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Dielectric Constants, Viscosities, and Related Physical Properties of Some Liquid Carbamates at Several Temperatures

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Dielectric constants, viscosities, densities, and refractive indices of five pure liquid carbamates and one binary liquid carbamate mixture were measured at several temperatures within the range of 25–105 °C. The experimental data, excepting refractive indices, were fitted precisely to appropriate equations as functions of temperature. Values of activation energies of viscous flow and Kirkwood correlation factors also were calculated. At comparable temperatures, the dielectric constants of these noncyclic carbamates were found to be much lower than those of the cyclic carbamates (or 2-oxazolidones) investigated previously. Among the noncyclic carbamates in this study, ethyl *N*-methylcarbamate has the most attractive combination of physical properties and appears to have the greatest potential for use as a new nonaqueous solvent.

Introduction

The preparation, properties, and chemistry of the noncyclic esters of carbamic acid, the carbamates, have been studied extensively since the beginning of the twentieth century. Recently there has been a number of articles dealing with carbamates as ligands in metal complexes (*2*, *4*, *8*).

Several carbamates are now commercially available. At least five of these moderately polar compounds have melting points of 60 °C or below and possibly may represent useful nonaqueous solvents. Although these five carbamates—methyl, ethyl, *n*-propyl, ethyl *N*-methyl, and ethyl *N*-ethyl—have received considerable attention from organic and inorganic chemists and biochemists, the literature contains indeed very little information relative to the physical properties of these compounds as highly purified liquids. This study, therefore, was undertaken to determine the dielectric constants, viscosities, and other physical properties of the five above-mentioned carbamates and a 1:1 mole mixture of ethyl and methyl carbamates as functions of temperature.

Experimental Section

Purification of the Carbamates. Methyl carbamate (MCB) and *n*-propyl carbamate (*n*-PCB) were generously donated by Millmaster Corp. Ethyl carbamate (ECB), ethyl *N*-methylcarbamate (ENMCB), and ethyl *N*-ethylcarbamate (ENECB) were obtained from Aldrich Chemical Co. and Eastman Kodak Co. MCB, ECB, and *n*-PCB were purified by successive fractional freezings under nitrogen until maximum freezing points of 54.0, 49.5, and 60.0 °C, respectively, were obtained. ENMCB was purified by vacuum distillation followed by successive fractional freezings under nitrogen until a maximum freezing point of −2.5 °C was obtained. ENECB was vacuum distilled twice and then passed through a column of activated alumina topped with Linde Type 4A molecular sieves. The 1:1 mole mixture of ECB and MCB, which was liquid at room temperature, was prepared on a weight basis using purified ECB and MCB.

Experimental Measurements. A General Radio Type 821-A Twin-T impedance measuring assembly (*14*, *19*) was used in conjunction with two-terminal parallel plate cells for capacitance measurements at 1 MHz. The assembly and cells were similar to those used in previous studies (*7*, *11*). The principal aspects for determining cell constants and for calculating dielectric constants have been described previously (*14*, *22*). The standard media used in the determination of cell constants were air and water which have dielectric constants of 1.0005 and 78.304 (*17*), respectively, at 25 °C. The capacitance measurements were made in duplicate with a precision of 0.2% being obtained.

The viscosities were determined by using size 25, 50, and 75 Cannon-Ubbelohde viscometers which previously had been calibrated by the Cannon Instrument Co. Efflux times always exceeded 200 s, making unnecessary any corrections due to kinetic energy effects. To minimize atmospheric contamination, a dry nitrogen atmosphere was maintained over the experimental liquids in the viscometers which were equipped with top adapters and vented through tubes filled with Drierite and Ascarite. Efflux times were measured to 0.1 s using electric timers. The measurements were made in duplicate, and a precision of 0.2% was achieved. The viscosities are reported relative to a viscosity of 1.0019 cP for water at 20 °C (*20*).

