Dielectric Constants and Viscosities of Some Mono-*N*-Substituted Amides and Cyclic Esters

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Dielectric constants, densities, and viscosities of four mono-*N*-substituted amides of acetic and formic acids and two sulfur-containing cyclic esters have been determined at several temperatures in the 25° to 75° C. range. Computer methods have been used to obtain least squares fitting of the experimental data to appropriate equations. Five of the six liquids have dielectric constants which are greater than that of water at a comparable temperature. The dielectric constants of the liquids are discussed with respect to structure and compared with those of closely related species. Activation energies of viscous flow have been calculated using a differentiated form of the Girifalco equation.

SEVERAL articles dealing with the high dielectric constants of mono-*N*-substituted amides (*2, 12, 13, 23*) and cyclic carbonates (*9, 19, 20*) have appeared in the literature within the past 15 years. Supplementary dielectric constant data as a function of temperature are reported herein for four more mono-*N*-substituted derivatives of acetamide and formamide and for two sulfur-containing heterocyclic esters. The names, symbols, and formulas for these compounds appear in Table I. No dielectric constant data have been reported previously for these liquids with the single exception that Mizushima *et al.* (*17*) remarked qualitatively that the dielectric constant of NM2CA exceeds 100. Densities, viscosities, and activation energies of viscous flow also have been determined for a more complete description of these media. In addition to providing quantitative data for the variations of selected physical properties as functions of structure and of temperature, the results also may be useful in making decisions about the possible utility of these liquids as new nonaqueous solvents.

EXPERIMENTAL

Using the method of Wenker (*24*), N2HEA was prepared by heating an equimolar mixture of monoethanolamine and glacial acetic acid in a distillation apparatus until the stoichiometric volume of by-product water was collected. The resulting N2HEA was purified by a method of fractional freezing (*6*). Several freezing cycles were required before a product having a constant maximum freezing point of about 32° C. was obtained. Owing to the extremely viscous nature of N2HEA and its tendency to supercool until it attains a glassy state, seeding was used to initiate crystallization in each cycle.

N2MEA (Eastman Grade) was fractionated at 1.5 mm. and 75° C. using a 30.5-cm. distillation column packed with 6-mm. porcelain saddles. The middle 60% was retained.

NM2CA (sample donated by Dow Chemical Co.) was subjected first to several freezing cycles, but this method was unsuccessful in yielding a low-conducting product. The conducting impurities were easily removed, however, by fractional distillation through a 30.5-cm. column at 4 mm. and 70° C. The final product had a melting point of 46.7° C., which is slightly higher than a literature value of 46° C. (*17*).

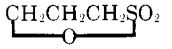
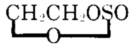
NEF (Eastman Grade) was fractionated at 1.5 mm. and 49° C. using a 1-meter distillation column packed with 6-mm. porcelain saddles. The middle 50% was retained.

1,3-PS (sample donated by Shell Chemical Co.) was purified by successive fractional freezings. After six cycles, the product was colorless and had a freezing point of 31.8° C.

ES (Eastman Practical Grade) was fractionated twice at 13 mm. and 61° C. using a 1-meter distillation column packed with porcelain saddles. The middle 60% was retained from each distillation.

A Twin-T impedance bridge assembly was used in conjunction with a two-terminal parallel plate cell for capacitance measurements at a frequency of 10^6 cycles per second. Similar cells have been found by other investigators (*1, 4, 9*) to be structurally satisfactory and convenient to use for measurements on low-conducting liquids having high dielectric constants. The ends of the external leads to the electrodes of the cell were fitted with special adapters so that the cell, which was suspended in an oil-filled thermostat during measurements, could be attached easily to the Twin-T bridge with a shielded coaxial cable with a dual banana plug connection on each end. For the measurements on N2HEA at several frequencies, another cell of the type which has been described by Leader (*11*) was used. The principal aspects of the procedures for determining the cell constants and for calculating dielectric constants have been described in detail (*11, 23*). The standard media, which were used in the determination of cell constants, were air

Table I. Experimental Compounds

Name	Symbol	Formula
N-(2-Hydroxyethyl)acetamide	N2HEA	$CH_3CONH(CH_2CH_2OH)$
N-(2-Methoxyethyl)acetamide	N2MEA	$CH_3CONH(CH_2CH_2OCH_3)$
N-Methyl-2-chloroacetamide	NM2CA	$ClCH_2CONH(CH_3)$
N-Ethylformamide	NEF	$HCONH(CH_2CH_3)$
1,3-Propanesultone	1,3-PS	 $CH_2CH_2CH_2SO_2$ (ring via O)
Ethylene sulfite	ES	 CH_2CH_2OSO (ring via O)

and water which have dielectric constants of unity and 78.30 (*14*), respectively, at 25° C. The cell constants were assumed to be independent of temperature over the experimental range. In check determinations on known systems, experimental values for the dielectric constants of water at 35°, 45°, 55°, 65°, and 75° C., acetone and nitrobenzene at 25° C., and *N*-methylacetamide at 40° C. in each case agreed within 0.1 dielectric constant unit with the best available comparison data in the literature (*13-15*).

