light flux is known within 1%. The light intensity can be controlled within 1% by controlling the current through the lamp within ±1 ma. or ±0.8% between 120 and 130 ma. and within ±0.1 ma. or ±0.6% between 15 and 30 ma., and by controlling the temperature of the lamp within ±0.1° and ±0.05° at 130 and 15 ma., respectively, under the conditions applying to the steep parts of the upper set of curves in Fig. 5. The same degree of control over the temperature, but less control over the current, is required as the lamp ages with use.

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

The Dielectric Constant of N-Methylamides

BY GORDON R. LEADER* AND JAMES F. GORMLEY

Dielectric constants have been determined in the temperature interval 15–35° for monomethyl-formamide, acetamide and propionamide, for dimethylformamide and acetamide and for ethyl N-methylcarbamate. The values observed are interpreted in terms of the influence of steric properties of the molecules upon association through hydrogen bonding.

Liquids associated through hydrogen bond formation have been shown by Kumler[1] to deviate markedly from a semi-empirical relationship which applies satisfactorily to many liquids in which the association is due largely or entirely to dipole interaction. The dielectric constants of hydrogen-bonded liquids are found to be either much higher than expected in cases where the hydrogen bonding produces extended "polymers" having increased dipole moments, or much lower in those cases where the association, as in acetic acid, leads to formation of a dimer of small or zero moment.

Measurements of the dielectric constants of monomethylamides which are here reported have shown them to be unusually high. These compounds are especially inclined to associate as extended polymers because of the presence in each molecule of only two sites able to participate in hydrogen bond formation, and because of a *trans* disposition of these sites, as shown by Mizushima[2] from Raman spectra and infrared studies on N-methylacetamide. For the structurally similar compound ethyl N-methylcarbamate a relatively low dielectric constant has been observed, indicating that the compound is largely dimerized because of a *cis* structure of the monomer. The data thus serve to illustrate the important role played by steric factors in determining the effect of hydrogen bonding on the orientation polarization of this class of compounds.

Experimental

Apparatus.—Dielectric constants were measured using a modified cell of the type devised by Conner, Clark and Smyth[3] together with a General Radio Twin-T Impedance Bridge as previously described.[4] For measurements with liquids of very high dielectric constant, a special cell having the constants: $C_0 = 1.9$ μμf. and $C_v = 1.765 \pm 0.003$ was constructed. The cells used were calibrated using purified benzene[5] methanol and water[6] as standard liquids. Measurements were made at a frequency of 10 mc. in most cases and were corrected for errors due to inductance in both the bridge circuit and cell by determining differences between measured capacities of the cell at 1 mc. and 10 mc. when filled with methanol, water and methanol–water mixtures. These sufficed to establish a partial correction curve for the inductance errors at low measured capacities and permitted estimation of the cell inductance by use of which the corrections at higher capacities could be calculated.[7]

Temperatures were measured with a 0.1° thermometer calibrated by the National Bureau of Standards. Refractive index measurements were made with a Spencer Abbe Refractometer. Density measurements were made using a Regnault pycnometer of 50-cc. capacity.

Materials.—N-Methylformamide was prepared by reaction of 98–99% formic acid with gaseous methylamine until the required weight was absorbed. The resulting concentrated salt solution was then heated at 160–170° at atmospheric pressure to drive off water and form the amide. When the water had been removed, the pressure was gradually reduced and the product was finally purified by fractionation under vacuum through a 35 × 1 cm. glass helices packed column. The distilled material was further purified by successive crystallizations. This procedure gave material of high purity as indicated by its melting point, but its conductivity was too high to permit dielectric constant measurements. To reduce the conductivity, about 200 cc. of purified liquid was slowly passed through a 10 × 1 cm. column packed with dried Amberlite IR-120 in the hydrogen form. This treatment effectively reduced the conductivity by converting methyl ammoniumformate to formic acid which, as has been observed for acetic acid in formamide,[8] is only slightly dissociated in the N-methylformamide medium. The first portions of N-methylformamide to come through the column were contaminated with water displaced from the resin, but later portions finally reached a limiting high value of dielectric constant, indicating that no more water was present. Conductivity of the material used for measurements was about 5×10^{-5} ohm^{-1} cm.$^{-1}$, d^{25}_4 0.9976, n^{25}_D 1.4310, m.p. −3.8°; lit.[9] 0.9961, 1.4300, −5.4°.

N-Methylacetamide.—A commercial product was purified by crystallization; sp. cond. about 10^{-6}; d^{30}_4 0.9512, n^{30}_D 1.4290, m.p. 29.7°; lit.[9] 0.9517 (25°), 1.4301 (25°), m.p. 28.0°.