Densities were determined pycnometrically and dilatometrically with 15-mL pycnometer–dilatometers which were calibrated with freshly distilled water at 25 °C and are based on 0.99704 g cm^{-3} as the density of water at this temperature. Volumes of the pycnometer–dilatometers at higher temperatures were calculated with a standard volume expansion formula using 9.6×10^{-6} $°C^{-1}$ as the cubical coefficient of expansion of Pyrex glass (*13*). Excess liquid in a pycnometer was removed when necessary by a strong suction through a capillary. Buoyancy corrections were applied to all experimental weights prior to calculations of densities (*13*). Duplicate determinations consistently agreed within 0.02%.

Refractive indices were measured with Spencer Abbe Model 2214 refractometers equipped with sodium D line compensating prisms and with jackets through which water from a constant-temperature bath could be rapidly circulated. Duplicate or triplicate refractive index measurements showed a precision of 0.02%.

The temperature for the dielectric constant, viscosity, and density determinations was controlled within 0.04 °C with a Cannon Model H-1 constant-temperature bath filled with light paraffin oil. The bath thermometers with 0.1 °C subdivisions were compared with a similar thermometer for which NBS calibration data were available; appropriate corrections were applied.

Mean values of the experimental data for the liquids were fitted as functions of temperature to various equations by least-squares analysis using an IBM 370-165-II computer. These equations then were used to calculate small corrections to the values of the physical constants, from the temperatures at which the measurements were made to the temperatures shown in Table I ($\Delta T < 0.4$ °C). The values in Table I, therefore, are corrected but not smoothed values.

Results and Discussion

The experimental data are summarized in Table I along with a few comparison data from other studies. Other existing dielectric constant, density, and refractive index data in the lit-

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Table I. Experimental Data

temp, °C	dielectric constant, 1 MHz	viscosity, cP	density, g cm^{-3}	refractive index
		MCB		
55	18.48	2.605	1.1352	1.4100
65	18.00	2.056	1.1248	
75	17.32	1.679	1.1146	
85	16.79	1.398	1.1039	
95	16.13	1.178	1.0932	
		ECB		
55	14.14	2.994	1.0511	1.4148
	13.98[a]			
65	13.68	2.310	1.0411	
	13.46[a]			
75	13.26	1.841	1.0311	
85	12.74	1.501	1.0209	
95	12.35	1.246	1.0105	
		n-PCB		
65	12.06	2.797	0.9970	
75	11.70	2.182	0.9875	
85	11.28	1.747	0.9779	
95	10.92	1.429	0.9680	
105	10.63	1.200	0.9584	
		ENMCB		
25	24.12	3.096	1.0075	1.4158
	23.5[b]		1.0042[b]	1.4179[b]
40	21.58	2.097	0.9932	
55	19.46	1.505	0.9787	1.4069
70	17.58	1.137	0.9639	
85	16.17	0.889	0.9490	
100	14.84	0.713	0.9338	
		ENECB		
25	21.10	3.584	0.9737	1.4192
		3.650[c]	0.9745[c]	1.4196[c]
40	18.82	2.369	0.9598	
55	16.96	1.658	0.9455	1.4098
70	15.28	1.225	0.9311	
85	13.90	0.943	0.9164	
100	12.60	0.745	0.9013	
		1:1 ECB:MCB		
25	18.05	7.716	1.1182	1.4218
40	17.18	4.410	1.1034	
55	16.31	2.804	1.0882	1.4106
70	15.47	1.960	1.0729	
85	14.65	1.449	1.0574	
100	13.87	1.119	1.0414	

[a] Reference 21. [b] Reference 15. [c] Reference 1.

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

system	A	$10^{-4}B$	$10^{-6}C$	% deviation × 100[a] mean	max
MCB	−44.131	3.560 88	−4.941 75	16	31
ECB	−14.134	1.360 20	−1.418 73	13	29
n-PCB	2.884	0.138 65	0.582 06	15	25
ENMCB	15.555	−1.146 70	4.181 08	14	31
ENECB	1.987	−0.288 81	2.558 14	13	22
1:1 ECB: MCB	−15.792	1.494 54	−1.447 49	3	4

[a] % deviation = $100|\epsilon_{\text{exptl}} - \epsilon_{\text{calcd}}|/\epsilon_{\text{exptl}}$.