A Cannon-Fenske viscometer of an appropriate size was selected for each liquid to obtain an efflux time exceeding 200 seconds at each temperature and thereby maintain negligible kinetic energy effects. Calibration data for the viscometers were provided by the Cannon Instrument Co. Experimental precautions with the use of the viscometers as discussed by Cannon and Fenske (*3*) were observed. To minimize atmospheric contamination of the nonaqueous media, the viscometers were equipped with top adapters which were vented through tubes filled with Drierite and Ascarite. Stopwatches were calibrated against NBS Station WWV time signals. The viscosity data are reported relative to a viscosity of 1.0019 centipoises for water at 20° C. (*21*).

Densities were determined pycnometrically and dilatometrically using 25-ml. pycnometers-dilatometers which were calibrated using freshly distilled water. Excess liquid in a pycnometer-dilatometer was removed when necessary by suction through a fine capillary. Appropriate buoyancy corrections were applied.

The temperature for all measurements was controlled within 0.03° C. with a Sargent S-84805 thermostatic bath assembly filled with light mineral oil. The bath thermometer with 0.1° C. subdivisions was compared periodically with a similar one which had been calibrated at the National Bureau of Standards; necessary corrections were applied.

All measurements were made in duplicate. Corresponding values agreed consistently within 0.1 unit for dielectric constants, 0.2% for viscosities, and 0.02% for densities. Mean values are listed in the tables of experimental data. A digital computer was used for the fitting of data by the method of least squares to the various polynomial equations.

RESULTS AND DISCUSSION

The experimental dielectric constant data are summarized in Table II. For each liquid the value of the dielectric constant is a linear function of the reciprocal of the absolute temperature. This pattern of behavior has been reported for several other systems by previous investigators (7, 10), and it may be described by the following empirical equation:

$$\epsilon = \frac{B}{T} - A \qquad (1)$$

The values of *A* and *B* obtained through a least squares analysis of the data for each liquid are summarized in Table III. As reflected by information concerning deviations (Table III), calculated values of the dielectric constant based on Equation 1 agree very well with the experimental values and show a maximum deviation of only 0.3 unit.

Table II. Experimental Dielectric Constant Data

Temp., °C.	Dielectric Constants at 1 Mc. N2HEA	N2MEA	NEF	NM2CA	ES	1,3-PS
25	96.6	80.7	102.7	...	39.6	...
35	91.6	75.2	94.9	...	38.0	86.3
45	86.7	70.2	87.9	...	36.4	83.0
50	...	...	...	92.3	...	...
55	82.1	65.7	81.7	88.7	35.0	79.9
65	77.8	61.4	75.9	81.8	33.6	76.9
75	73.8	57.4	...	75.7	...	74.0

The mono-*N*-substituted amides have high dielectric constants as expected from the results of closely related preceding investigations (*2, 12, 13, 23*). The results of the present study also reveal significant effects of structural modifications on the dielectric constant. This applies especially to two cases in which a substituent group or atom makes possible competitive interactions and, thereby, alters the specificity of the hydrogen bonding responsible for the linear association and high dielectric constants of the mono-*N*-alkylamides. NM2CA and N2HEA have structural characteristics which provide a basis for hydrogen bonding which leads not only to linearly associated species but also to more viscous cross-associated species. Comparison of data at 50° C. for NM2CA and its parental *N*-methylacetamide (*5*) shows that 2-chloro-substitution reduces the dielectric constant from 151.8 to 92.3 and increases the viscosity from 2.411 to 3.824 centipoises. A similar comparison of data at 25° C. for N2HEA and its parental *N*-ethylacetamide (*23*) reveals that the dielectric constant decreases from 129.0 to 96.6 and that the viscosity increases strikingly from 6.0 to 201 centipoises. The more normal viscosity of N2MEA suggests that cross-association through hydrogen bonding is not significantly characteristic of that species.

