, it is worthwhile to note that the results in Table II would be altered less than 0.5% if Me_3PhNO_3SPh were used as the reference electrolyte instead of $OctdMe_3NOctdSO_4$. On the basis of data for aqueous and NMA solutions, therefore, Me_3PhNO_3SPh is potentially applicable as a reference electrolyte for approximating limiting ionic equivalent conductances in other solvents. Inherent advantages may be utilized also inasmuch as Me_3PhNO_3SPh, NaO_3SPh and Me_3PhNI are commercially available, easily purified and readily soluble in several common solvents in which $OctdMe_3NOctdSO_4$ and $KOctdSO_4$ are practically insoluble.

Based on the data in Table III, the limiting equivalent conductance–viscosity products for the Bu_4N^+ and the Pi^- ions in NMA are 0.236 and 0.356 ohm^{-1} $cm.^2$ $equiv.^{-1}$ poise and are about 35% greater than the corresponding products for aqueous solutions. Nevertheless, the ratio of the limiting equivalent conductance of the picrate ion to that of Bu_4N^+ ion in NMA differs less than 3% from the same conductance ratio for aqueous solutions and consequently indicates considerable parallelism in the relative conductance behavior of these large ions in NMA and in water.

Although the ratio of the viscosity of NMA at 40° to that of water at 25° is 3.4, the ratio of the limiting equivalent conductance of an ion in water at 25° to that of the same ion in NMA at 40° varies from 2.5 for the Bu_4N^+ ion to 8.7 for the potassium ion, excluding the solvated proton and several ions for which proper comparison data are unavailable. The broad range of values for the conductance ratio together with the very high values for the conductance–viscosity products for the Bu_4N^+ and Pi^- ions suggests that unusual relative solute–solvent interactions and perhaps significant variations between the macroscopic viscosities of the solutions and the microscopic viscosities in the immediate vicinities of the ionic species may be operative in NMA solutions. Novel positions which are occupied by several ionic species in series of decreasing cationic and anionic limiting equivalent conductances are readily discernible from the data presented in Table III.

In comparing the behavior of hydrogen chloride and 2,4,6-trinitrophenol (picric acid) in the isomeric amides, N-methylacetamide and N,N-dimethylformamide, it is interesting to note that the former and the latter[8] act as leveling and differentiating solvents, respectively, toward the acidic solutes. The extent of substitution on the amide-N not only drastically affects the magnitudes of physical properties but also apparently is reflected in the proton-accepting properties of the medium.

Other conductance studies involving the behavior of multivalent electrolytes in NMA and also the behavior of uni-univalent electrolytes in iso-viscous mixtures of NMA and tertiary butyl alcohol and in mixtures of isomeric NMA and N,N-dimethylformamide are in progress in this Laboratory.

LEXINGTON, KENTUCKY

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[15] W. J. McDowell and C. A. Kraus, THIS JOURNAL, **73**, 2173 (1951).

[16] G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 400 (1932).

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

Interaction of Polyelectrolytes with the Electrical Double Layer on Mercury–Water Interfaces. II. Influence of Added Ionized Polyacids on the Differential Capacity*

BY ISRAEL R. MILLER[1] AND DAVID C. GRAHAME

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The differential capacity of the electrical double layer at the interface between mercury and aqueous 0.1 *N* NaF solutions containing various amounts of the salts of dibasic and polybasic acids at different temperatures has been measured. A series of polyacids has been investigated, starting with simple dibasic acids, through the relatively low molecular weight polyaspartic and polyglutamic acids, and extending finally to very high molecular weight samples of polymethacrylic acid of various degrees of polymerization. It has been found that the results can be interpreted by assuming (a) that even short hydrocarbon chains produce a squeezing-out effect which appears as an adsorption of anions, and (b) that polybasic anions are completely expelled from the interface when the mercury carries even a small negative charge, and strongly attracted when the charge is slightly positive. Adsorption–desorption peaks are produced at the potential of the electrocapillary maximum through the operation of this effect. It seems clear that a monolayer of anions is formed.

Introduction

From the electrocapillary properties of soluble acetates and oxalates it is known,[2-4] that the car-

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[1] On leave of absence from the Weizmann Institute, Rehovot, Israel, during the execution of the experimental part of this work.

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