Table III. Results for Density Data Fitted to Equation 2

system	a	$-b \times 10^4$	$-c \times 10^7$	% deviation × 10^3 [a] mean	max
MCB	1.188 32	9.2078	8.450	6	13
ECB	1.102 74	8.9482	8.030	4	8
n-PCB	1.057 15	8.9885	4.018	8	16
ENMCB	1.030 76	9.1979	5.014	3	7
ENECB	0.996 30	8.8785	6.258	5	11
1:1 ECB:MCB	1.142 32	9.5075	5.771	5	13

[a] % deviation = $100|\rho_{\text{exptl}} - \rho_{\text{calcd}}|/\rho_{\text{exptl}}$.

Table IV. Kirkwood Correlation Factors

compd	μ_0, D	temp, °C	g
MCB	2.59[a]	55	1.04
ECB	2.59[b]	55	0.99
n-PCB	2.59[a]	65	1.04[c]
ENMCB	2.59[a]	25	1.94
		55	1.77
ENECB	2.59[a]	25	1.96
		55	1.79

[a] Estimated to be equal to that of ECB. [b] Reference 16. [c] Based on an estimated value of 1.416 for refractive index.

erature concerning the carbamates (*3*, *18*, *23*, *24*, *26*) do not correspond to the temperatures at which measurements were made in this study and, therefore, were deemed unsuitable for inclusion in this table for comparison.

The dielectric constant data for each system as a function of temperature were fitted to the empirical equation

$$\epsilon = A + B/T + C/T^2 \qquad (1)$$

The values obtained for A, B, and C through least-squares analyses of the data for the systems studied are summarized in Table II. The excellent fitting of the data to eq 1 is manifest from the average and maximum deviations between experimental and calculated values being ≤0.16 and ≤0.31%, respectively.

The dielectric constant of ENMCB is about 50% greater than that of isomeric *n*-PCB at a comparable temperature, e.g., 16.17 vs. 11.28 at 85 °C. More interesting, however, is the observation that the noncyclic carbamates in this study have dielectric constants which are about only one-third as large as those of their cyclic analogues, the 2-oxazolidones, which have been studied previously in this laboratory (*10*). Comparable data at 25 °C reveal that the dielectric constants of ENMCB and ENECB are 53.4 and 45.7 units lower than those of 3-methyl-2-oxazolidone and 3-ethyl-2-oxazolidone, respectively.

The density data for each liquid as a function of temperature are described excellently by the equation

$$\rho = a + bt + ct^2 \qquad (2)$$

The calculated least-squares values for a, b, and c are compiled in Table III which also contains data showing that the mean and maximum deviations between experimental and calculated densities are ≤0.008 and ≤0.016%, respectively.

The experimental data in Table I indicate that the density decreases with increasing molecular weight within an homologous series as expected. On the other hand, at the comparable temperature of 85 °C, the density of ENMCB is about 3% less than that of isomeric *n*-PCB suggesting differences in the packing or ordering of molecules of these isomeric species in the liquid state.

Experimental dielectric constant, density, and refractive index data were used with dipole moment data from the literature to gain insight into the nature and extent of association of the carbamates. Hence, values of the Kirkwood correlation factor, g, were calculated from appropriate data using the Kirkwood–Fröhlich equation (*9*, *12*) in the form

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

For the calculations, the value of 2.59 D for ECB (*16*) was used for the dipole moment of each of the carbamates since no other

Table V. Results for Viscosity Data Relative to Equations 4 and 5

system	$-\alpha$	β	$-\gamma$	$\delta \times 10^{-8}$	% deviation × 100[a] mean	% deviation × 100[a] max	E_{vis}(85 °C), cal mol^{-1}	std dev in E_{vis}, cal mol^{-1}
MCB	61.959 15	62 558.59	21 646 710	25.901 35	1	2	4482	4
ECB	30.827 63	29 970.15	10 340 930	12.942 02	1	1	4951	3
n-PCB	−24.883 90	−28 673.49	−10 205 250	−10.946 04	5	10	5390	32
ENMCB	9.157 65	6 520.188	1 902 765	2.603 836	8	17	3942	17
ENECB	6.950 17	4 164.020	1 092 050	1.734 990	12	21	4218	23
1:1 ECB:MCB	13.307 39	12 041.31	4 211 651	5.922 022	16	33	4711	28

