The gas was then expanded through a fine capillary into a series of low pressure traps. N_2O_4 was frozen out at Dry Ice temperatures, and nitrous oxide + some nitric oxide frozen subsequently at liquid nitrogen temperatures. Any oxygen and nitrogen formed in the decomposition were pumped away.

The trap containing nitrous oxide was allowed to warm, the pressure noted, and the contents analyzed on the mass spectrometer. The content of N₂O, 5 to 16% of the gas analyzed, was ample to allow an unambiguous identification. For example, a large m/e = 44 peak might result from CO₂ as well as from N₂O. But CO₂ possesses a 22 peak $^{1}/_{32}$ as large as its 44 peak, while N₂O has none. Our 44 peaks were large enough so that the absence of a 22 peak meant that not more than 2% of the 44 peak could have been due to CO₂.

Single runs were made at 1277 and 1357°, and two at 1485°K. 0.3 mole of NO was fed as $N_2O_4 + NO_2$ at each run. Residence times were 31 and 43

seconds at the lower temperatures, 24 and 54 seconds at 1485°. Very little decomposition of NO occurred at the lowest temperature, about 4% at 1357°, and 13 and 30% decomposition at 1485°. The extent of decomposition was calculated from the ratio of NO₂ + N₂O₄ recovered to that fed. The ratio of [N₂O]/[NO] in the reacting mixture was calculated from the N₂O found and from the NO recovered as NO₂ + N₂O₄. At 1277°, the ratio was 3×10^{-5} at 1357°, 2×10^{-5} ; and at 1485°, the ratio was 2×10^{-5} for 24 sec. residence time, and 1.5×10^{-5} for 54 sec.

It was pointed out previously that $[N_2O]/[NO]$ would be about 10^{-4} if all NO decomposed via the intermediate formation of N₂O and if N₂O in turn decomposed only by the catalytic influence of NO. Since an uncatalyzed decomposition of N₂O also occurs, the ratio might be a good deal less than 10^{-4} . Our experimental values are reasonable, therefore, and provide evidence that NO decomposes in the manner predicted by the determination of k_1 .

DIELECTRIC CONSTANTS AND VISCOSITIES OF SEVERAL N-SUBSTITUTED AMIDES AS FUNCTIONS OF THEIR STRUCTURE AND OF TEMPERATURE¹

By JOE W. VAUGHN AND PAUL G. SEARS²

Department of Chemistry, University of Kentucky, Lexington, Kentucky Received July 17, 1957

The dielectric constants of nine N-alkylamides of carboxylic acids and also the N-methyl- and N,N-dimethylamides of methanesulfonic and benzenesulfonic acids were measured at 5°-intervals in the range 25-55° except for cases in which an amide exists as a solid. These measurements were made at 1 and 10 megacycles. Where pronounced frequency dependence was observed, measurements were made also at other frequencies. Eleven of these amides were found to have a dielectric constant greater than that of water at the same temperature. For the amides of a given carboxylic acid, the dielectric constant was observed to decrease somewhat regularly with increasing size of the N-alkyl substituent. For the amides of a given amine, the dielectric constant was found to vary in an unpredictable manner as the acid was varied. The observed difference in the dielectric constant of mono- and di-N-substituted amides of the sulfonic acids is very small in comparison to that which has been reported previously for the carboxylic acids and therein indicates much less dependence of the dielectric constant upon selective hydrogen bonding. Viscosities and densities of the amides were measured also at several temperatures and from these data the activation energies of viscous flow and temperature gradients of density were calculated.

Introduction

In 1951, Leader and Gormley³ reported that Nmethylformamide, N-methylacetamide and Nmethylpropionamide are characterized by exceptionally high dielectric constants which more than twice exceed that of water at a comparable temperature. More recently Dawson, Graves and Sears⁴ have reported a lesser but nevertheless very high dielectric constant of 128.4 for N-methylbutyramide at 25°. Since these four mono-N-substituted amides are characterized by such unusual dielectric constants, the present research was designed to supplement these previous studies from this laboratory by investigating the properties of nine other mono-N-substituted amides as a function of

(1) Taken from a thesis submitted by Joe W. Vaughn in partial fulfillment of the requirements for the degree of Master of Science.

