Dielectric Constants, Viscosities, and Related Physical Properties of Five Cyano- and Halopyridines at Several Temperatures

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Dielectric constants, viscosities, densities, and refractive indices of five monosubstituted liquid pyridines are measured at several temperatures ranging from 25° to 125°C. The experimental data as functions of temperature are fitted to appropriate equations. Values of activation energies of viscous flow and Kirkwood correlation factors also are calculated. At comparable temperatures, the dielectric constants and viscosities of the isomeric cyanopyridines are significantly affected by the position of the substituent group. The calculated Kirkwood correlation factors range from 0.73 to 1.56, implying only slight amounts of net parallel or antiparallel configurations of dipoles in the liquids.

Pyridine and its monosubstituted derivatives have been studied extensively, and their preparations, properties, and chemistry have been reviewed comprehensively by Mertel (*18*) and Oliveto (*19*). Dipole moments and other related physical properties have been determined by Cumper and Vogel (*6*). Microwave (*17*), electron spin resonance (*10*), and nitrogen-14 nuclear quadrupole resonance spectroscopy (*4, 9, 20*) studies also have been carried out on several monosubstituted pyridines. Low-frequency dielectric constants, viscosities, and densities of most monosubstituted pyridines, however, have not been determined.

The convenient liquid range, moderate to very high dipole moments, and commercial availability of several of the halo- and cyanopyridines provided a basis for interest in these compounds as potentially useful nonaqueous solvents. Although many monosubstituted pyridines have received considerable attention from both organic and inorganic chemists, the literature is essentially devoid of data relative to some of the most important physical properties of these compounds as highly purified liquids. This study was undertaken to determine the dielectric constants, viscosities, and other physical properties of five monosubstituted pyridines as functions of temperature.

Experimental

2-Cyanopyridine (2CNP), 3-cyanopyridine (3CNP), 4-cyanopyridine (4CNP), 2-bromopyridine (2BrP), and 2-chloropyridine (2ClP) were obtained from the Aldrich Chemical Co. The pyridines were vacuum distilled two or more times. 2CNP was further purified by fractional freezing techniques (*3*).

A Twin-T impedance bridge assembly was used in conjunction with two-terminal parallel plate cells for capacitance measurements at 1 MHz. Similar glass cells with platinum electrodes have been found (*1, 5, 11*) to be structurally satisfactory and convenient to use for measurements of low-conducting liquids at several temperatures. The ends of the external leads to the cell electrodes were fitted with special adapters so that the cell, which was suspended in an oil bath during measurements, could be easily attached to the Twin-T bridge by a shielded coaxial cable having a dual banana plug connection at each end. The principal aspects for determining the 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 (*15*), respectively, at 25°C. The cell constants were assumed to be temperature-independent 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, and of methanol, acetone, and nitromethane at 25°C in each case agreed within 0.1 dielectric constant unit with widely accepted data in the literature (*15, 16*).

The viscosities were measured with size-25 Cannon-Ubbelohde viscometers which were previously calibrated by the Cannon Instrument Co. Corrections for kinetic energy effects were unnecessary since flow times always exceeded 200 sec. 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 with electric timers. The viscosities are reported relative to a viscosity of 1.0019 cP for water at 20°C (*21*).

Densities were determined pycnometrically and dilatometrically using 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 other temperatures were calculated with a standard volume expansion formula and by using 9.9×10^{-6} $°C^{-1}$ as the cubical coefficient of expansion of Pyrex glass (*13*). Excess liquid in a pycnometer was removed when necessary by strong suction through a fine capillary. Appropriate buoyancy corrections were applied to weights of liquid prior to calculations of densities (*13*).

Refractive indices were measured with a Spencer Abbe Model 2214 refractometer equipped with sodium D-line compensating prisms and with jackets through which water from a constant temperature bath could be rapidly circulated.

The temperature for the dielectric constant, viscosity, and density determinations was controlled within 0.03°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 an NBS-calibrated thermometer; appropriate corrections were applied.

All determinations were made in duplicate or triplicate. The precision of multiple experimental values was within 0.2% for dielectric constants and viscosities and 0.02% for densities and refractive indices. Mean values of experimental data were fitted to various equations by least-squares analyses performed with an IBM 360/65 computer using double-precision Fortran IV programming.