[a] % deviation $100 |\eta_{exptl} - \eta_{calcd}|/\eta_{exptl}$.

dipole moment data were available. The values for the Kirkwood correlation factors for the five carbamates, which are presented in Table IV, range from 0.99 to 1.96. These results generally indicate nonspecific or essentially random orientation of dipoles for the simple unsubstituted carbamates and slightly parallel alignment of dipoles for the N-substituted compounds.

The viscosity and the activation energy of viscous flow for each liquid may be described as functions of temperature by the following equations, respectively

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

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

The viscosity data were fitted to eq 4 by a nonlinear least-squares program of the type described by Wentworth (*25*). Resulting values of α, β, γ, and δ are compiled in Table V along with data showing that the average and maximum deviations between experimental and calculated values of viscosity never exceed 0.16 and 0.33%, respectively.

It is evident from data in Table I that viscosities typically increase with increasing molecular weights within a particular homologous series. A perhaps more noteworthy observation, based on data in Tables I and V at the comparable temperature of 85 °C, is that the N-substituted carbamates have both lower viscosities and lower activation energies of viscous flow relative to those of the unsubstituted carbamates.

Although the molecular weights of ENMCB and ENECB are greater than those of MCB and ECB, the viscosities of the former two are less. This inverse relationship between viscosities and molecular weight has been observed to apply to pyridine *N*-oxide and its 2-methyl and 2,6-dimethyl derivatives (*6*) and for sulfolane and its 3-methyl and 2,4-dimethyl derivatives (*5*). Another interesting comparison reveals that the viscosities of noncyclic ENMCB and ENECB are approximately 0.7 cP greater than the viscosities of their cyclic analogues, 3-methyl-2-oxazolidone and 3-ethyl-2-oxazolidone, at 25 °C (*10*).

Other Findings Relative to Ethyl *N*-Methylcarbamate

Among the noncyclic carbamates studied, ENMCB has the best overall combination of physical properties. It is a liquid at room temperature and is capable of a high degree of purification by a combination of fractional distillation and fractional freezings. A number of alkali metal and quaternary ammonium salts were found to be soluble in ENMCB to the extent of more than 0.06 mol L^{-1}. Water and ENMCB are miscible in all proportions. The minimum specific conductance thus far observed for purified ENMCB is 2.5×10^{-9} Ω^{-1} cm^{-1} at 25 °C.

Conclusion

The convenient liquid range, ease of purification, low specific conductance, intermediate dielectric constant, moderate viscosity, and fairly good dissolving power of ENMCB indicate that it has potential and is indeed worthy of investigation as a new nonaqueous solvent. The other carbamates discussed in this study show less potential.

Glossary

MCB	methyl carbamate
ECB	ethyl carbamate
n-PCB	*n*-propyl carbamate
ENMCB	ethyl *N*-methylcarbamate
ENECB	ethyl *N*-ethylcarbamate
n_D	refractive index (sodium D line)
T	temperature, K
t	temperature, °C
g	Kirkwood correlation factor
M	formula weight in g mol^{-1}
k	Boltzmann constant
N	Avogadro number
E_{vis}	activation energy of viscous flow in cal mol^{-1}
R	molar gas constant in cal mol^{-1} deg^{-1}
cP	centipoise
A, B, C	constants in eq 1
a, b, c	constants in eq 2

Greek Symbols

ϵ	low-frequency dielectric constant
ϵ_∞	high-frequency dielectric constant, approximated as $1.10\, n_D^2$
η	viscosity in cP
ρ	density in g cm^{-3}
μ_0	dipole moment in D
α, β, γ, δ	constants in eq 4 and 5

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