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

Solvents Having High Dielectric Constants. IX. Conductimetric Behavior of Some Alkaline Earth Salts in N-Methylacetamide at 40°[1,2]

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The equivalent conductance of each of twenty alkaline earth salts in N-methylacetamide (NMA) has been determined at several concentrations in the range 1–280 × 10^{-4} *N*. The resulting phoreograms are very slightly anabatic for all salts except barium and strontium nitrates. Excellent agreement exists between the observed results and those predicted theoretically by the Onsager equation. Values of Λ_0 have been determined from Shedlovsky plots of Λ'_0 *versus* *C*. The behavior of corresponding anhydrous and hydrated salts appears to be identical within experimental error. The limiting ionic equivalent conductances of the alkaline earth ions in NMA have been calculated by differences utilizing previous results based on the octadecyltrimethylammonium octadecyl sulfate method. The barium ion unexpectedly is slightly less conducting than the calcium and strontium ions in NMA.

Introduction

Preceding papers from this Laboratory[4–6] describe the conductance behavior of more than fifty uni-univalent electrolytes in NMA, an unusual solvent characterized at 40° by an exceptionally high dielectric constant (165.5 at 10 megacycles), moderate viscosity (3.02 centipoise), and extensive dissolving and dissociating power. Excellent agreement between the experimental results and those predicted theoretically by the Onsager equation[7] indicates that all of the ionophores and also ionogens such as hydrogen chloride and 2,4,6-trinitrophenol are dissociated completely in dilute NMA solutions. The availability of values for limiting ionic equivalent conductances[6] also permits an extension of theoretical analyses to conductance data for unsymmetrical multivalent electrolytes in NMA.

The objectives of the research described herein were to study the conductances of several alkaline earth salts in dilute NMA solutions, to compare the behavior of corresponding anhydrous and hydrated salts and to extend generally the existing knowledge concerning the potentialities of NMA as an important electrolytic solvent.

Experimental

Apparatus and Procedure.—These have been described in detail previously.[4,5]

Salts.—Reagent grade salts which were purchased from the Mallinckrodt Chemical Company and the G. Frederick Smith Chemical Company were used without further purification. The non-hydrated salts were dried to constant weight in a vacuum oven at an appropriate temperature. All of the salts were analyzed for water content by the Karl Fischer method using Fisher stabilized single-solution Karl Fischer reagent after it had been standardized against sodium acetate trihydrate.[8] Also, all the halides were analyzed by the Fajans method[9] and were found to be very pure. The molecular weights of the hydrated solutes were adjusted in necessary cases to conform with the analytical data. For convenience, each hydrate is listed in the following tables as the one containing the nearest integral number of associated water molecules.

Solvent.—The preparation and purification of NMA has been described previously.[4,5] The solvent which was used in this study had a freezing point of 30° and the following physical properties at 40°: conductivity, 1–5 × 10^{-7} ohm^{-1} cm.$^{-1}$; density, 0.9421 g./ml.; dielectric constant, 165.5; viscosity, 0.0302 poise.

Results

The very extensive tabulation of corresponding values of the equivalent conductance and the equivalent concentration for each of the twenty electrolytes is omitted herein to conserve valuable space but is available elsewhere.[10] However, the more useful results which were derived from these data are conveniently summarized in Tables I and II.