(2) Research Department, Inorganic Chemicals Division, Monsanto Chemical Company, St. Louis 24, Missouri.

(3) G. R. Leader and J. F. Gormley, J. Am. Chem. Soc., 73, 5731 (1951).

(4) L. R. Dawson, R. H. Graves and P. G. Sears, *ibid.*, **79**, 298 1957).

their structure and of temperature. The selection of amides enables comparisons to be made within homologous series and among several combinations of isomers. Included also in the investigation which is described herein were the N-methyland N,N-dimethylamides of methanesulfonic and benzenesulfonic acid which have properties somewhat analogous to those of the carboxylic acids.⁵ Viscosity determinations were included in this study in order to correlate the viscosity behavior with the dielectric behavior and also to give further insight into the possible application of some of the amides as electrolytic solvents.

Experimental

1. Preparation and Purification of Amides.—Each amide was prepared by the reaction of two moles of amine with one mole of acid chloride in benzene solution at approximately 0° . A combination of extractions and fractional distillations at reduced pressure yielded low-conducting final products for which analyses confirmed the % N within at least 0.3% of the theoretical.

(5) E. Wertheim, "Textbook of Organic Chemistry," The Blakiston Company, Philadelphia, Pa., 1945, p. 438.

Name	Symbol	t, °C.	Refractive index, $n^t D$	Density d ⁱ 4 (g./ml.)	Viscosity (centipoise)
N-Ethylacetamide	NEA	25	1.4318	0.9204	6.01
			(1.4318)10	(.9200)10	
N-n-Propylacetamide	NPA	25	1.4356	. 9066	10.7
			(1.4355)11		
N-n-Butylacetamide	NBA	25	1,4388	.8961	14.0
			$(1.4388)^{10,12}$	(.8960)10	
N-n-Amylacetamide	NAA	25	1.4418	.8898	19.7
			$(1.4412)^{13}$	•	
N-Ethylpropionamide	NEP	25	1.4348	.9055	7.29
N-n-Propylpropionamide	NPP	25	1.4377	.8958	12.1
N-n-Butylpropionamide	NBP	25	1.4401	.8892	15.1
N-Ethylbutyramide	NEB	25	1.4366	.8923	11.8
N-n-Propylbutyramide	NPB	40ª	1.4322	.8761	11.2
N-Methylmethanesulfonamide	NMMSA	25	1.4493	1.2757	9.17
				$(1.275)^{14}$	
N,N-Dimethylmethanesulfonamide	DMMSA	50^a	1.4368	1.1632	3.15
N-Methylbenzenesulfonamide	NMBSA	30ª	1.5403	1.2569	52.5
N, N-Dimethylbenzenesulfonamide	DMBSA	50ª	1.5223	1.1856	7.46

TABLE I

^a Amide exists as a solid at lower experimental temperatures.

2. Apparatus and Procedure.—The bridge assembly, capacitance cells, temperature control and principal aspects of the procedure for calibrating the cells, measuring capacitance changes and calculating the dielectric constants have been described in detail previously.^{3,6-8} The standard media which were used in the calibration of the capacitance cells were air and water which have dielectric constants of unity and 78.54,⁹ respectively, at 25°. To check the calibrations of the cells and the experimental procedure in general, measurements of the dielectric constant of water were made at 5°-intervals in the range 25–55°. The results thus obtained (and which are included in Table II) duplicate those of Wyman⁹ within 0.1%. The dielectric constant of each amide at the various temperatures was measured in two cells of considerably different dimensions and the corresponding values always agreed excellently. Mean values of the dielectric are reported in Table II.

Density and refractive index measurements were made by standard procedures. Viscosity determinations were made using Cannon-Fenske viscometers manufactured and calibrated by the Cannon Instrument Company. A viscometer of size 50, 100 or 200 was used as the case required in order to obtain a flow time of sufficient magnitude that kinetic energy corrections would be negligible. The viscosity of each amide was measured in two viscometers and in all cases the duplicate determinations agree within 0.3%. For the density and viscosity measurements, temperature control within 0.02° was provided with a Sargent S-84805 thermostatic water-bath assembly.