N-Methylpropionamide was prepared from propionic acid and methylamine as described for N-methylformamide. The product was purified by fractionation under vacuum; b.p. 134° at 60 mm.; sp. cond. about 10^{-6}; d^{25}_4 0.9306, n^{25}_D 1.4350; lit.[9] 0.9304, 1.4345.

N,N-Dimethylformamide and N,N-Dimethylacetamide.—Commercial material was purified by fractionation at atmospheric pressure after treatment with solid KOH and CaO; d^{25}_4 0.9442, n^{25}_D 1.4290(DMF); d^{25}_4 0.9365, n^{25}_D 1.4363-(DMA); lit.[10] 0.9445, 1.4269; 0.9366, 1.4351.

Ethyl N-Methylcarbamate.—Commercial material was purified by distillation; b.p. 169–170 at 740 mm.; d^{25}_4 1.0042, n^{25}_D 1.4179; lit.[11] 1.0087 (19°), 1.4200 (19°).

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* Mallinckrodt Chemical Works, St. Louis, Mo.

[1] W. D. Kumler, THIS JOURNAL, **57**, 600 (1935).

[2] S. Mizushima, *et al.*, *ibid.*, **72**, 3490 (1950).

[3] W. P. Conner, R. P. Clark and C. P. Smyth, *ibid.*, **64**, 1379 (1942).

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

[5] R. M. Davies, *Phil. Mag.*, **21**, 1 (1936).

[6] P. S. Albright and L. J. Gosting, THIS JOURNAL, **68**, 1062 (1946).

[7] I. G. Easton, "Corrections for Residual Impedances in the Twin-T," General Radio Co., Cambridge, Mass.

[8] W. J. McCreary, M.S. Thesis, Univ. of Kentucky, 1948.

[9] G. F. D'Alelio and E. E. Reid, THIS JOURNAL, **59**, 109 (1937).

[10] J. R. Ruhoff and E. E. Reid, *ibid.*, **59**, 402 (1937).

[11] O. Schmidt, *Ber.*, **36**, 2476 (1903).

The Dielectric Constant of Acetamide.—For comparative purposes, it was thought desirable to obtain a value for the dielectric constant of acetamide at 25°. (The dielectric constant of formamide has already been reported.[4]) This was accomplished by measurement of the dielectric constant of solutions of acetamide in purified formamide. The acetamide used was purified as described by Wagner[12]; m.p. 81°. The results obtained are shown in Table I.

TABLE I

Wt., % acetamide	$\epsilon^{25°}$ (10 mc.)
0.0	109.5
31.39	98.8
36.43	96.4
47.60	92.8
64.01	87.1
100.0 (Extrapolated)	(74)

The extrapolation to obtain a hypothetical dielectric constant for acetamide as a liquid at 25° was made using a straight line plot of ϵ *versus* weight per cent. acetamide. In general, dielectric constants of mixtures are not a linear function of composition expressed in per cent. by weight, but in an analogous case of mixtures of water and methanol, data have been reported[6] which also show a very nearly linear relationship between these quantities. There is, however, no apparent theoretical justification for the use of this relationship, hence no great significance can be attached to the extrapolated value obtained. It is, nevertheless, of value in the present study as an indication of the nature of the association of acetamide as reflected in its dielectric constant. It is of interest that a similar series of measurements using dimethyl formamide as solvent also gave a straight line extrapolating to 74 as the dielectric constant of acetamide, even though the maximum concentration of acetamide that can be dissolved in dimethyl formamide is only about 36% by weight.

Results

The dielectric constants observed for the pure liquids studied are shown in Table II. The estimated probable error of the values reported is ±0.3%.

TABLE II

DIELECTRIC CONSTANTS OF N-METHYLAMIDES AT 10 MC.

Compound	15°	20°	25°	30°	35°
N-Methylformamide	200.1	190.5	182.4	174.3	167.1
N-Methylacetamide[a]	....	....	....	....	169.7
N-Methylpropionamide	188.1	179.8	172.2	164.3	156.7
N,N-Dimethylformamide	38.42	37.65	36.71	35.87	35.05
N,N-Dimethylacetamide	40.09	38.93	37.78	36.81	35.83
Ethyl N-methylcarbamate	25.3	24.3	23.5	22.7	21.9

[a] Other values determined for N-methylacetamide were: 30.5°, 175.7; 32.5°, 172.9; 37.5°, 166.1; 40°, 162.7.