TABLE I

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

Salt	Λ_0	Exptl. slope (S_E)	Theor. slope (S_T)	$\frac{(S_E - S_T)\,100}{S_T}$
$BaCl_2$	21.61	22.9	25.3	−10
$BaCl_2 \cdot 2H_2O$	21.61	22.9	25.3	−10
$BaBr_2$	22.90	23.5	25.5	− 8
$BaBr_2 \cdot 2H_2O$	22.90	23.5	25.5	− 8
BaI_2	24.58	22.1	25.7	−14
$BaI_2 \cdot 2H_2O$	24.65	22.1	25.7	−14
$Ba(NO_3)_2$	24.64	28.0	25.7	9
$Ba(ClO_4)_2$	27.05	24.3	26.0	− 7
$Ba(ClO_4)_2 \cdot 3H_2O$	27.05	24.4	26.0	− 6
$SrCl_2 \cdot 6H_2O$	21.93	23.9	25.4	− 6
$SrBr_2 \cdot H_2O$	23.13	23.9	25.5	− 6
$SrBr_2 \cdot 6H_2O$	23.13	23.9	25.5	− 6
$Sr(NO_3)_2$	24.95	29.3	25.8	12
$Sr(ClO_4)_2 \cdot 3H_2O$	27.25	24.1	26.0	− 7
$Sr(ClO_4)_2$	27.26	24.0	26.0	− 8
$CaBr_2 \cdot 4H_2O$	23.12	23.6	25.5	− 8
$Ca(ClO_4)_2 \cdot 4H_2O$	27.00	24.9	26.0	− 4
$Ca(NO_3)_2 \cdot 4H_2O$	24.66	24.9	25.5	− 3
$MgCl_2 \cdot 6H_2O$	21.28	23.3	25.3	− 8
$Mg(NO_3)_2 \cdot 5H_2O$	24.20	25.8	25.6	1

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[2] Taken from a dissertation submitted by George R. Lester in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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

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

[6] L. R. Dawson, E. D. Wilhoit, R. R. Holmes and P. G. Sears, *ibid.*, **79**, 3004 (1957).

[7] L. Onsager, *Physik. Z.*, **28**, 277 (1927).

[8] G. G. Warren, *Can. Chem. Process Inds.*, **29**, 370 (1945).

[9] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1952, p. 543.

[10] A complete tabulation of corresponding equivalent conductance and concentration data has been deposited as Document number 5524 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 II

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

Salt	Λ_0	B
$BaCl_2$	21.67	18
$BaCl_2 \cdot 2H_2O$	21.64	19
$BaBr_2$	22.93	18
$BaBr_2 \cdot 2H_2O$	22.92	21
BaI_2	24.66	29
$BaI_2 \cdot 2H_2O$	24.71	38
$Ba(NO_3)_2$	24.60	−25
$Ba(ClO_4)_2$	27.07	19
$Ba(ClO_4)_2 \cdot 3H_2O$	27.07	19
$SrCl_2 \cdot 6H_2O$	21.93	20
$SrBr_2 \cdot H_2O$	23.13	25
$SrBr_2 \cdot 6H_2O$	23.13	18
$Sr(NO_3)_2$	24.92	−33
$Sr(ClO_4)_2 \cdot 3H_2O$	27.26	20
$Sr(ClO_4)_2$	27.30	20
$CaBr_2 \cdot 4H_2O$	23.13	24
$Ca(ClO_4)_2 \cdot 4H_2O$	27.00	22
$Ca(NO_3)_2 \cdot 4H_2O$	24.69	4
$MgCl_2 \cdot 6H_2O$	21.33	15
$Mg(NO_3)_2 \cdot 5H_2O$	24.20	0

Discussion

The phoreogram[11] for each electrolyte is linear over the entire concentration range which is included within 1-280 × 10^{-4} N. Results from duplicate series of measurements always agree within 0.1%. In order to compare the observed results with those predicted theoretically, utilization is made of the Onsager equation[7] which may be written conveniently in the general form

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

in which C is the concentration of solute in gram equivalents per liter, Λ and Λ_0 are the equivalent conductances at concentration C and infinite dilution, respectively, and α and β are constants the values of which are fixed by the dielectric constant and viscosity of the solvent, the number of unit charges on each of the ions and the absolute temperature. For a multivalent electrolyte having an anion and a cation with different valences, the value of α is dependent also upon transference data. For NMA solutions of alkaline earth salts having univalent anions at 40°, $\beta = 22.04$ and $\alpha = 0.388/(1 + T_0^- + 0.816\sqrt{1 + T_0^-})$ in which T_0^- is the limiting value of the transference number of the anion. Existing values of the limiting equivalent conductances, λ_0^-, of the pertinent anions from an earlier study[6] make possible the convenient evaluation, $T_0^- = \lambda_0^-/\Lambda_0$. The experimental slope of the phoreogram in most cases shows good agreement with the Onsager slope, $-(\alpha\Lambda_0 + \beta)$, therein indicating essentially complete dissociation. Comparison data are summarized in Table I.