These results show that the dielectric constant of NM2CA is several units lower that the value previously estimated by Mizushima *et al.* (*17*). Also, the dielectric constant of NEF is unexpectedly low relative to that of *N*-ethylacetamide (*23*), since corresponding *N*-alkyl derivatives of formic and acetic acids usually have dielectric constants within a few units of each other (*12, 23*).

The values of the dielectric constants of 1,3-PS and ES generally conform to expectations in view of results from other studies involving heterocyclic liquids (*9, 19, 20*). The structure of 1,3-PS is less symmetrical than that of ES, and it is reasonable that its dielectric constant is considerably greater. Comparison of corresponding properties of tetramethylene sulfone ($\overline{CH_2CH_2CH_2CH_2SO_2}$) with those of 1,3-PS ($\underline{CH_2CH_2CH_2O}\overline{SO_2}$) at 35° C. reveals that the substitution of an oxygen atom for a methylene group in the ring results in significantly increasing the dielectric constant from 42.4 to 86.3, whereas the viscosity concomitantly decreases slightly from 9.03 to 7.45 centipoises (*22*). At 40° C., ES has a dielectric constant which is less than half that of corresponding ethylene ester of carbonic acid (*20*), reflecting the effects of substituting a sulfur atom for a carbon atom in the ring structure.

Table III. Results for Dielectric Constant Data Fitted to Equation 1

Compound	A	$B \times 10^{-4}$	$(\epsilon_{obsd} - \epsilon_{calcd})100$ Std.	Max.
N2HEA	62.6	4.7499	6	9
N2MEA	81.3	4.8247	14	17
NEF	123.8	6.7452	29	30
NM2CA	139.4	7.4861	14	16
ES	11.1	1.5131	3	3
1,3-PS	20.5	3.2937	6	7

Table IV. Dielectric Constant of N2HEA at Several Frequencies

Temp., °C.	Megacycles 1	2	3	4	6	7	10
25	96.6	96.4	95.9	95.2	93.4	92.0	87.6
35	91.6	91.6	91.5	91.4	91.0	90.5	89.3

Table V. Experimental Density Data

Temp., °C.	N2HEA	Densities, Grams/Ml.				1,3-PS
		N2MEA	NEF	NM2CA	ES	
25	1.1113	1.0121	0.9447	...	1.4158	...
35	1.1041	1.0041	0.9364	...	1.4032	1.3996
45	1.0967	0.9958	0.9282	...	1.3903	1.3893
50	...	...	...	1.2110	...	...
55	1.0900	0.9877	0.9202	1.2065	1.3777	1.3795
65	1.0828	0.9795	0.9118	1.1963	1.3646	1.3694
75	...	0.9714	0.9037	1.1865	1.3523	1.3595

Table VI. Results for Density Data Fitted to Equation 2

Compound	a	$b \times 10^4$	$(d_{\text{obsd}} - d_{\text{calcd}}) \times 10^4$	
			Std.	Max.
N2HEA	1.1290	7.110	1.9	2.8
N2MEA	1.0325	8.154	0.6	1.0
NEF	0.9651	8.194	0.9	1.3
NM2CA	1.2605	9.868	2.3	2.6
ES	1.4477	12.740	1.8	2.7
1,3-PS	1.4345	10.010	1.3	1.7

Table VII. Experimental Viscosity Data

Temp., °C.	N2HEA	Viscosities, Cp.				1,3-PS
		N2MEA	NEF	NM2CA	ES	
25	206.3	10.84	2.212	...	2.056	...
35	101.1	7.515	1.838	...	1.734	7.447
45	54.19	5.437	1.549	...	1.483	5.915
50	...	...	...	3.824	...	...
55	32.05	4.096	1.328	3.398	1.287	4.816
65	20.22	3.178	1.153	2.687	1.130	3.980
75	...	2.542	1.005	2.186	1.002	3.362

Table VIII. Results for Viscosity Data Fitted to Equations 3 and 4

Compound	α	β	γ	E_{vis}, Cal./Mole	Std. Dev. in E_{vis}, Cal./Mole
N2HEA	4.68043	−4389.153	1,098,363	13,629 (25°)	87
N2MEA	0.61639	−1256.082	411,714	6,889 (25°)	14
NEF	−1.32786	252.506	73,391	3,408 (25°)	37
NM2CA	−1.04368	−90.377	199,109	5,225 (50°)	193
ES	−0.99927	91.485	89,388	3,162 (25°)	7
1,3-PS	−0.36766	−233.619	189,710	4,565 (35°)	35

As N2HEA is very viscous near room temperature, it is not surprising that anomalous dispersion (decrease of dielectric constant with increasing frequency) is observable in the radiofrequency range. Such is illustrated by the data in Table IV. Similar behavior is not exhibited by the less viscous N2MEA.

