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## Dielectric Constants, Viscosities, and Related Physical Properties of Several Substituted Liquid Ureas at Various Temperatures

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**Dielectric constants, viscosities, densities, and refractive indices of three urea derivatives were measured at various temperatures ranging from 25 to 100 °C. The experimental data as functions of temperature were fitted precisely to appropriate equations. Dielectric constant data indicated a significant increase in dielectric constant of the cyclic ureas over that of the acyclic homologs. Kirkwood correlation factors and the activation energies of viscous flow were also evaluated. Values for Kirkwood correlation factors ranged from 1.07 to 1.21. This range indicates but does not substantiate parallel dipole association. Activation energies ranged from 3.3 to 4.4 kcal/mol.**

Tetramethylurea (TMU) has been a very versatile solvent for a number of investigations (2, 8, 14); however, analogs such as tetraethylurea (TEU) and the substituted cyclic ureas (Figure 1) have not been so thoroughly investigated. Available physical data for these interesting compounds are limited even though they have been available for some time (5, 24, 26, 28). [The dielectric constant of TEU has been previously investigated by Beguin and Gäumann (5) over the temperature range -68 to 134 °C.] Their relatively high polarities, large liquid ranges, and slightly basic nature make these substituted ureas potentially useful dipolar aprotic solvents. Tetraethylurea, for example, has recently been successfully used as a solvent for electrical conductivity studies (3). Presently, in this laboratory, *N,N'*-dimethylethyleneurea (DMEU) and *N,N'*-dimethylpropylene urea (DMPU), shown in Figure 1, are also being investigated as electrolytic solvents. The cyclic ureas have larger polarities with dipole moments of 4.09 (26) and 4.23 (26) for DMEU and DMPU, respectively, as compared with 3.45 for acyclic TEU (5). In addition, their dielectric constants are at least twice as high as will be shown below.

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### Experimental

**Reagents.** TEU was obtained from the RSA Corp. (Ardsley, N.Y.) and was purified by vacuum distillation as previously described (8). The specific conductance of TEU was  $7.9 \times 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$ . DMEU was synthesized by combining 2-imidazolidinone (Eastman), 80% formic acid (MCB reagent ACS), and 37% formaldehyde solution (Mallinkrodt Analytical reagent), in molar ratios of 5:50:8, respectively (20). Initially, the mixture warmed and the solution yellowed. Distinct color changes from yellow to orange, red, and finally brown were observed during the initial 8 h of the 48-h reflux period. Excess reagent solvents were removed under vacuum using a rotoevaporator; after the solution was made basic with saturated NaOH, the product was distilled at 65–72 °C (~2 mm Hg). Another distillation, over BaO at 65 °C (2 mm Hg), provided a colorless liquid in contrast to the yellow appearance of the crude distillate. Successive fractional freezings (17) then gave a very pure product with a specific conductance ranging from  $1-7 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The liquid range for DMEU was determined as 8.2–220 °C (~754 mm Hg).

DMPU was prepared in a similar manner using 5 moles of 2-(1H)-tetrahydropyrimidinone (Eastman) in the starting mixture. No dramatic color change occurred as with DMEU, and the solution remained yellow. Fractional freezings were not practical due to the low freezing point (below -20 °C) of the substance. DMPU has a boiling point of 230 °C (~754 mm Hg). The pure distillate, distilled over BaO, had a specific conductance of  $4.73 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$  and a boiling point of 81 °C (2.8 mm Hg). Boiling points agreed very well with literature data of 67 °C (2 mm Hg) (26), 84 °C (2 mm Hg) (26), and 30 °C (~2 mm Hg) (3) for DMEU, DMPU, and TEU, respectively.