The values of the limiting ionic equivalent conductances which were used to evaluate the T_0^- data are based upon the octadecyltrimethylammonium octadecyl sulfate approximation method. However, the relative contributions of the asymmetric effect, $\alpha\Lambda_0$, and the electrophoretic effect, β, to the theoretical slope of a phoreogram for a 2–1 salt in NMA are about 15 and 85%, respectively, and the transference data are needed only in the evaluation of $\alpha\Lambda_0$. Calculations reveal that a 10% change in a typical anionic transference number would alter the value of the theoretical slope by only 0.5%.

With an exception for some of the nitrates, the phoreograms for the alkaline earth salts are slightly anabatic. This is quite interesting inasmuch as the phoreograms for 1–1 salts have been observed previously to be always very slightly catabatic. If ionic association were operative, however, the phoreograms for the 2–1 salts should be more catabatic than those for the 1–1 salts. The most probable explanation is that both types of salts are dissociated completely in dilute NMA solutions and that the somewhat illusory relative natures of the slopes of the phoreograms for the different types of salts is attributable to relative viscosity effects. For both types of salts the viscosities of NMA solutions increase very rapidly with concentration, *e.g.*, the relative viscosities of 0.01, 0.5 and 1.0 N solutions of a typical 1–1 salt in NMA are 1.01, 1.55 and 2.25, respectively, with corresponding relative viscosities for solutions of 2–1 salts being slightly greater.[12] If the equivalent conductance data were corrected by multiplying them by the corresponding relative viscosities, the resulting phoreograms for 1–1 salts then would be anabatic and those for the 2–1 salts even more so thereby exhibiting parallelism with the observations for aqueous solutions.[13]

The Shedlovsky modification of the Onsager equation[14] provides the best means for analyzing the conductance data. In accordance with his equation which may be written as follows for alkaline earth salts with univalent anions in NMA at 40°

$$\Lambda_0^1 \equiv \frac{\Lambda + 22.04\sqrt{C}}{1 - 0.388(1 + T^-_0 + 0.816\sqrt{1 + T_0^-})\sqrt{C}} = \Lambda_0 + BC \qquad (2)$$

The plot of Λ_0^1 *versus* C for each salt is linear over the experimental concentration range. Values of Λ_0 and B which were obtained analytically by the method of least squares are summarized in Table II. The corresponding values of Λ_0 in Tables I and II usually agree very closely; however, those in Table II are based upon a preferable extrapolation procedure and have been used for comparison purposes.

The results clearly illustrate that the behavior of corresponding anhydrous and hydrated salts is almost identical. Apparently the water originally associated with a hydrate loses its identity as such upon dissolution of the solute in NMA and effectively becomes a part of the solvent medium. In a 0.01 N solution of an alkaline earth salt hexahydrate, for example, the NMA/water mole ratio is greater than 400/1. As a result of this preponderance in concentration and also the greater dipole moment of NMA,[15] the ions of an alkaline

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(11) R. M. Fuoss, *J. Chem. Educ.*, **32**, 527 (1955).

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

(13) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939, p. 331.

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

(15) J. F. Gormley, Dissertation, University of Kentucky, 1952

earth salt hydrate in NMA should be preferentially solvated with NMA. Furthermore, the properties of the resulting mixed solvent should differ negligibly from those of pure NMA.

The limiting equivalent conductances of the strontium, calcium, barium and magnesium ions in NMA at 40° are 10.4, 10.2, 10.1 and 9.8 ohm^{-1} cm.^{2} equiv.$^{-1}$, respectively. These are based on the values of anionic conductances which were reported in a previous paper.[6] Insofar as the series of alkaline earth ions is concerned, the barium ion is generally the most conducting; however, in NMA its limiting equivalent conductance is intermediate in the series. This behavior is very much analogous to sodium salts having greater limiting equivalent conductances than corresponding potassium salts in N,N-dimethylacetamide[16] and N,N-dimethylpropionamide.[17] In comparison to aqueous solutions, obviously unusual relative ionic solvation effects are operative in the amides. This is further illustrated by the limiting equivalent conductance of each of the alkaline earth ions in NMA being 15–20% greater than that of the potassium ion which is the most conducting of the alkali metal ions which have been studied.