Discussion

The results in Table II show that the *trans* configuration of carbonyl and N–H linkages which Mizushima has deduced for N-methylacetamide from spectroscopic evidence is also present in N-methylformamide and N-methylpropionamide as seen from the equally high dielectric constants of these compounds. It is worthy of note that, in these compounds, the large orientation polarization is due not only to the existence of a chain type of association, but also to the fact that the moments of the individual molecules are all directed more or less parallel to the general direction of the chain itself. The large temperature coefficient of dielectric constant shown by the N-methylamides is also indicative of the presence of molecular units of large dipole moment.[13]

The dielectric constants of the monomethylamides are found to be considerably higher than those of the unsubstituted amides. This can be explained as due to the fact that whereas the monosubstituted amides are associated as chain polymers, the two amino hydrogens in the unsubstituted amides permit a larger variety of associated forms, even if it be assumed that only one hydrogen atom of the amino group is involved in hydrogen bonding at any given time. The possible associated forms range from the extended type of increased moment, involving the *trans* hydrogen atom, through intermediate random forms which would involve a considerable degree of mutual cancellation among the contributions made by each molecule to the net moment of the polymeric group, and finally to a dimer of small or zero moment. The observed dielectric constant is largely determined by the composite effect of all of these associated groups, and hence is smaller for the unsubstituted amides.

A comparison of the value 74 obtained by extrapolation for the dielectric constant of acetamide as a liquid at 25° with the value 110 reported for formamide indicates that, in acetamide, association leads to a relatively greater proportion of dimer and randomly associated polymeric groups than is the case with formamide. The dipole moments of formamide and acetamide have been shown to be not significantly different.[14] The trend here observed is in the same direction as the change observed in going from formic acid (58.5) to acetic acid (6.15) which is attributed to a much greater degree of dimerization of the latter.

The variation with frequency of the dielectric constant of the N-methylamides has not been studied, but would be of interest. The region of anomalous dispersion for such compounds apparently lies at frequencies considerably above 10 mc. as shown by the fact that no change from the 10 mc. value was observed in the dielectric constant of N-methylpropionamide when the measurement was made at 1 mc.

In the dimethyl amides, association through hydrogen bonding is no longer possible, and hence a large decrease in dielectric constant occurs. The dipole moments of unsubstituted, monoalkyl and dialkyl amides do not differ much, as shown by Kumler and Porter[15] by measurements on dilute solutions in dioxane; hence this factor is probably of little effect in causing the observed differences in dielectric constant within this class of compounds.

The relatively low dielectric constant shown for ethyl N-methylcarbamate in Table II is of interest since this compound differs from N-methylacetamide only in the substitution of an ethoxy group for a methyl group on the carbonyl carbon. Its low dielectric constant may be attributed to the fact that it is most stable in the *cis* configuration, and hence exists in the pure liquid largely as a dimer having a relatively small or zero moment. The low dielectric constant of acetic acid has been

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(12) E. C. Wagner, *J. Chem. Ed.*, **7**, 1135 (1930).

(13) J. Wyman, THIS JOURNAL, **58**, 1485 (1936).

(14) W. W. Bates and M. E. Hobbs, *ibid.*, **73**, 2151 (1951).

(15) W. D. Kumler and C. W. Porter, *ibid.*, **56**, 2549 (1934).

attributed to this same effect.[16] The difference in the temperature coefficients of dielectric constant of acetic acid and ethyl N-methylcarbamate is also of interest. Acetic acid shows very unusual behavior in this respect in that its dielectric constant increases slightly with increasing temperature. This can be explained as due to dissociation of the dimer in sufficient amount to counteract the effects which normally cause dielectric constant to decrease with increasing temperature. The dielectric constant of ethyl N-methylcarbamate shows a normal decrease in dielectric constant with increasing temperature. Since the temperature coefficient of density is very nearly the same for both compounds, this may be taken to indicate little change in the degree of dissociation of the dimer of ethyl N-methylcarbamate with change in temperature, and hence a small heat content change for the dimerization process.

LEXINGTON, KY. RECEIVED JUNE 8, 1951

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(16) C. P. Smyth and H. E. Rogers, THIS JOURNAL, **52**, 1824 (1930); R. J. W. LeFevre, *Trans. Faraday Soc.*, **34**, 1127 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DAVIS CAMPUS OF THE UNIVERSITY OF CALIFORNIA]

The Argentation of Organic Iodides

BY L. J. ANDREWS AND R. M. KEEFER

By measurement of the solubilities in aqueous silver nitrate of the 1,2-diiodoethylenes, *o*- and *m*-diiodobenzene and methylene iodide, equilibrium constants for the formation of water soluble organic halide–silver ion complexes have been obtained. All of these iodo compounds show a marked tendency to undergo such coördination to form complexes containing either one or two silver ions, except for methylene iodide which forms only a 1:1 complex in measurable amounts. Structurally related dichlorides and dibromides are only feebly disposed to interact with silver ion. Possible structures for the several organic iodide complexes are discussed in this report.

