should be obtained between the two methods; the results of this study are summarized in Tables III–VII. The detailed example in Table III is representative of the basic experimental data. The standard deviation of this example for the 12 single flow rate diffusivities is ±0.0004. The basic experimental data are recorded in the thesis (*13*).

Typical plots of the data are shown in Figures 3–5. All of the systems showed the density-diffusivity products to be independent of the density for the range of this investigation (Figure 3). One example of the multiflow rate calculation is shown in Figure 4 for the radioactive system. As shown in Figure 5, the systems exhibited linear behavior on an isobaric plot of log *D* vs. log absolute temperature.

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Dielectric Constants, Viscosities, and Related Physical Properties of Four Liquid Pyridine–*N*-Oxides at Several Temperatures

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Dielectric constants, viscosities, densities, and refractive indices of four liquid pyridine–*N*-oxides, were measured at several temperatures ranging from 25° to 125°C. The experimental data as functions of temperature were fitted precisely to appropriate equations. Values of activation energies of viscous flow and Kirkwood correlation factors were also calculated. At comparable temperatures, the dielectric constants and viscosities of the pyridine–*N*-oxides were significantly affected by the position of the methyl group. The viscosity also tended to increase as the molecular weight decreased. The Kirkwood correlation factors ranged from 0.65 to 1.21, implying only slight amounts of net parallel or antiparallel configurations of dipoles in the liquids.

Pyridine–*N*-oxides and other aromatic amine oxides have been studied extensively since about 1940, and their preparations, properties, and chemistry have been reviewed comprehensively by Ochiai (*18*). During the last five years, there has been an unusually large number of articles dealing with aromatic–*N*-oxides as ligands in metal complexes (*2, 8–10, 26*).

Several pyridine–*N*-oxides are now commercially available. At least three of these highly polar compounds have melting points below 50°C and may possibly represent a new type of useful nonaqueous solvent. Although the pyridine–*N*-oxides have received considerable attention from both organic and inorganic chemists, the literature contains a paucity of data concerning 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 pyridine–*N*-oxide and three of its methyl derivatives as functions of temperature.

Experimental

Pyridine–*N*-oxide (PO), 2-methylpyridine–*N*-oxide (2MPO), 3-methylpyridine–*N*-oxide (3MPO), and 2,6-dimethylpyridine–*N*-oxide (2,6DMPO) were obtained from the Reilly Tar and Chemical Corp. The *N*-oxides were

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vacuum distilled two or more times and then further purified by slow fractional freezing under a dry nitrogen atmosphere in a 2- or 6-liter fractional freezing flask (*3*). Each pyridine-*N*-oxide gave white opaque crystals if it was frozen rapidly, whereas, upon slow fractional freezing, it gave large crystals which were completely clear and "ice-like" in appearance.

The fractional freezings for the lower melting pyridine–*N*-oxides were carried out in a Precision Scientific Freas 815 incubator and a Thelco Model 4 oven. Pyridine–*N*-oxide was frozen in a Precision Scientific Thelco Model 17 oven. The temperatures were controlled better than ±1.0°C.

The *N*-oxides are very hygroscopic, and their melting points are quite sensitive to the amount of adsorbed moisture. It is very important that the compounds be virtually void of water before the fractional freezing process is started, since it has been observed in this laboratory that at least one of the pyridine-*N*-oxides (2,6DMPO) forms a hydrate which has a melting point higher than that of the pure compound. Similar hydrate formation has been observed for the 2-pyrrolidone–water system (*4*).

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 by other investigators (*1, 11*) to be structurally satisfactory and convenient to use for measurements on 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 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, 24*). The standard media used in the determination of cell constants were air and water which have dielectric constants of 1.0005 and 78.304 (*16*), 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 (*16, 17*).

The viscosities were measured with size 50 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 (*22*).