Precautions were observed at all times to minimize the atmospheric contamination of the amides.

Results and Discussion

Table I contains values of the refractive index, density and viscosity for each of the amides at a convenient temperature which will be useful for future analytical identification purposes, and also convenient symbols for the relatively long names

(6) G. R. Leader, J. Am. Chem. Soc., 73, 856 (1951).

(7) W. P. Conner, R. P. Clarke and C. P. Smyth. *ibid.*, **64**, 1379 (1942).

(8) F. E. Critchfield, J. A. Gibson and J. L. Hall, *ibid.*, 75, 1991 (1953).

(9) J. Wyman, Jr., Phys Rev., 35, 623 (1930).

(10) B. V. Ioffe, Zhur. Obshchei Khim., 25, 902 (1955); C. A., 49, 13717f (1955).

(11) K. W. F. Kohlrausch and R. Seka, Z. physik. Chem., B43, 355 (1939).

(12) R. H. Wiley, O. H. Borum and L. L. Bennett, Jr., J. Am. Chem. Soc., 71, 2899 (1949).

(13) M. E. Smith and H. Adkins, ibid., 60, 657 (1938).

(14) B. Helferich and H. Grunert, Ber., 73B, 1133 (1940).

which are used frequently hereafter. The few comparable data in the literature (which are provided in parentheses below the corresponding data in Table I) exhibit close agreement.

Data pertinent to the dielectric constant of each of the amides at one megacycle (mc.) are presented in Table II together with comparable data for water. As discernible from these results, all of the amides except the two benzenesulfonamides have a dielectric constant which is greater than that of water at a given temperature.

The very high values for the dielectric constants of the mono-N-substituted amides of the carboxylic acids can be attributed to association as chain polymers^{3,15} through a selective type of hydrogen bonding inherently related to the *trans*-configuration of the hydrogen and oxygen atoms in the H

planar (-C-N-) group.¹⁶ Including data for N-

methylformamide (NMF), N-methylacetamide (NMA), N-methylpropionamide (NMP) and N-methylbutyramide (NMB) from previous studies, 3,4,17 it is interesting to compare trends within homologous series and among groups of isomers. For the amides of a given acid, the dielectric constant decreases with increasing size or formula weight as shown by the examples

At 30°: 55.4 10.5 16.3 10.0 NMA > NEA > NPA > NBA > NAA (178.9) (123.5) (113.0) (96.7) (86.7) At 25°: 45.4 8.7 17.5 NMP > NEP > NPP > NBP (172.2) (126.8) (118.1) (100.6)

⁽¹⁵⁾ S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954, p. 120.

⁽¹⁶⁾ W. W. Bates and M. W. Hobbs, J. Am. Chem. Soc., 73, 2151 (1951).

⁽¹⁷⁾ L. R. Dawson, P. G. Sears and R. H. Graves, *ibid.*, 77, 1986 (1955).