Results and Discussion

Mean values of experimental data are summarized in Table I. Existing density and refractive index data in the

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Table I. Experimental Data

Temp, °C	Dielectric constant, 1 MHz	Viscosity, cP	Density, g cm^{-3}	Refractive index
		2CNP		
30	93.77	1.816	1.0785	1.5245
40	87.46	1.528	1.0694	1.5203
50	81.72	1.306	1.0601	1.5159
75	69.73	0.946	1.0377	
100	60.01	0.722	1.0145	
125	52.14	0.574	0.9912	
		3CNP		
50	20.54	1.731	1.0744	1.5252
60	19.79	1.463	1.0650	1.5207
75	18.76	1.177	1.0511	
100	17.20	0.861	1.0276	
125	15.80	0.665	1.0043	
		4CNP		
80	5.23	0.977	1.0392	
90	5.10	0.860	1.0292	
100	5.02	0.770	1.0198	
110	4.91	0.694	1.0103	
125	4.77	0.598	0.9955	
		2BrP		
25	23.18	1.754	1.6169	1.5695
30	22.69	1.622	1.6101	1.5671
40	21.71	1.403	1.5969	1.5625
50	20.79	1.231	1.5837	1.5582
75	18.75	0.927	1.5508	
100	16.98	0.729	1.5170	
125	15.45	0.592	1.4829	
		2ClP		
25	27.32	1.187	1.2039	1.5310
30	26.62	1.106	1.1986	1.5287
40	25.29	0.971	1.1880	1.5239
50	24.05	0.863	1.1775	1.5190
75	21.32	0.663	1.1513	
100	19.04	0.529	1.1239	
125	17.05	0.434	1.0966	

Table II. Results for Dielectric Constant Fitted to Equation 1

				% Deviation, 100	
Compound	A	$B \times 10^{-4}$	$C \times 10^{-6}$	Mean	Max
2CNP	1.659	−0.48308	9.92774	3	7
3CNP	−7.464	1.01913	−0.36971	2	4
4CNP	1.347	0.13158	0.01895	12	28
2BrP	−6.982	0.87332	0.07842	3	5
2ClP	−7.609	0.80477	0.70584	3	7

Table III. Results for Density Data Fitted to Equation 2

				% Deviation × 10^3	
Compound	a	$-b \times 10^4$	$c \times 10^7$	Mean	Max
2CNP	1.10530	8.8947	−1.833	8	22
3CNP	1.12123	9.3671	0.098	2	4
4CNP	1.11498	9.3649	−1.492	12	24
2BrP	1.64916	12.9056	−3.120	7	14
2ClP	1.22956	10.2146	−3.389	10	24

literature concerning these pyridine derivatives (*2, 23*) 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 liquid as a function of temperature were fitted to the following empirical equation:

$$\epsilon = A + B/T + C/T^2 \tag{1}$$

The values obtained for A, B, and C through least-squares analyses of the data for the five halo- and cyanopyridines studied are presented in Table II. The excellent fitting of the data to Equation 1 is manifest from the average and maximum deviations between experimental and calculated values being ≤ 0.12 and $\leq 0.28\%$, respectively.

Trends in dielectric constants and dipole moments of the experimental compounds exhibit significant similarities. For comparison purposes, the dielectric constant of pyridine (Py) at 25°C is 12.3 (*16*), and the dipole moments of pyridine and its five derivatives in benzene solution at 25°C are as follows (*6*): Py, 2.21 D; 4CNP, 1.63 D; 3CNP, 3.46 D; 2CNP, 5.24 D; 2BrP, 3.21 D; 2ClP, 3.25 D. Cyano-substitution in the 4-position of pyridine causes decreases in both the dielectric constant and dipole moment. Cyano-substitution in the 3-position or bromo- or chloro-substitution in the 2-position causes approximately equally large increases in both the dielectric constant and dipole moment. Most strikingly, cyano-substitution in the 2-position of pyridine results in very large increases in both of these quantities; as a point of special emphasis, the dielectric constant for 2CNP is greater than that for water at all comparable temperatures.

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

$$\rho = a + bt + ct^2 \tag{2}$$

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 differences between experimental and calculated densities are ≤ 0.012 and $\leq 0.024\%$, respectively. From the experimental data in Table I, the density is a function of the substituted group and its position on the pyridine ring. 2-Bromopyridine, as expected, has a significantly greater density than 2ClP or any of the cyanopyridines studied. Also, 3CNP has the greatest density of the cyanopyridines studied, with 2CNP being the least dense at comparable temperatures. These differences in the densities of the isomeric pyridine derivatives are probably due to steric effects since 3-cyano-substitution would perhaps allow closer packing of the molecules compared to 2-cyano- or 4-cyano-substitution.