Mass spectral, IR, and NMR data confirmed the DMEU and DMPU structures. The mass spectral data were gathered using a Hitachi Perkin-Elmer Model RMU-7 mass spectrometer. IR spectra were taken on a Perkin-Elmer 337 grating spectrometer and revealed virtually no OH stretch from 3350 to 3650  $\text{cm}^{-1}$  when the solvent was transferred under anhydrous conditions to the cell. NMR spectra were taken using a

Varian A-60 spectrometer. The spectra agreed well with those in the literature (19, 26). A Model 4666 Leeds and Northrup Dyke-Jones conductivity bridge unit, described in detail elsewhere (11), in conjunction with a Freas-type conductance cell (12) was used to measure the specific conductivities of TEU, DMEU, and DMPU.

Capacitance measurements were obtained at 1 MHz using a Twin-T impedance bridge assembly, described in detail elsewhere (6), in conjunction with two glass cells having parallel plate electrodes of different geometries (6, 18). Cells of this type with platinum electrodes have been used by other investigators, and their results indicate the suitability of these cells for such measurements (7, 18, 21). Procedures for calculating cell constants and dielectric constants, as well as bridge and cell calibration procedures, have been previously described (25, 27, 31). The cells were suspended in an oil-filled thermostat during measurements. Air and water having dielectric constants of 1.0005 and 78.304, respectively, were the standard media used for cell constant determinations (27). Cell constants were assumed constant over the temperature range considered as in similar investigations (6, 7, 18). In checking determinations (6, 7) on known systems, experimental values for the dielectric constant of water at 25, 35, 45, 55, 65, and 75 °C, as well as acetone, methanol, and nitrobenzene at 25 °C, agreed to within 0.1 dielectric unit of accepted literature data (27).

Three Cannon-Ubbelohde size 25 and 50 viscometers were used to obtain efflux times greater than 200 s. Flow times greater than 200 s were chosen so that kinetic energy corrections would be negligible (6, 7). Calibration data for the viscometers were provided by the Cannon Instrument Co. Experimental precautions and special adaptations of setups previously established (18) were followed.

Densities were measured pycnometrically and dilatometrically using two 15-ml pycnometer-dilatometers (6). The appropriate corrections were applied for calculating densities (6, 16, 23).

An Abbe Model 3L refractometer in conjunction with a Haake FJ temperature control assembly was used for measuring the refractive indices for TEU, DMEU, and DMPU at 25, 35, and 45 °C. Readings were taken in duplicate and agreed to within 0.02%.

Control of temperature for dielectric constant, viscosity, and density measurements was within 0.03 °C using a Cannon Model H-1 thermostatic bath assembly filled with a silicone oil. Bath thermometers sectioned into 0.1 °C divisions were compared with an NBS-calibrated thermometer, and the appropriate corrections were applied.

The precision for duplicate dielectric constant measurements was within 0.3%. Triplicate viscosity and duplicate density measurements agreed to within 0.2 and 0.02%, respectively. An IBM 370/65 computer was used to fit the data to the appropriate equations. The addition of higher terms to any given equation was considered not significant when an F test as described by Wentworth (32) at 99% confidence was not passed. The data are presented in Table I.

## Results and Discussion

Table I summarizes the experimental data for dielectric constants, densities, viscosities, and refractive indices.

The dielectric constant data were analyzed by fitting them to the linear empirical Equation 1 (10, 18):

$$\epsilon = A + B/T \quad (1)$$

Values for *A* and *B* are given in Table II. The average deviation between experimental and calculated values does not exceed 0.07% and has a maximum of 0.16% which indicates an excellent fit. At 25 °C the cyclic compounds DMEU and DMPU have moderately high dielectric constants of 37.6

and 36.1, respectively, while acyclic TEU is a relatively low dielectric media of dielectric constant 14.4. Beguin and Gäumann (5) have investigated TEU's dielectric properties. Over the temperature range considered in this present investigation, dielectric constant agreement with their data appears good. Here, the addition of a methylene group into the ring system decreases the dielectric constant much less than the addition of a methyl group to the aliphatic portion of the acyclic system (Figure 1). This addition to the acyclic structure lowers the dielectric constant from about 23.4 (4) for TMU to 14.4 for TEU, a 10-unit decrease. DMEU has a consistently higher dielectric constant than DMPU at all temperatures.