	Frequency	CINIC CONS	TANIS OF DEV	DIGAL MAIDES	Femneratura (°C	()	6000	
Amide	(megacycles)	25	30	35	40	45	50	55
NEA	1	129.0	123.5	118.9	114.5	110.7	106.6	102.3
	10	126.8						
NPA	1	117.8	113.0	108.7	104.9	101.2	97.5	93.4
	10	111.0	107.7	105.3	102.4	99.1	96.1	92.6
NBA	1	100.3	96.7	92.9	89.6	86.4	83.7	80.4
	10	85.5						
NAA	1	89.9	86.7	83.7	80.8	77.8	75.2	72.2
	10	68.8						
NEP	1	126.8	121.2	115.7	111.2	106.4	102.4	98.0
	10	118.8						
NPP	1	118.1	112.6	107.4	102.2	98.1	94.6	90.8
	10	102.5						
NBP	1	100.6	96.2	92.3	88.8	85.2	81.9	78.7
	10	78.5	82.6	83.1	83.0	80.9	78.8	76.3
NEB	1	107.0	102.9	98.7	95.1	91.7	88.4	84.8
	10	94.9						
NPB	1				90.8	87.3	84.4	80.6
	10				80.1		•	
NMMSA	1	104.4	101.2	98.3	95.2	92.5	90.0	87.4
	10	104.4	101.2	98.3	95.2	92.5	90.0	87.4
DMMSA	1						80.4	78.2
	10						80.3	78.2
NMBSA	1		67.1	65.4	63.6	62.1	60.1	58.2
	10		66.2	64.7	63.1	61.7	59.8	58.0
DMBSA	1						48.6	47.3
	10						48.5	47.2
H ₂ O	1	78.5	76.7	75.0	73.3	71.6	70.0	68.4
	10	78.5	76.7	75.0	73.3	71.6	70.0	68.4

TABLE II DISTRUCTOR CONSTANTS OF SEVERAL AMONG AN ONE AND THE MEGAGING

At 40°:

 $\begin{array}{c} 22.1 & 4.3 \\ \mathrm{NMB} > \mathrm{NEB} > \mathrm{NEB} \\ (117.2) & (95.1) & (90.8) \end{array}$

For mono-N-substituted amides of a given amine, except for derivatives of formic acid, the dielectric constant also decreases with increasing molecular size. Parallelism of this trend is exhibited also by the data for the N,N-dimethylamides of the same acids.^{3,18,19} It may be seen also from the following examples that the decrease in the dielectric constant between corresponding propionic and butyric acid derivatives is several times greater than that between corresponding acetic and propionic acid derivatives

At 30°:

$\begin{array}{ccc} 4.6 & 14.6 & 39.6 \\ \mathrm{NMF} < \mathrm{NMA} > \mathrm{NMP} > \mathrm{NMB} \\ (174.3) & (178.9) & (164.3) & (124.7) \end{array}$)
At 25°:	At 40°:
$\begin{array}{ccc} 2.2 & 19.8 \\ \mathrm{NEA} > \mathrm{NEP} > \mathrm{NEB} \\ (129.0) & (126.8) & (107.0) \end{array}$	$\begin{array}{ccc} 2.7 & 11.4 \\ \mathrm{NPA} > \mathrm{NPP} > \mathrm{NPB} \\ (104.9) & (102.2) & (90.8) \end{array}$

For isomeric amides both butyric and propionic acid derivatives have greater dielectric constants than those of corresponding acetic acid derivatives therein indicating that the size of the N-alkyl group affects the magnitude of the dielectric constant to a

(18) R. A. Hovermale and P. G. Sears, THIS JOURNAL, 60, 1579 (1956).

(19) R. A. Hovermale, unpublished data, University of Kentucky, 1956.

greater extent than does the size of the acid alkyl group. However, consistent parallelism is not exhibited by the data for the corresponding isomers of propionic and butyric acids although this may result in part from slightly anomalous behavior usually displayed by derivatives of butyric acid.

At 25°:	At 25°:
$\begin{array}{ccc} 1.6 & 9.0 \\ \text{NMB} > \text{NEP} > \text{NPA} \\ (128.4) & (126.8) & (117.8) \end{array}$	$\begin{array}{c} 11.1 & 17.8 \\ \text{NEB} > \text{NPP} > \text{NBA} \\ (107.0) \ (118.1) \ (100.3) \end{array}$
At 40°:	
2.0 8.0	
NPB > NBP > NAA	
(90.8) (88.8) (80.8)	

For the amides of the carboxylic acids, it appears than an unsubstituted hydrogen atom on the amide nitrogen atom is necessary for a high dielectric constant. This is illustrated very strikingly by the examples which are presented in Table III and which show that there is at least 100 units of difference between the dielectric constants of the Nmethyl- and the N,N-dimethylamides. In contrast to this behavior, corresponding N-methyl-and N,N-dimethylsulfonamides have dielectric constants which differ by only a few units as illustrated also by the data in Table III. This provides convincing evidence that the properties which are responsible for the high dielectric constants of the sulfonamides must differ basically from those of the amides of the carboxylic acids. As other evidence of structural or association dif-



Fig. 1.—The dielectric constants of NPA and NBP at frequencies of 1 and 10 mc. as a function of temperature: A, NPA at 1 mc.; B, NPA at 10 mc.; NBP at 1 mc.; F, NBP at 10 mc.