The experimental dielectric constant, density, and refractive index data were used with the dipole moment data from the literature to gain insight concerning the nature and extent of association of polar liquids such as the

Table IV. Kirkwood Correlation Factors

Compound	Temp, °C	Correlation factor, g
2CNP	30	1.56.
3CNP	50	0.79
4CNP	80	0.73
2BrP	25	0.91
2ClP	25	1.08

Table V. Results for Viscosity Data Relative to Equations 5 and 6

Compound	$-\alpha$	β	$-\gamma$	$\delta \times 10^{-8}$	% Deviation, 100		E_{vis} (100°C), cal/mol	SD in E_{vis}, cal/mol
					Mean	Max		
2CNP	8.39484	6390.947	1909939.0	2.421694	10	18	2726	15
3CNP	6.56917	4575.603	1317503.0	1.881229	11	20	3114	24
4CNP	45.65510	48567.64	17836050.0	22.51479	3	6	2940	20
2BrP	6.48221	4418.443	1182717.0	1.465513	3	7	2458	4
2C1P	5.81420	3375.051	794146.3	0.953837	5	8	2332	6

cyano- and halopyridines. The Kirkwood-Frohlich equation (*7, 12*) in the form:

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

makes possible a description of polar liquids having specific short-range forces which hinder orientation of a molecule with respect to its surrounding neighbors. The significance of the calculated g value is that it gives an indication of the type of dipole–dipole alignment taking place. Values of g greater than unity indicate parallel orientation of the dipoles, whereas values of g less than unity indicate an antiparallel orientation. If g is equal to or nearly equal to one, the compound is essentially nonassociated, and the intermolecular forces are nonspecific or perfectly random.

Since the melting point of 4CNP was too high to permit the determination of its refractive index by regular experimental procedure, the approximate refractive index of 4CNP was calculated by Equation 4b to be 1.504 at 80°C, using $[R]$ = 29.66 cm^3 mol^{-1} (the average of five values for 2CNP and 3CNP). This calculation was based on the generally accepted fact that the molar refraction, $[R]$, of a compound is essentially independent of temperature (*8*) and on the assumption that molar refractions are equal for isomeric compounds such as 2CNP, 3CNP, and 4CNP. The reasonableness of the assumption of equal molar refractions for related isomers was supported by calculations based on appropriate handbook data (*23*), showing that molar refractions of isomers differed less than 1% in each of four sets of three ring-substituted isomers which were checked.

$$[R] = (n^2_{\rm D} - 1)M/(n^2_{\rm D} + 2)\rho \quad (4a)$$

or

$$n_{\rm D} = \sqrt{(M + 2\rho[R])/(M - \rho[R])} \quad (4b)$$

The calculated Kirkwood correlation factors for the pyridines studied are presented in Table IV. These results indicate that the most probable types of dipole–dipole orientations are slightly antiparallel for 3CNP and 4CNP, essentially random or no net alignment for 2BrP and 2ClP, and parallel to a small extent for 2CNP. Although approximate, these calculated results are probably of the correct relative order.

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

$$\eta = \exp(\alpha + \beta/T + \gamma/T^2 + \delta/T^3) \quad (5)$$

$$E_{\rm vis} = Rd(\ln \eta)/d(1/T) = R(\beta + 2\gamma/T + 3\delta/T^2) \quad (6)$$

The viscosity data were fitted to Equation 5 by a nonlinear least-squares program of the type described by Wentworth (*24*). Resulting values of α, β, γ, and δ are provided in Table V along with data showing that the average and maximum deviations between experimental and calculated values never exceed 0.11 and 0.20%, respectively. Equation 5 may be converted to the base 10 by dividing the constants listed in Table V by 2.30258. The viscosity of 2BrP is higher than that of 2ClP at all temperatures; this probably results from both the larger size and the greater density of 2BrP relative to that of 2ClP. Typically for similar molecules which have comparable dipole moments and dielectric constants, the viscosity is a function of the position of a given constituent. For example, the viscosity of 3CNP is higher than that of 2CNP. Another study in this laboratory has revealed similarly that the viscosity of 3-methylpyridine-*N*-oxide is higher than that of 2-methylpyridine-*N*-oxide.

The fairly high dielectric constants, moderate viscosities, and large dipole moments coupled with reasonable liquid ranges provide a basis for 2CNP, 3CNP, 2BrP, and 2ClP, representing potentially useful nonaqueous solvents. The low dielectric constant and high melting point of 4CNP practically prohibit its use as an electrolytic solvent. In view of its convenient melting point, high dielectric constant, moderate viscosity, and very low specific conductance, 2-cyanopyridine seems to offer the most promising potential among these compounds as a nonaqueous solvent for various physicochemical studies.

