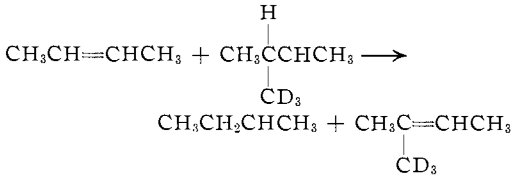


$$CH_3CH{=}CHCH_3 + CH_3\overset{H}{\underset{CD_3}{C}}CHCH_3 \longrightarrow CH_3CH_2CHCH_3 + CH_3\underset{CD_3}{C}{=}CHCH_3 \quad (24)$$

$$CH_3CH_2CHCH_3 \longrightarrow CH_3 + CH_2{=}CH{-}CH_3 \quad (25)$$

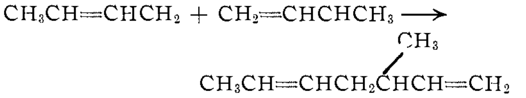
Butene-1 is formed rapidly in this reaction and could be the source of ethylene and ethane.

***cis*-Butene-2.**—The photolysis of acetone in the presence of *cis*-butene-2 at 374° was carried out to identify the products. The products were CO, CH_4, and small amounts of ethane, propylene, propane, butene-1, pentane and approximately equal amounts of three isomers of octadiene. The butenyl radical may be represented by two equivalent formulas.

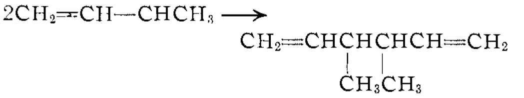
$$CH_2CH{=}CHCH_3 \longleftrightarrow CH_2{=}CH{-}CHCH_3 \quad (2)$$

There are three combinations of these radicals to give three octadienes.

$$2CH_3CH{=}CHCH_2 \longrightarrow CH_3CH{=}CHCH_2CH_2CH{=}CHCH_3 \quad (26)$$



$$CH_3CH{=}CHCH_2 + CH_2{=}CHCHCH_3 \longrightarrow CH_3CH{=}CHCH_2\overset{CH_3}{C}HCH{=}CH_2 \quad (27)$$

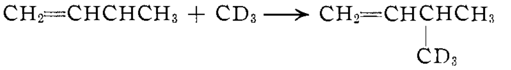


$$2CH_2{=}CH{-}CHCH_3 \longrightarrow CH_2{=}CH\underset{CH_3}{C}H\underset{CH_3}{C}HCH{=}CH_2 \quad (28)$$

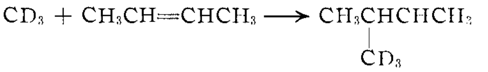
An experiment on the addition of CD_3 to *cis*-butene-2 was performed. Slight isomerization to butene-1 is again observed at 370°, with about 10% of the butene-1 having one D atom. Two pentenes and a pentane containing three D's each were recovered.

$$R + CH_3CH{=}CHCH_3 \longrightarrow CH_2CH{=}CHCH_3 + RH \quad (29)$$

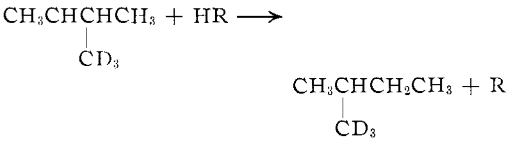
$$CH_2CH{=}CHCH_3 + CD_3 \longrightarrow CD_3CH_2CH{=}CHCH_3 \quad (30)$$



$$CH_2{=}CHCHCH_3 + CD_3 \longrightarrow CH_2{=}CH\underset{CD_3}{C}HCH_3 \quad (31)$$



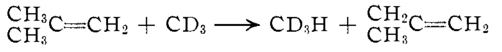
$$CD_3 + CH_3CH{=}CHCH_3 \longrightarrow CH_3\underset{CD_3}{C}HCHCH_3 \quad (32)$$



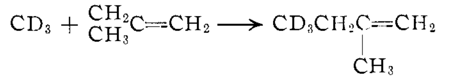
$$CH_3\underset{CD_3}{C}HCHCH_3 + HR \longrightarrow CH_3\underset{CD_3}{C}HCH_2CH_3 + R \quad (33)$$

No ethylene, ethane, propylene or propane appears in the products.