Fig. 2.—Variation of the dielectric constants of NEA, NAA and NBP with the frequency in mc. at 25°.

TABLE I	I	1
---------	---	---

Comparison of the Dielectric Constants of Monoand Di-N-substituted Amides of Some Carboxylic and Sulfonic Acids

•¢.	N- Methyl- amide	D	N,N- Dimethyl- amide	D	Dif- ference
25	NMF ³	182.4	DMF ³	36.7	145.7
30	NMA ¹⁷	178.9	DMA ³	36.8	142.1
25	NMP ³	172.2	$\rm DMP^{18}$	32.9	139.3
25	NMB^4	128.4	DMB19	28.0	100.4
50	NMMSA	90.0	DMMSA	80.4	9.6
50	NMBSA	60.1	DMBSA	48.6	11.5

ferences, the variation in the dielectric constant with temperature is 35% less for the amides of the sulfonic acids than for the amides of the carboxylic acids; nevertheless, the variation in the dielectric constant is many times greater than the variation in the number of dipolar molecules per unit volume. Hence, it is postulated that the high dielectric constant which is characteristic of the sulfonamides is principally related to the net permanent dipole moment resulting primarily from the sulfur-oxygen bonds and perhaps to a small extent from the sulfur-nitrogen bond, and that an ordered liquid structure and a high viscosity results from dipole-dipole attraction. It is probable that N-H-O hydrogen bonding does occur to some extent in the cases of the N-methylsulfonamides, but from a statistical standpoint it could produce dimers as well as chain polymers, or stated differently, it could result in the effective cancellation as well as the additivity of dipole moments. As a somewhat analogous example, the polarity of the sulfur-oxygen linkage is the only feasible explanation for the relatively high dielectric constant and viscosity of dimethyl sulfoxide (CH₃SOCH₃) which has been reported recently.²⁰

Values of the dielectric constants at 10 mc. for some of the amides are presented also in Table II. A comparison of these data with those immediately above them for 1 mc. reveals that the observed value of the dielectric constant in some cases decreases several units as the frequency is increased from 1 to 10 mc. Although the values of the dielectric constants of the sulfonamides exhibit very little frequency dependence, those of the amides of the carboxylic acids at the lowest temperatures decrease from 2.2 to 22.1 units. For most liquids, a decrease in dielectric constant with increasing frequency, which is a phenomenon usually termed "anomalous dispersion,"^{21,22} is not observed in the radiofrequency range. According to Smyth,²² however, when the polar molecules are very large and the viscosity of the medium is fairly great, the rotary motion of the molecules is not sufficiently rapid for the attainment of equilibrium or full alignment with a rapidly alternating electrical field. This is illustrated very well in the two homologous series of acetamide and propionamide derivatives. As the formula weight or size and the viscosity simultaneously increase, there is a correspondingly greater difference in the dielectric constants at 1 and 10 mc. For isomeric amides, such as NBA, NPP and NEB, the dielectric decrements with increasing frequency are approximately of the same magnitude.

The dielectric constants of NPA and NBP at 1 and 10 mc. as a function of temperature are illustrated in Fig. 1. These results clearly show that the frequency dependency of the dielectric constant decreases as the temperature increases. In the case of NPA which is represented by curves A and B in Fig. 1, the dielectric constant at both frequencies decreases with increasing temperature not only because of a reduction in the number of dipoles per unit volume but principally because the thermal energies have increased sufficiently to disrupt some of the hydrogen bonds and also to decrease the ordered nature of the liquid. This is associated also with a concomitant decrease in viscosity. Since the liquid becomes less viscous and the effective sizes of the polymeric aggregates probably also are reduced, a greater proportion of the dipolar species composing the liquid are capable of more nearly attaining equilibrium or gaining complete alignment with the alternating electrical field and, consequently, the effect of anomalous dispersion approaches a minimum with increasing temperature.