Nomenclature

A, B, C = constants in Equation 1
a, b, c = constants in Equation 2
cP = centipoise
D = Debye units
E_{vis} = activation energy of viscous flow, cal mol^{-1}
g = Kirkwood correlation factor
k = Boltzmann constant
M = formula weight, g mol^{-1}
N = Avogadro number
n_D = refractive index (sodium D-line)
R = molar gas constant, cal mol^{-1} deg^{-1}
$[R]$ = molar refraction, cm^3 mol^{-1}
T = temperature, K
t = temperature, °C

Greek Letters

$\alpha, \beta, \gamma, \delta$ = constants in Equations 5 and 6
ϵ = low-frequency dielectric constant
ϵ_∞ = high-frequency dielectric constant, approximated as 1.10 $n^2_{\rm D}$
η = viscosity, cP
μ_0 = dipole moment
ρ = density, g cm^{-3}

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Vapor Pressure of 2,4-Tolylene Diisocyanate

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Vapor pressures of 2,4-tolylene diisocyanate between 20° and 40°C (determined by a gas saturation technique) and between 100° and 170°C (directly measured) are reported. They are well represented by the equation, $\log_{10} p$ (torr) = $38.179 - 4821/T - 9.612 \log_{10} T$, for the temperature range 20–170°C.

2,4-Tolylene diisocyanate (1-methyl-2,4-diisocyanatobenzene) is widely used, especially in the manufacture of polyurethanes. Because of its toxicity, its atmospheric concentration must be kept to a very low level, and accordingly, the vapor pressure above the pure liquid and above partially cured polyurethane is of considerable interest.

Three reports of vapor pressures above 100°C exist. Cole (*1*) reports vapor pressures of 2,4-tolylene diisocyanate and its 2,6-isomer from 100° to 180°C in the form of three-constant (Kirchhoff) equations. Molard's (*4*) data from 120° to 190°C, in the form of two-constant (Clausius) equations, are 3–11% lower than those of Cole, which represents quite good agreement. In contrast, Gol'dberg et al. (*3*) report vapor pressures of the 2,4-isomer at 100° to 155°C, which are two to three times higher than those of Cole and Molard. That the results of Gol'dberg et al. are erroneous, possibly owing to the presence of gaseous impurities during the static determination, is made manifest by the boiling point quoted by them (125° at 15 torr), which is much closer to the prediction of Cole's equation (130° at 15 torr) than to their own (103° at 15 torr).

Neither Cole (*1*) nor Molard (*4*) gives the data points used in deriving their correlating equations. Moreover, the literature contains no reports of room temperature vapor pressures, which are of special interest for health reasons. Hence, the purpose of this paper is twofold: to report the original data points between 100° and 170°C, on which the equation given by Cole (*1*) is based; and to report vapor pressures between 20° and 40°C obtained by a gas saturation method.

Health and Safety Considerations

Tolylene diisocyanates are highly irritating materials and have to be handled with great care. Their atmospheric concentration must be held to very low levels. The present threshold limiting value is 0.02 parts per million by volume (*2*), and an even lower standard (0.005 ppm) has been proposed (*5*).

These low standards should be kept in mind when handling these materials and, in addition, provide the rationale for the present measurements.

Experimental

Materials. The 2,4-tolylene diisocyanate used in these measurements was a sample of commercial material specially selected for its purity. It contained 99.5% or more tolylene diisocyanate by titration, of which 98.9% was the 2,4-isomer by infrared analysis. The major expected impurity is the 2,6-isomer.

High-temperature measurements. Vapor pressures above 100°C were measured directly by means of an isoteniscope [as described by Weissberger (*7*)] connected to manometer, vacuum pump, 5-l. surge tank, and a controlled leak. The closed-end mercury manometer was made of 15-mm tubing and read to the nearest 0.1 mm with a cathetometer. Readings were corrected to 0°C (mercury vs. brass scale).

The isoteniscope was immersed in a vigorously stirred, baffled oil bath equipped with a bare-wire heater. A mercury thermometer, which had been calibrated against a platinum-resistance thermometer and could be read to the nearest 0.05°C, was located with its bulb near the reservoir of the isoteniscope.

To initiate a series of measurements, freshly redistilled 2,4-tolylene diisocyanate was introduced into the isoteniscope and degassed. Measurements were started at the lowest pressure, which was then increased stepwise. At each pressure, equilibrium was obtained by adjusting the temperature until the liquid levels in the two legs of the isoteniscope were equal. Then the temperature was raised a few degrees to boil out any low-boiling impurities, and finally equilibrium was reestablished. This procedure took only a few minutes, and the two equilibrium temperatures never differed by more than 0.1°C.

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