Isobutene-Acetone-d_6 Photolysis.—At 381° a single pentene-d_3 peak and two pentane-d_3 peaks are observed.



$$\substack{CH_3\\CH_3}C{=}CH_2 + CD_3 \longrightarrow CD_3H + \substack{CH_2\\CH_3}C{=}CH_2 \quad (34)$$



$$CD_3 + \substack{CH_2\\CH_3}C{=}CH_2 \longrightarrow CD_3CH_2\underset{CH_3}{C}{=}CH_2 \quad (35)$$

Only one pentene can be formed from this butene.

The pentanes are formed by the terminal and non-terminal addition of CD_3 to the double bond, followed by the pentyl radicals abstracting H.

CHINA LAKE, CALIFORNIA

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

Solvents Having High Dielectric Constants. VIII. The Conductimetric Behavior of Several Salts in Formamide at 25°[1]

BY LYLE R. DAWSON, EUGENE D. WILHOIT AND PAUL G. SEARS

RECEIVED MAY 18, 1957

The conductivities of eight electrolytes in formamide at 25° have been measured at several concentrations within the range 3–100 × 10^{-3} *N*. The limiting equivalent conductance in each case has been determined by a mathematical extrapolation of a Shedlovsky plot of Λ'_0 *versus C*. The results illustrate the additivity of limiting ionic conductances in formamide. In most cases, the slopes of the plots of Λ *versus* $\sqrt{C}$ (for the above concentration range) are 10–30% numerically less than those calculated by the Onsager equation. Limiting ionic equivalent conductances based upon the approximation method using trimethylphenylammonium benzenesulfonate as the reference electrolyte agree within 3% with those which have been determined by the Hittorf method.

The first unit in this series[2] describes the conductances of hydrogen and potassium chlorides in formamide at 3, 20 and 40°. Anabatic phoreograms[3] characterize the conductimetric behavior of these electrolytes in formamide. The magnitude of Λ_0 for HCl also indicates the absence of any unique mechanism for the conductance of the solvated proton in this medium.

Despite the numerous inherent difficulties associated with the purification and preservation of formamide of desirable quality, there is need for additional information concerning the properties of solutions of electrolytes in un-N-substituted amide solutions. The melting points of acetamide and propionamide being above 80° presents concomitant experimental difficulties which eliminate any advantages in selecting these solvents preferentially with respect to formamide.

The objectives of the present study were to extend generally the previous studies using form-

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[1] This research was supported in part by a contract with the Office of Ordance Research.

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

[3] R. M. Fuoss, *J. Chem. Educ.*, **32**, 527 (1955).

amide as an electrolytic solvent and to evaluate limiting ionic equivalent conductances by an approximation method.

Experimental

Solvent.—The best available commercial grade of formamide was refluxed for several hours in contact with calcium oxide and then was distilled twice at a pressure of 1 mm. through a fractionating column. The retained middle fractions were subjected to several fractional freezing cycles in which the unfrozen liquid was removed very effectively by suction provided by a vacuum pump. The formamide which was used in the preparation of solutions had the following physical properties at 25°: conductivity, 0.9–1.5 $\times 10^{-5}$ ohm^{-1} cm.$^{-1}$; density, 1.1296 g. ml.; viscosity, 0.0331 poise; dielectric constant, 109.6 (at ten megacycles). The conductivity is lower than that which has been reported in any previous study involving formamide. The values for the remaining physical properties agree very well with data in the literature.[4–6]

Salts.—The preparation and/or purification of the electrolytes have been discussed in previous papers.[7–9]

Apparatus and Procedure.—The bridge assembly, conductance cells, temperature bath and control, and the procedures involved in the preparation of solutions and the measurement of resistances also have been described previously.[8,10]

Results and Discussion

The equivalent conductance in formamide at 25° was determined at several concentrations in the range of 3–100 $\times 10^{-3}$ N for each of the following salts: NaI, KI, KCl, Me_3PhNCl, Me_3PhNI, NaO_3SPh, Me_3PhNO_3SPh and Bu_4NI. Very large solvent corrections severely restricted the utilization of more dilute solutions. Tabulated data concerning corresponding values of Λ and C are omitted herein for conciseness but are available elsewhere.[11]

With an exception for Bu_4NI, the phoreogram for each salt is anabatic and has a slope which is 8 to 29% numerically less than that calculated by the Onsager equation. The slope for the catabatic phoreogram for Bu_4NI is 18% numerically greater than the theoretical slope.

The data for each salt were analyzed using the Shedlovsky rearrangement of the Onsager equation[12] which may be written as follows for a 1-1 salt in formamide at 25°

$$\Lambda'_0 \equiv \frac{\Lambda + 13.77\sqrt{C}}{1 - 0.1389\sqrt{C}} = \Lambda_0 + BC \qquad (1)$$

All plots of Λ *versus* C are illustrated in Fig. 1 and the results from them based on a least squares treatment are summarized in Table I.