The experimental density data, which were determined primarily to permit the calculation of absolute viscosities, are summarized in Table V. The density data for each liquid as a function of temperature may be fitted excellently to an empirical equation of the following type:

$$d = a - bt \tag{2}$$

The least squares values of the constants in Equation 2 and the deviations between experimental and calculated data are presented in Table VI.

The experimental viscosity data are compiled in Table VII. The viscosity-temperature relationship for each liquid is described excellently by the Girifalco equation (*8, 16*):

$$\log \eta = \alpha + \frac{\beta}{T} + \frac{\gamma}{T^2} \tag{3}$$

Upon differentiation, this equation makes possible the evaluation of the activation energy of viscous flow (*18*).

$$\frac{E_{\text{vis}}}{2.303\,R} = \frac{d(\log \eta)}{d(1/T)} = \beta + \frac{2\gamma}{T} \tag{4}$$

The results obtained through fitting the viscosity data to Equation 3 and calculating the activation energy of viscous flow with Equation 4 are given in Table VIII. The unusually large value of E_{vis} for N2HEA probably arises from complex cross-association through hydrogen bonding.

NOMENCLATURE

ϵ = dielectric constant
d = density in g./ml. or g./cc.
η = viscosity in centipoises
t = temperature in °C.
T = temperature in °K.
E_{vis} = activation energy of viscous flow in cal./mole
R = molar gas constant, 1.987 cal./mole deg.
A, B = constants in Equation 1
a, b = constants in Equation 2
α, β, γ = constants in Equation 3

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Binary Freezing Point Behavior of Some Normal Octadecenoic Acids

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Complete binary freezing point data have been obtained for the following fatty acid systems: oleic-elaidic, oleic-petroselinic, oleic-petroselaidic, elaidic-petroselinic, elaidic-petroselaidic, and petroselinic-petroselaidic. All these systems, representing the various binary combinations of two pairs of geometrical and positional isomers, were of the simple eutectic type. Calculated heats of fusion were obtained for each of the acids. Mixtures rich in elaidic acid acid gave two freezing points, proving the existence of two polymorphic forms. The common form, f.p. 43.7° C., is metastable and the new form, f.p. 44.8° C., is stable.

SINCE the classical work of de Visser (*2*) in 1898, solid-liquid phase diagrams have been published for binary systems involving various long-chain fatty acid combinations (*6*). Those systems involving two homologous saturated acids exhibit molecular compound formation. Combinations of a saturated and an unsaturated fatty acid or of fatty acids of two different degrees of unsaturation give simple eutectic freezing point diagrams. Griffiths and Hilditch (*1*, *3*) published simple eutectic diagrams for the oleic–elaidic acid and the petroselinic-petroselaidic acid systems but observed only one polymorphic form of oleic and elaidic acids. The present report deals with the complete freezing point data for all six binary systems involving oleic, elaidic, petroselinic, and petroselaidic acids including polymorphic solid phases. These systems represent the various binary combinations of two pairs of geometrical and positional isomers.

EXPERIMENTAL

The pure oleic acid (f.p. stable form 16.3° C., f.p. unstable form 13.5° C.) and petroselinic acid (f.p. 29.8° C.) were prepared from olive oil and parsley seed oil, respectively, by methanolysis, fractionation on a Podbielniak column, conversion to the acids, and recrystallization from acetone until no further increase in freezing point was observed. The elaidic acid (f.p. 43.7° C.) and petroselaidic acid (f.p. 52.7° C.) were prepared by elaidinization of the pure cis acids followed by repeated recrystallization from acetone as above.

The freezing point determinations were made by the thermostatic sealed tube method (*5*), which involves finding two temperatures about 0.2° C. apart, one at which the last crystals disappear and the other at which a few crystals persist after prolonged agitation at constant temperature. The freezing point was taken as a mean of these two temperatures corrected for thermometer calibration and emergent stem.

RESULTS AND DISCUSSION

The results are given in Table I and are represented graphically in Figure 1. All six binary systems are of the simple eutectic type.

Compositions of both the elaidic and oleic acid branches of the diagrams had two freezing points, indicating that elaidic acid as well as oleic acid crystallizes in two polymorphic forms. The broken lines represent the binary freezing point curves for the low-melting modifications.

When mixtures rich in oleic acid were cooled to about