The density data as a function of temperature were fitted precisely to Equation 2 (18):

$$\rho = a + bt \quad (2)$$

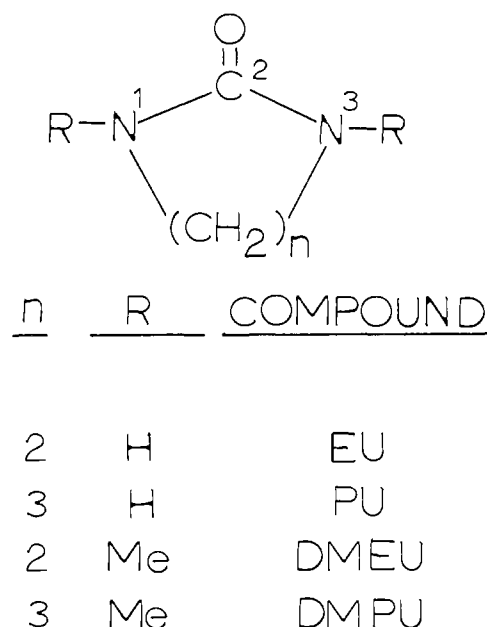


Figure 1. Structure of cyclic ureas

Table I. Experimental Data (Mean Values)

Temp, °C	Dielectric constant, 1 MHz	Viscosity, cP	Density, g/cm <sup>3</sup>	Refractive index
TEU				
25	14.39	2.363	0.9027	1.4448
35	13.78	1.879	0.8941	1.4403
45	13.16	1.531	0.8854	1.4360
55	12.60	1.276	0.8768	
75	11.55	0.935	0.8599	
100	10.42	0.676	0.8382	
DMEU				
25	37.60	1.944	1.0519	1.4707
35	35.97	1.633	1.0431	1.4664
45	34.43	1.393	1.0342	1.4621
55	32.96	1.204	1.0253	
75	30.35	0.938	1.0080	
100	27.42	0.720	0.9862	
DMPU				
25	36.12	2.934	1.0596	1.4881
35	34.47	2.371	1.0512	1.4837
45	32.88	1.960	1.0428	1.4795
55	31.40	1.650	1.0344	
75	28.75	1.233	1.0181	
100	25.86	0.909	0.9970	

The average and maximum deviations between experimental and calculated densities does not exceed 0.02% (Table III).

DMPU has a consistently higher density (Table I) than DMEU, and both are greater than water up to 75 °C. TEU has a density less than that of water at all measured temperatures and is comparable to the density of TMU (4).

Utilizing dipole moments, indicated in Table IV, along with densities and refractive indices from Table I, the Kirkwood correlation factor was obtained using Equation 3:

$$g = [(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)9 MkT] / [\epsilon(\epsilon_\infty + 2)^2 4 \pi N \rho \mu_0^2] \quad (3)$$

which is obtained by rearranging the Kirkwood-Frohlich equation (12, 22, 29).

Table II. Dielectric Constant Data Fitted to Equation 1

Compound	-A	B × 10 <sup>-3</sup>	% Dev <sup>a</sup> × 10 <sup>2</sup>	
			Mean	Max
TEU	5.43302	5.9154	7	16
DMEU	13.03731	15.1003	3	6
DMPU	15.02797	15.2468	2	6

<sup>a</sup> % Deviation = 100|ε<sub>exp</sub> - ε<sub>calc</sub>|/ε<sub>exp</sub>.

Table III. Density Data Fitted to Equation 2

Compound	a	-b × 10 <sup>4</sup>	% Dev <sup>a</sup> × 10 <sup>3</sup>	
			Mean	Max
TEU	0.92409	8.584	10	20
DMEU	1.07370	8.764	10	10
DMPU	1.08038	8.337	10	19

<sup>a</sup> % Deviation = 100|ρ<sub>exp</sub> - ρ<sub>calc</sub>|/ρ<sub>exp</sub>.