The limiting equivalent conductance data for NaI, KI and KCl in Table I are approximately 7% greater than the corresponding results which have been reported by Davis, Putnam and Jones.[13] Values of 121.4 and 142.6 ohm^{-1} cm.^{2} equiv.$^{-1}$ for Λ_0 for NaI and KI, respectively, in water at 25°, which are based on the method of Jones and collaborators,[14] indicate that about 6% of the difference is inherent in their experimental technique or equipment. Other smaller differences probably arise from the variations in the physical properties of batches of formamide. However, excellent agreement is obtained with an interpolated value for Λ_0 for KCl in formamide at 25° as reported previously from this Laboratory.[2]

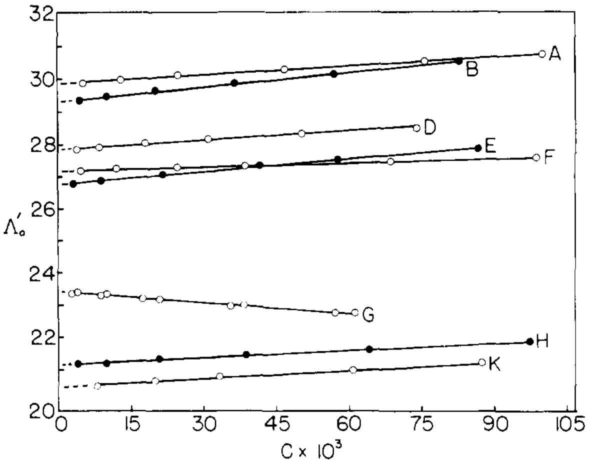

Fig. 1.—Plots of the Shedlovsky modification of the Onsager equation for some salts of formamide at 25°: A, KCl; B, KI; D, Me_3PhNCl; E, NaI; F, Me_3PhNI; G, Bu_4NI; H, Me_3PhNO_3SPh; J, NaO_3SPh.

Table I

Data Derived from Plots of the Shedlovsky Modification of the Onsager Equation for Some Salts in Formamide at 25°

Salt	Λ_0	B
Bu_4NI	23.37	−10.5
NaI	26.74	14.3
Me_3PhNI	27.25	4.3
NaO_3SPh	20.46	8.6
Me_3PhNO_3SPh	21.09	8.3
KI	29.31	14.8
KCl	29.85	8.8
Me_3PhNCl	27.84	9.0

Normalized values of B, $B' = B/\Lambda_0$, which have been omitted from Table I, exhibited no comprehensive trends of parallelism with comparable data for water and hydrogen cyanide solutions.[15]

Several combinations of Λ_0 data in Table I substantiate the additivity of limiting ionic equivalent conductances in formamide. This reflects consistency within the results; nevertheless, the accuracy (estimated to be within 0.5%) is difficult to evaluate owing to the use of large solvent corrections.

An attempt to approximate limiting ionic equivalent conductances in formamide by the $OctdMe_3NOctdSO_4$ method[16] was initiated and later aban-

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[5] P. L. Magill, *Ind. Eng. Chem.*, **26**, 611 (1934).

[6] G. R. Leader, This Journal, **73**, 856 (1951).

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

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

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

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

[11] Tables of equivalent conductance and concentration data have been deposited as Document number 5224 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 payable in advance to Chief, Photoduplication Service, Library of Congress.

[12] T. Shedlovsky, This Journal, **54**, 1405 (1932).

[13] P. B. Davis, W. S. Putnam and H. C. Jones, *Carnegie Inst. Pub.*, **230**, 16 (1915).

[14] C. G. Carroll and H. C. Jones, *ibid.*, **80**, 43 (1907).

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[16] W. E. Tompson and C. A. Kraus, This Journal, **69**, 1016 (1947).

doned because of the apparent insolubility of OctdMe$_3$NOctdSO$_4$ and KOctdSO$_4$ in formamide. Recourse was made, therefore, to the Me$_3$PhNO$_3$-SPh method which previously has been shown to yield essentially the same results as the OctdMe$_3$-NOctdSO$_4$ method for N-methylacetamide solutions.[9] The approximate values thus obtained for the limiting ionic equivalent conductances in formamide are summarized in Table II. On the basis of these findings, the potassium ion for potassium chloride in formamide is characterized by a limiting transference number of 0.415 which differs only 2% from the corresponding value of 0.406 which was determined independently by Dawson and Berger[17] using the Hittorf method.