(20) P. G. Sears, G. R. Lester and L. R. Dawson, This Journal, 60, 1433 (1956).

(21) P. Debye, "Polar Molecules," The Chemical Catalog Company, Inc., New York, N. Y., 1929, pp. 77, 95.

(22) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp. 53, 74.

SUMMARY OF DENSITY AND VISCOSITY DATA FOR SEVERAL AMIDES							
Amide	t Range, °C.	to	d_{04} (g./ml.)	$k \times 10^4$ (g./ml. deg.)	A	В	$E_{ m vis}$ (kcal./mole)
NEA	25 - 50	25	0.9204	7.35	-2.0870	1069	4.9
NPA	25 - 50	25	. 9066	7.49	-3.3239	1298	5.9
NBA	25 - 50	25	.8961	6.87	-3.4792	1378	6.3
NAA	25 - 50	25	.8898	6.59	-3.8182	1524	7.0
NEP	25 - 50	25	. 9055	7.07	-2.9143	1126	5.2
NPP	25 - 50	25	. 8958	7.20	-3.4070	1337	6.1
NBP	25 - 50	25	.8892	7.12	-3.4048	1366	6.3
NEB	25 - 50	25	. 8923	7.00	-3.2780	1297	5.9
NPB	40-60	40	.8761	7.25	-3.6454	1470	6.7
NMMSA	25 - 50	25	1.2757	8.96	-2.9880	1177	5.4
DMMSA	50 - 65	50	1.1632	9.60	-2.4138	941	4.3
NMBSA	30 - 50	30	1.2569	7.55	-5.9577	2327	10.7
DMBSA	50 - 65	50	1.1856	8.35	-3.2649	1378	6.3

 TABLE IV

 Summary of Density and Viscosity Data for Several Amides

In the case of NBP which is represented by curves E and F in Fig. 1, an interesting trend is observed at 10 mc. in which the dielectric constant passes through a maximum with increasing temperature. The explanation of curve E is the same as that above for curve A or B. The nature of curve F results from the net effect of two opposing factors: (1) an increase in dielectric constant (or decrease in anomalous dispersion effects) with increase in temperature because of rapidly decreasing viscosity, and (2) a decrease in the dielectric constant with increasing temperature because of increasing thermal energies rupturing some of the hydrogen bonds and decreasing the ordered nature of the liquid. Below 35° the first factor is predominant whereas above 40° the second factor is controlling. Be-tween 35 and 40° , the opposing factors are comparable in magnitude thereby producing a peak or plateau. The anomalous dispersion effects reduce from 22.1 units at 25° to 2.4 units at 55° .

The frequency dependencies of the dielectric constants of NEA, NAA and NBP are illustrated in Fig. 2. Evidence for the variation of the dielectric constant of NEA is not apparent below 6 mc. However, for NAA and NBP incipient variation is observable at 1 mc. A few measurements which were made at 0.55 mc. differed only 0.1 or 0.2 of a unit from those at 1 mc. Available experimental equipment prevented an investigation at lower frequencies. Nevertheless, even in the most pronounced cases represented by NAA and NBP at 25° , it appears that the static dielectric constant (that is, the value as the frequency approaches zero) probably does not exceed that reported for 1 mc. by more than 0.3 unit and, in most cases, the difference probably is less than experimental error.