Table IV. Kirkwood Correlation Factors (Calculated from Equation 3)

Compound	Debye	Temp, °C	g
TEU	3.45 (5)	25	1.11
		35	1.11
		45	1.11
		55	1.10
		75	1.09
DMEU	4.09 (6)	100	1.07
		25	1.20
		35	1.20
		45	1.21
		55	1.21
DMPU	4.23 (6)	75	1.20
		100	1.19
		25	1.17
		35	1.17
		45	1.16
		55	1.16
		75	1.15
		100	1.13

Table V. Viscosity Data Fitted to Equation 4

Compound	-α	β × 10 <sup>-2</sup>	γ × 10 <sup>-5</sup>	δ × 10 <sup>-8</sup>	% Dev <sup>a</sup> × 10 <sup>2</sup>		E <sub>vis</sub> (°C), cal/mol
					Mean	Max	
TEU	9.19233	68.8206	-20.7591	2.73598	7	15	4352 (25)
DMEU	4.53320	23.9496	-5.3189	0.83463	7	15	3266 (25)
DMPU	7.02574	50.7676	-14.6990	2.01703	9	18	4021 (25)

<sup>a</sup> % Deviation = 100|η<sub>exp</sub> - η<sub>calc</sub>|/η<sub>exp</sub>.

The dipole moments (Table IV), μ<sub>0</sub>, used in Equation 3 for TEU, DMEU, and DMPU were obtained in dioxane (5, 26). ε<sub>∞</sub> (the high-frequency dielectric constant characteristic of induced polarization) was estimated as 1.1 × n<sub>D</sub> where n<sub>D</sub> is the refractive index (9, 10). The factor takes into account that the atomic polarization is about 10% of the electric polarization (9, 10, 30). Though ε<sub>∞</sub> is only an approximation, it gives a common basis for the three compounds studied here. This factor "g", when greater than unity, depicts a system where neighboring dipoles are parallel with respect to one another. When g is less than unity, an antiparallel or random configuration of dipoles is described. For normal polar liquids, g is unity, and Equation 3 reduces to the Onsager equation (29).

For TEU, DMEU, and DMPU, the Kirkwood correlation factors (Table IV) are greater than unity but are not sufficiently greater to support or deny predominantly parallel dipole association.

Viscosity data were fitted to the Girifalco Equation 4 (13):

$$\ln \eta = \alpha + \beta/T + \gamma/T^2 + \delta/T^3 \quad (4)$$

with viscosity as a function of temperature. Values obtained for α, β, γ, and δ for the three solvents studied are shown in Table V. The average and maximum deviations between experimental and calculated values do not exceed 0.09% and 0.18%, respectively. The activation energy of viscous flow was calculated by using Equation 5, and the results are listed in Table V.

$$E_{vis} = R d(\ln \eta) / (d(1/T)) = R(\beta + 2 \gamma/T + 3 \delta/T^2) \quad (5)$$

The viscosities of DMEU and DMPU and TEU decrease in the order DMPU > TEU > DMEU. The activation energy for viscous flow (E<sub>vis</sub>) is less for DMEU than for that of DMPU and TEU. For slightly associated dipolar liquids, E<sub>vis</sub> is typically between 3-5 kcal/mol. The energy for viscous flows of DMEU, DMPU, and TEU falls within this range.

TEU, DMEU, and DMPU possess a variety of useful properties within the alkylated urea system. The experimental and derived data presented should be of interest to those who pursue investigations involving these interesting liquids.