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 and using 9.9×10^{-6} 1/°C 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 a 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%

Table I. Dielectric Constants, Viscosities, Densities, Melting Points, Boiling Points, and Indices of Refraction of Several Pyridine–*N*-Oxides at Various Temperatures

Compound	Mp, °C	Bp, °C	Temp, °C	Dielectric constant, 1 MHz	Viscosity, cP	Density, g/cm^3	Index of refraction, sodium D-line
PO	67.8	95 (0.8)	70.0	35.94	2.995	1.1553	...
	66[a]	138 (*15*)[a]	75.0	35.38	2.734	1.1514	...
	66–67[b]		87.5	34.04	2.206	1.1413	...
	67[c]		110.0	32.74	1.834	1.1313	...
			112.5	31.56	1.557	1.1219	...
			125.0	30.38	1.333	1.1117	...
2MPO	49.8	75 (0.8)	50.0	36.40	3.792	1.1132	1.5768
	49.5[d]	127 (*12*)[a]	75.0	32.87	2.228	1.0930	...
			100.0	29.93	1.483	1.0728	...
			125.0	27.20	1.074	1.0521	...
3MPO	41.0	100 (0.8)	45.0	28.26	5.975	1.1194	1.5839
	33–36[a]	146–49 (*15*)[a]	50.0	27.92	5.133	1.1156	...
	40.5[e]	156–58 (*16*)[a]	75.0	26.20	2.794	1.0961	...
			100.0	24.58	1.785	1.0765	...
			125.0	23.09	1.264	1.0568	...
2,6DMPO	23.3	80 (0.8)	25.0	46.11	6.165	1.0901	1.5679
		115–19 (*18*)[a]	50.0	38.72	2.904	1.0695	1.5571
			75.0	33.02	1.732	1.0493	...
			100.0	28.52	1.182	1.0292	
			125.0	24.91	0.869	1.0086	...

[a] (*21*). [b] (*20*). [c] [*19* (a)]. [d] [*19* (b)]. [e] [*19* (c)].

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 along with some comparison data from other studies. The melting points are the highest recorded for these particular pyridine-*N*-oxides. The boiling points compare favorably with those previously reported.

The dielectric constant data for each pyridine-*N*-oxide as a function of temperature were fitted to the following 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 four pyridine-*N*-oxides studied are summarized 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 ≤ 0.10 and $\leq 0.16\%$, respectively. The dielectric constants are significantly dependent on the position of the methyl group. Methyl substitution of pyridine-*N*-oxide in the 3-position causes a significant decrease in the dielectric constant. Such 3-methyl substitution has been known to cause similar reduction of the dielectric constant between sulfolane and 3-methylsulfolane (*23*). The dielectric constant reductions for the various substitutions relative to pyridine-*N*-oxide at 75°C are 7.46, 2.51, and 1.86 for 3MPO, 2MPO, and 2,6DMPO, respectively.

The density data for each compound as a function of temperature are described excellently by the following 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 maximum and mean differences between experimental and calculated densities are ≤ 0.023 and $\leq 0.011\%$, respectively. From the experimental data in Table I, the density is a function of the size of the molecule. Also, 3MPO has a greater density than 2MPO. This is probably due to steric hindrance since 3-methyl substitution would allow closer packing of the molecules compared to 2-methyl substitution.

The experimental dielectric constant, density and refractive index data may be used with dipole moment data from the literature to gain insight concerning the nature and extent of association of polar liquids such as the pyridine-*N*-oxides. The Kirkwood-Frohlich equation (*7, 12*) in the form:

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

makes possible a description of polar liquids having specific short-range forces which hinder rotations of molecules. The correlation factor, *g*, is a measure of the short-range effects 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 imply 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.

The calculated Kirkwood correlation factors for the pyridine-*N*-oxides studied are presented in Table IV. The values used in the above equation were the observed dielectric constants and densities. The refractive indices were calculated based on a temperature differential of 4×10^{-4}/°C. The index of refraction of PO was estimated as 1.60 at 75°C. Since the dipole moments of two of the compounds were unknown, the dipole moments of each pyridine-*N*-oxide was approximated to be 4.3 *D*. This is reasonable in view of the reported dipole moment values of 4.33 *D* (*20*) for 3MPO and 4.13 *D* (*5*), 4.19 *D* (*20*), and 4.32 *D* (*15*) for PO. The calculations indicate that the most probable type of dipole-dipole orientation for PO, 2MPO, and 2MPO is slightly antiparallel at all temperatures. The results for 2,6DMPO, however, indicate that a parallel alignment at low temperatures converts to an antiparallel alignment at high temperatures. Although these calculations are approximate, they are probably of the correct relative order, assuming that the dipole moments of 2MPO and 2,6DMPO do not differ significantly from 4.3 *D*.