In determining aromatic ring argentation constants by measuring the solubilities of a series of substituted benzenes in aqueous silver nitrate it was noted that iodobenzene and *p*-diiodobenzene showed a pronounced capacity for coördination with silver ion.[1] The argentation constants found for these compounds were considerably larger than those for benzene, while the constants for the corresponding chloro- and bromobenzenes were less than those for benzene. These observations were interpreted as an indication that in the complexes of the iodine compounds the silver ions are bonded preferentially to the iodine atoms rather than to the aromatic nucleus.

Experiments have now been performed which were designed to demonstrate that vinyl iodides and saturated iodides as well as aromatic iodides will coördinate silver ions in aqueous solution. This report presents evidence for the iodine atom argentation of *cis*- and *trans*-1,2-diiodoethylenes and of methylene iodide as based on measurements of the solubilities of these diiodides in aqueous silver nitrate.[2] The results of similar measurements on related organic chlorides and bromides and also on *o*- and *m*-diiodobenzene are reported.

Experimental

The Dihaloethylenes.—Samples of the 1,2-dichloroethylenes remaining from earlier work[3] were refractionated (*trans*, b.p. 47.9–48.5°; *cis*, b.p. 60.0°). A sample of 1,2-dibromoethylene (Eastman Kodak Co.) was distilled and a cut of b.p. 111–112°, n^{25}_{D} 1.5395 was collected. On the basis of its refractive index[4] it was estimated that this cut was approximately 35% of the *trans* configuration. The *cis*- and *trans*-diiodoethylenes were prepared by the methods of previous investigators.[4,5] The *trans* isomer melted at 71.5–72.0° and the *cis* at −13°.[6]

The Halomethanes.—Methylene iodide, b.p. 71.0–71.5° (18 mm.), and methylene bromide, b.p. 96.5–98.0° (763 mm.), were prepared, respectively, from iodoform and bromoform.[7] Mallinckrodt Analytical Reagent grade chloroform was used without purification.

***o*- and *m*-Diiodobenzene.**—The ortho (m.p. 23–24°) and meta (m.p. 34–35°) diiodides were prepared from Eastman *o*- and *m*-nitroaniline.[8]

The Solubility Measurements.—Saturated solutions of the several organic halides in aqueous silver nitrate solutions of varying concentrations were prepared at 25° by methods described previously.[1,9] The ionic strengths of the original silver nitrate solutions were adjusted to unity by the addition of potassium nitrate. The organic halide concentrations of these saturated solutions were determined by extracting measured volumes with known volumes of hexane and determining the halide concentrations of the hexane phases by spectrophotometric methods, using the previously devised techniques.[1,9]

Table I contains the wave length and slit width settings of the Beckman spectrophotometer used in measuring the optical densities of the hexane solutions of the halides and also contains the corresponding experimentally determined extinction coefficients of solutions of the halides in hexane. The compounds for which extinction coefficients are reported obeyed Beer's law in hexane solution in the concentration range in which analytical measurements were made.

Recovery of the Diiodoethylenes from Silver Nitrate Solution.—To check the possibility that *cis*–*trans* isomerization may have been induced when *trans*-diiodoethylene was dissolved in aqueous silver nitrate, 50 ml. of a saturated solution of the diiodide in 1 *N* silver nitrate was extracted repeatedly with a total of 50 ml. of hexane. The hexane extract was evaporated to dryness at room temperature under a stream of air. Only white needles of the *trans*-dihalide (m.p. 70–71°) remained as residue. The quantitative aspects of the experiment were destroyed by the

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(1) Andrews and Keefer, THIS JOURNAL, **72**, 3113 (1950).

(2) Sabanejeff, *Ann.*, **216**, 275 (1883), reported the isolation of a solid addition compound, $C_2H_2I_2\cdot 4AgNO_3$. Scholl and Steinkopf, *Ber.*, **39**, 4393 (1906), obtained a solid, $CH_2I_2\cdot AgNO_3$. In both compounds the silver ions presumably were coördinated with the iodine atoms.

(3) Volman and Andrews, THIS JOURNAL, **70**, 457 (1948).

(4) *Cf.* Noyes, Noyes and Steinmetz, *ibid.*, **72**, 33 (1950).

(5) Noyes, Dickinson and Schomaker, *ibid.*, **67**, 1319 (1945).

(6) Miller and Noyes, *ibid.*, **73**, 2376 (1951), have presented evidence suggesting that this so-called "*cis*" isomer as prepared in this investigation is a eutectic mixture containing about 20% of the *trans* isomer.

(7) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, pp. 349, 350.

(8) (a) Baeyer, *Ber.*, **38**, 2760 (1905); (b) Körner, *Gazz. chim. ital.*, **4**, 385 (1874); (c) Körner and Wender, *ibid.*, **17**, 491 (1887).

(9) Andrews and Keefer, THIS JOURNAL, **71**, 3644 (1949); **72**, 5034 (1950).