TABLE II

LIMITING IONIC EQUIVALENT CONDUCTANCES IN FORMAMIDE AT 25° BASED ON THE TRIMETHYLPHENYLAMMONIUM BENZENESULFONATE APPROXIMATION METHOD

Cation	Λ^+_0	Anion	Λ^-_0
K$^+$	12.5	PhSO$_3^-$	10.6
Me$_3$PhN$^+$	10.5	I$^-$	16.8
Na$^+$	10.0	Cl$^-$	17.3
Bu$_4$N$^+$	6.7		

An analysis of the pattern of results reported herein for formamide solutions with comparable data for water, N-methylacetamide and N,N-dimethylformamide solutions reveals no consistent trends of pronounced parallelism.

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[17] L. R. Dawson and C. Berger, THIS JOURNAL, **79**, 4269 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Diffusion Measurements in Aqueous Solutions of Different Viscosities

BY AMILCARE BIANCHERIA[1] AND GERSON KEGELES

RECEIVED JUNE 3, 1957

The diffusion of approximately 0.5% glycolamide or acetamide has been studied by the Gouy method in various aqueous solutions, whose viscosity was adjusted by the addition of small amounts of a third component to be from 2 to 7% above that of water. Deviations from ideal diffusion behavior were studied to assure that no appreciable interaction of flow occurred between the diffusing and non-diffusing solutes. It was found that the relative decrements of the diffusion coefficients of glycolamide and acetamide were never as great as the relative increments of solvent macroscopic viscosity. Moreover, at a constant increment of macroscopic viscosity, the decrement in diffusion coefficient depended markedly on the nature of the third component. All the diffusion data could be correlated accurately, however, with the volume fraction of third component added, an experimental correlation suggested by the theory developed by Wang to explain the obstruction of the self-diffusion of water by dissolved macromolecules.

Introduction

The Stokes–Einstein–Sutherland equation[2–4] relating diffusion to the observed macroscopic viscosity, was derived on the basis that the solvent medium presents a continuum to the diffusing particle. In many cases, the general form of the relation has appeared to be applicable even outside its intended range of validity. The data of Stokes, Dunlop and Hall[5] for the diffusion of iodine in several organic solvents exemplifies this point. However, the data of Lamm and Sjöstedt[6] for the diffusion of water in glycerol, the study of Polson[7] on diffusion *versus* molecular weight, and the data of Longsworth[8] for the temperature dependence of diffusion indicate that in those cases where the solvent media can no longer be considered a continuum, the diffusion process is not determined simply by the macroscopic viscosity. Similar considerations have been discussed by Schachman and Harrington[9] for the case of sedimentation.

This investigation was undertaken to provide precise additional data on diffusion in discontinuous media for the purposes of examining the validity of the general form of the Stokes–Einstein relation and of furnishing a possible basis for future theoretical considerations.

Basically, the investigation entailed the observation of diffusion of glycolamide and acetamide in various aqueous solutions. The viscosities of these solutions were held at approximately 3 or 6% above that of pure water by controlling the concentration of a third component added to increase the viscosity. In general, third components of zero average charge and low dipole moment were selected to avoid effects due to charge interaction. The molecular size of the third component, was varied in the hope that this parameter could be used to correlate the solvent viscosity with its effect on the diffusion of glycolamide or acetamide.

Experimental

Measurements of diffusion coefficients were made by the Gouy interference method.[10–13] The cell employed was of the Tiselius type,[14] but with clamped optical flats for win-

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[1] Presented to the faculty of Clark University, 1957, in partial fulfillment of the requirements for the Ph.D. degree.

[2] G. Stokes, *Trans. Cambridge Phil. Soc.*, **9**, 5 (1856).

[3] A. Einstein, *Ann. Physik*, **19**, 371 (1906).

[4] W. Sutherland, *Phil. Mag.*, **9**, 781 (1905).

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[8] L. G. Longsworth, *ibid.*, **58**, 770 (1954).

[9] H. K. Schachman and W. F. Harrington, THIS JOURNAL, **74**, 3965 (1952).

[10] L. G. Longsworth, *ibid.*, **69**, 2510 (1947).

[11] G. Kegeles and L. J. Gosting, *ibid.*, **69**, 2516 (1947).

[12] C. A. Coulson, J. T. Cox, A. G. Ogston and J. St. L. Philpot, *Proc. Roy. Soc.* (*London*), **A192**, 382 (1948).

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[14] A. Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).