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

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

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

The viscosity data were fitted to Equation 4 by a nonlinear least-squares program of the type described by Wentworth (*25*). Resulting values for 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 0.18 and 0.39%, respectively. Equation 4 may be converted to base 10 by dividing the constants listed in Table V by 2.30258. An in-

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

Compound	A	$B \times 10^{-4}$	$C \times 10^{-6}$	% Deviation, 100[a] Mean	% Deviation, 100[a] Max
PO	−13.351	2.0535	−1.24223	2	6
2MPO	−14.164	1.7082	−0.24082	10	16
3MPO	−9.701	1.6931	−1.5435	2	3
2,6DMPO	8.945	−0.77180	5.6047	2	3

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

Table III. Results for Density Data Fitted to Equation 2

Compound	a	$-b \times 10^4$	% Deviation × 10^3 Mean	% Deviation × 10^3 Max
PO	1.21078	7.9242	11	23
2MPO	1.15400	8.1413	11	17
3MPO	1.15477	7.8335	7	9
2,6DMPO	1.11034	8.1334	11	17

Table IV. Kirkwood Correlation Factors

Compound	Temperature, °C 25	50	75	100	125
PO	...	...	0.74	0.76	0.78
2MPO	...	0.88	0.88	0.88	0.88
3MPO	...	0.65	0.68	0.71	0.73
2,6DMPO	1.21	1.13	1.07	1.02	0.98

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

Compound	$-\alpha$	β	$\gamma \times 10^{-5}$	$\delta \times 10^{-8}$	% Deviation, 100		E_{vis}, 75°C (cal/mol)	SD in E_{vis}, cal/mol
					Mean	Max		
PO	1.06359	−725.87	5.03448	0	18	39	4304	57
2MPO	0.56883	−1292.5	6.16212	0	10	16	4466	15
3MPO	8.85022	8201.1	−29.8894	4.63374	6	13	4966	18
2,6DMPO	13.20954	12390.9	−43.6212	5.97413	3	5	4209	6

verse correlation exists between the viscosities and molecular weights of pyridine-*N*-oxide and its 2-methyl, 3-methyl, and 2,6-dimethyl derivatives. This type of relationship also has been noted for sulfolane and its 3-methyl and 2,4-dimethyl derivatives in another study recently conducted in this laboratory (*6*). Values of E_{vis} for each liquid at one temperature are listed also in Table V.

The fairly high dielectric constants, moderate viscosities, and large dipole moments coupled with reasonable liquid ranges provide a basis for these pyridine-*N*-oxides, representing potentially interesting nonaqueous solvents. Their apparent disadvantages are hygroscopicity and tendency to decompose slightly when exposed to light for long periods of time. 2MPO seems to have the best long-term stability and also is relatively easy to purify by a combination of vacuum distillation and fractional freezing. In view of its melting point, viscosity, dielectric constant, and low specific conductance, 2MPO appears worthy of investigation as a new electrolytic solvent at 50°C or above. Several salts of various types are sufficiently soluble in 2MPO to warrant conductance and other physicochemical studies. The other pyridine-*N*-oxides investigated are more difficult to purify to the extent of obtaining colorless, low-conducting products. However, once highly purified, these compounds have low specific conductances and, when stored in the dark, apparently are stable and remain uncolored for several weeks.

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
g = Kirkwood correlation factor
k = Boltzmann constant
M = formula weight, g/mol
N = Avogadro number
n_D = refractive index (sodium D-line)
R = molar gas constant, cal/(mol deg)
T = temperature, K
t = temperature, °C

Greek Letters

$\alpha, \beta, \gamma, \delta$ = constants in Equations 4 and 5
ϵ = low-frequency dielectric constant
ϵ_∞ = high-frequency dielectric constant, approximated as $1.10\, n^2{}_D$
η = viscosity, cP
μ_0 = dipole moment in Debye units
ρ = density in g/cm^3

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