The density of each amide was found to be a linear function of the temperature and can be described by an equation of the form

$$d'_4 = d'_{0_4} - k(t - t_0)$$

where d, t, t_0 and k are the density in g./ml., any temperature in the experimental range, the reference temperature, and the temperature gradient of density in g./ml. deg., respectively. The results based upon this equation are summarized in Table IV and describe within 0.03% the experimental data which, except for those included in Table I, have been omitted for conciseness.²³ The variation of the viscosity of each amide with temperature can be described very well by the equation

$$\log \eta = A + B(1/T)$$

in which η is the numerical value of the viscosity expressed in poise, A and B are constants corresponding to the ordinate intercept and the slope, respectively, of a plot of log η versus 1/T, and T is the absolute temperature. Glasstone, Laidler and Eyring²⁴ have shown that the above relationship has a theoretical basis and that $B = E_{\rm vis}/2.303R$, where $E_{\rm vis}$ and R are the activation energy of viscous flow and the molar gas constant, respectively. The results based upon the above equation are summarized in Table IV and describe within 1% the experimental data which, except for those incorporated in Table I, also have been omitted for conciseness.²³

The plot of $\log \eta$ versus 1/T in some cases, and especially for NMBSA, exhibits a slight amount of curvature. This not only accounts in major part for the deviations between the experimental data and those calculated using the equations, but it also indicates that the slope of the plot of $\log \eta$ versus 1/T, and consequently $E_{\rm vis}$, varies slightly with temperature. As usually observed, $E_{\rm vis}$ increases with increasing size or formula weight within any homologous series. For isomeric amides, values of $E_{\rm vis}$ are of the same magnitude although acetamide derivatives are always characterized by the largest value.

Several conductimetric studies in this Laboratory have dealt with NMA, NMP and NMB as electrolytic solvents.^{4,17,25-27} Because of its extremely high

(25) L. R. Dawson, E. D. Wilhoit and P. G. Sears, J. Am. Chem. Soc., 78, 1569 (1956).

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

(27) "A Study of the Conductances of Multivalent Electrolytes in NMA," a current research program sponsored by the National Science Foundation and directed by P. G. Sears.

⁽²³⁾ Material supplementary to this article has been deposited as Document number 5351 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 35 mm. microfilm, or \$1.25 for photoprints, payable in advance by check or money order payable to: Chief, Photo-duplication Service, Library of Congress.

⁽²⁴⁾ S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 484, 505.

dielectric constant, relatively low viscosity and adaptability to a very high degree of purification by the fractional freezing technique, NMA offers very promising potentialities as an electrolytic solvent for a variety of theoretical studies. However, even though all of the other amides which are under consideration are characterized by very high dielectric constants and are media in which many electrolytes are soluble, their high viscosities handicap the use of most of the amides as solvents at room temperature. Nevertheless, the viscosities change rapidly with temperature and in most cases reduce to the reasonable range of 2–3 centipoise at about 60°. This coupled with concomitant high dielectric constant and low vapor pressure should make them advantageous for studies at elevated temperatures. Another asset is their extremely broad liquid range; at normal pressure, the amides of the carboxylic and sulfonic acids are liquids up to 210–225° and 275–300°, respectively.

THERMODYNAMIC PROPERTIES OF THE SYSTEM WATER-p-DIOXANE

By J. REX GOATES AND RALPH J. SULLIVAN

Contribution from the Department of Chemistry, Brigham Young University, Provo, Utah

Received July 22, 1957

Calorimetric heats of mixing and a phase diagram were obtained for the system water-p-dioxane at 25° over the entire range of composition. From these data are derived values for the partial molar heat contents, activities and free energies and entropies of mixing. The excess free energy-composition curve, which reaches a maximum of 267 cal./mole at a mole fraction of 0.5 is roughly parabolic in shape. The heats of mixing, however, range from 115 cal./mole endothermic to 142 cal./mole exothermic. A sharp exothermic dip occurs at a mole fraction of 0.143, which corresponds to a ratio of 6.00 water molecules to each dioxane molecule. Minimum values for the freezing points and entropies of mixing also occur at approximately this same composition. Possible short range structures that could contribute to the properties of this system are discussed.

The physical properties of water and p-dioxane are in many respects quite similar. For example, their freezing points are within 12° of each other; their boiling points are within 1.5° ; and their heats of vaporization, which are high, are within 2 kcal. The difference in size and shape of the water and p-dioxane molecules, and the ability of dioxane to H-bond to water and not to itself, however, provide opportunity for interesting molecular interactions in the system water-p-dioxane. A fairly complete thermodynamic study of this system was undertaken.