As indicated earlier in the discussion, the results presented in Table II are based on the Shedlovsky equation[14] which at low concentrations reduces to the limiting theoretical Onsager equation. Since this same method of analysis has been used for treating the data for alkaline earth salts in aqueous solutions,[18] convenient comparisons are facilitated. An analysis of the data by the new Fuoss method[19] is inapplicable since the method has been worked out only for the symmetrical valence type of electrolyte.

This research involving the use of NMA as a solvent represents by far the most comprehensive study of the conductances of alkaline earth salts in a non-aqueous medium. Additional work involving the behavior of NMA solutions of several other 2–1, 3–1, 2–2, 1–2 and 1–3 salts is in progress in this Laboratory.

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[16] G. R. Lester, T. A. Gover and P. G. Sears, *J. Phys. Chem.*, **60**, 1076 (1956).

[17] E. D. Wilhoit and P. G. Sears, *Trans. Ky. Acad. Sci.*, **17**, 123 (1956).

[18] T. Shedlovsky and A. S. Brown, THIS JOURNAL, **56**, 1066 (1932).

[19] R. M. Fuoss, *ibid.*, **79**, 3301 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND ELECTRICAL ENGINEERING RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Dielectric Dispersion in Symmetric Top Molecules[1]

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The dielectric constants of CH_3CN, CHF_3, $CHCl_3$ and CH_3CCl_3 have been measured at 9400 megacycles over a range of pressures and temperatures. For these gases, as well as CH_3Cl and CH_3Br reported earlier, the orientation polarization at 9400 megacycles is appreciably lower than the static value. The difference is shown to be due to dispersion associated with low-frequency inversion transitions. The dielectric constant measurements are correlated with published data on microwave absorption by the pressure-broadened inversion transitions. Moreover, the measured dielectric constants can be accurately predicted by application of the Van Vleck–Weisskopf theory of the intensity of spectral lines to an inversion transition occurring at zero frequency.

Most studies of the dielectric constants of gases have been made at relatively low frequency, generally of the order of 1 megacycle. In the range between 0 and 10 megacycles the dielectric constant has been found to be frequency-independent for all gases. At the other extreme of frequency, refractive index measurements of high accuracy are available in the optical region where the dielectric constant is found to be much lower. Between the frequency regions accessible by these two methods there is a wide range of frequency where measurements were not possible before the development of microwave techniques.

For gases at moderate or low pressure, it has been presumed generally that the dielectric constant would be independent of frequency until the measuring frequency approached the lowest resonance frequency of the molecule, normally for the $J = 0 \rightarrow J = 1$ rotational transition. Boggs, Crain and Whiteford,[2] however, have measured the dielectric constant of a number of gases at a frequency of 9400 megacycles and have found that while some gases show the static value of dielectric constant, others (CH_3Cl, $CHClF_2$, $CHCl_2F$, CH_3Br, and possibly $CClF_3$ and CCl_3F) have a distinctly lower dielectric constant at 9400 megacycles than at low frequency. This result cannot be attributed to dispersion involving a pure rotational transition, since, for CH_3Cl and CH_3Br at least, the measurement frequency is well below the frequency of the first rotational spectral line. More recently, Boggs, Thompson and Crain[3] have shown that no measurable variation in the dielectric constant occurs in the frequency region surrounding the first rotational line of cyanoacetylene or the third rotational line of *t*-butyl iodide. While such a variation would certainly be expected to be present, its magnitude must be below the ± 0.5% level which could be detected. These workers also have shown[3] that the dielectric constants of CH_3Cl and CH_3CCl_3, which are lower at 9400 megacycles than at low frequency, are still decreasing at 9400 megacycles.

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[1] A portion of this work was supported by Air Force Contract AF 33(616)-2842.

[2] J. E. Boggs, C. M. Crain and J. E. Whiteford, *J. Phys. Chem.*, **61**, 482 (1957).

[3] J. E. Boggs, C. M. Thompson and C. M. Crain, *ibid.*, **61**, 1625 (1957).