#### Acknowledgment

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#### Nomenclature

n<sub>D</sub> = refractive index  
t = temperature, °C  
T = temperature, K  
g = Kirkwood correlation factor  
M = formula weight, g/mol  
k = Boltzmann constant, erg/deg Kelvin  
N = Avogadro number, l./mol  
E<sub>vis</sub> = activation energy of viscous flow, cal/mol  
R = molar gas constant, cal/mol-deg  
cP = centipoise  
A, B = constants in Equation 1  
a, b = constants in Equation 2

## Greek Letters

$\epsilon$  = low-frequency dielectric constant

$\epsilon_{\infty}$  = high-frequency dielectric constant (approximated as  $1.1 \times n_D^2$ )

$\eta$  = viscosity, cP

$\rho$  = density, g/cm<sup>3</sup>

$\mu_0$  = dipole moment, Debye units [which are (esu-cm)<sup>2</sup>]

$\alpha, \beta, \gamma, \delta$  = constants in Equations 4 and 5

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# Heats of Dilution of Lithium Perchlorate in Anhydrous Acetonitrile, Propionitrile, and Isobutyronitrile at 25 °C

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**Heats of dilution of lithium perchlorate in anhydrous acetonitrile, propionitrile, and isobutyronitrile at 25 °C using solution and dilution calorimeters are reported. The results indicate that electrostatic treatments do not consistently predict the behavior of these systems even in the millimolar range, probably because of ion association.**

Two recent surveys of thermochemical data for nonaqueous electrolytes (3, 6) indicate that determinations of heats of dilution have been confined largely to alcoholic solvents. It is of interest to examine the predictions of the Debye-Hückel model in a negligibly hydrogen-bonded solvent from the point of view of heats of dilution.

Heats of dilution data are reported for lithium perchlorate in acetonitrile, propionitrile, butyronitrile, and isobutyronitrile at 25 °C.

## Experimental

**Acetonitrile.** Fisher ACS reagent grade acetonitrile was purified by a method reported previously (4, 13). Alternatively, a purer grade of acetonitrile was used as a starting material (MCB Spectroquality) and was of high purity as received (2). The only treatment required was a 6-h period standing over calcium hydride followed by a high vacuum room temperature distillation to remove residual water and dissolved air. After degassing, the void in the flask was refilled with dry nitrogen (Linde) to a pressure of 350-400 torr before warming to room temperature.

An analysis by the Karl Fischer method using the Photovolt "Aquatest II" titrator showed a water content of 30-40 ppm

immediately after distillation and 50-60 ppm after standing in a stoppered flask in the drybox for 24 h. A blank titration showed that 30 ppm was close to the lower limit of detection for this instrument. Therefore, nitriles treated with calcium hydride were considered to have a water content between 0 and 10 ppm if used very soon after distillation.

**Propionitrile.** Propionitrile was far more sensitive to acid-catalyzed polymerization than acetonitrile, and heating with phosphorus pentoxide was not an efficient method of drying. Instead, propionitrile [Eastman Organic Chemicals or MCB (99% purity)] was first dried in 1-l. batches by standing for 5 days over dried silica gel (Tel-Tale, Davison Chemical Co.), followed by standing over ~30 g phosphorus pentoxide for 2 days. A small amount of polymerization was noted at this point. Drying was completed by refluxing over calcium hydride, followed by fractionation and degassing as described for acetonitrile, except that a 2-ft column with glass packing was used for fractionation. This permitted distillation to be carried out in a fume hood, as the higher nitriles are noticeably toxic (11).

The butyronitriles (Eastman Organic Chemicals) were purified by the same procedure as propionitrile.

**Lithium perchlorate.** Lithium perchlorate (K & K Laboratories) contained approximately 70 ppm halide by potentiometric titration with aqueous silver nitrate and a small amount of unidentified tan-colored, water-insoluble matter. Both of these were removed to within the limits of detection (10 ppm for halide, visibility on sintered glass filter for other matter) by a single recrystallization from water.

Differential thermal analysis of dried lithium perchlorate indicated a melting point range (235-237 °C) above which temperature no salient features appeared on the thermogram