Experimental

Materials.—Reagent grade *p*-dioxane was further purified by both fractional distillation and crystallization. The resulting product had a freezing point of 11.78°, which is the same as others^{1,2} have reported. The water was freshly distilled and CO_2 -free.

Heats of Mixing.—Measurements of the heats of mixing per mole of solution, ΔH_{\star}^{M} , were made calorimetrically. The calorimeter consisted of a stainless steel mixing vessel suspended in a silvered glass tube, which was evacuated and immersed in a 25.00° water-bath.

The calorimeter to instead of a statistics steel mixing vessel and immersed in a 25.00° water-bath. The mixing vessel was similar to that described by Moelwyn-Hughes and Missen.³ It consisted of two 15-ml. compartments separated by an aluminum foil disc seated between polyethylene gaskets. Mixing was accomplished by turning the vessel upside down, causing a steel plunger to pierce the metal foil disc. The calorimeter was turned end for end every ten seconds during a run. The fall of the plunger through the solution produced efficient, gentle stirring.

The concentration of the solution produced was varied by using plungers of varying sizes, thereby varying the amount of liquid that could be put into the compartment containing the plunger. To obtain solutions with very high and very low volume fractions, pure liquid was used in one compartment and solution in the other; and heats of dilution were measured.

(1) A. L. Bacarella, A. Finch and E. Grunwald, THIS JOURNAL, 60, 573 (1956).

(2) F. Hovorka, R. A. Schaefer and D. Dreisbach, J. Am. Chem. Soc., 58, 2264 (1936).

(3) E. A. Moelwyn-Hughes and R. W. Missen, Trans. Faraday Soc., 53, 607 (1957). Temperature changes in the mixing vessel were detected by a single junction copper-constantan thermocouple, one end of which was soldered to the mixing vessel, and the other end was in a Dewar flask of oil immersed in the 25° water-bath. The thermocouple leads were connected to a galvanometer with a sensitivity of fapproximately 0.2 $\mu v./$ mm. Galvanometer deflection as a function of time was recorded.

The heat capacity of the calorimeter and its contents in each run was determined by use of an electrical heating coil of known resistance that was wound around the mixing vessel. The wire was insulated from the vessel by a strip of tissue paper impregnated with shellac.

Corrections for loss or gain of heat from the calorimeter after mixing (or heating) were made by extrapolating the deflection-time data back to the time of mixing (or heating). The time of heating was so regulated that the amount of deflection produced by the heating was made to approximate the deflection produced by the mixing.

The extent of the correction for gain or loss of heat from the calorimeter was less than 10% of the total deflection obtained on mixing. An error of 5% in the extrapolation would result in an error of 0.5% in the heat of mixing from this source. Other uncertainties were 0.1% in the time of heating, 0.01% in the resistance of the heating coil, 0.01% in the potential drop across the heater, and 0.01% in composition. To accommodate the change in volume on mixing approximately 2 ml. of air space was left inside the mixing vessel. The uncertainty introduced by a change in composition of this volume of vapor phase is negligible for the water-dioxane system. The over-all limit of uncertainty is considered to be 0.6% in the range $x_2 = 0.1-0.3$. Above and below this range it was necessary to calculate the heats of mixing from heats of dilution. This involved two measurements of heats to get ΔH_x^m in the range $x_2 = 0.3-0.85$, and three measurements beyond $x_2 = 0.85$, introducing an uncertainty for the values in these ranges of 1.2 and 1.8%, respectively.

Freezing Points.—Measurements of freezing points proved to be a convenient and accurate method for obtaining the activities in this system. The freezing points were determined from cooling curves. A ten junction thermocouple connected to a 10 mv. recorder allowed measurements of the equilibrium temperature to within 0.02°. Previous freezing point studies² of water-dioxane solutions showed a eutectic point composition of approximately $x_2 =$ 0.15, below which pure water separates as the solid phase; and above which, pure dioxane freezes out.

Derived Properties .- Relative partial molar heat con-