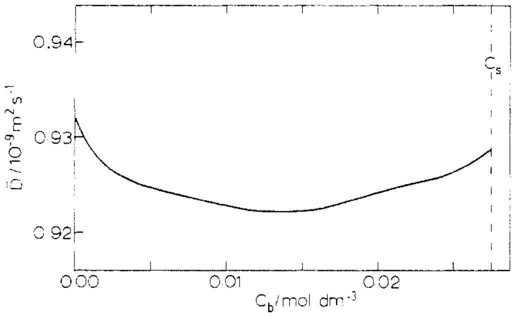

Figure 2. Integral diffusion coefficients of aqueous benzoic acid at 25 °C calculated from eq 6.

mass-transfer coefficients for dissolution of benzoic acid are independent of acid concentration.

Glossary

a	cell height, m
C	total acid concentration, mol dm^{-3}
C_b	bulk concentration, mol dm^{-3}
C_s	saturation concentration, mol dm^{-3}
D	binary diffusion coefficient, m^2 s^{-1}
$\bar{D}$	integral diffusion coefficient, m^2 s^{-1}
D_m	limiting molecular diffusion coefficient, m^2 s^{-1}
$D_\pm$	limiting ionic diffusion coefficient, m^2 s^{-1}
F	Faraday constant, C mol^{-1}
I	ionic strength, mol dm^{-3}
K_a	dissociation constant, mol dm^{-3}
K_B	bottom reciprocal resistance, ohm^{-1}
K_T	top reciprocal resistance, ohm^{-1}
k_B	bottom electrode cell constant, m^{-1}
k_T	top electrode cell constant, m^{-1}
R	gas constant, J K^{-1} mol^{-1}
r	cell constant ratio
T	temperature, K
t	time, s
$y_\pm$	mean molar ionic activity coefficient
α	degree of dissociation
Δ_1	first order electrophoretic correction, m^2 s^{-1}
Δ_2	second order electrophoretic correction, m^2 s^{-1}
Λ	molar conductance, m^2 ohm^{-1} mol^{-1}
λ_+^0	limiting cation molar conductance, m^2 ohm^{-1} mol^{-1}
λ_-^0	limiting anion molar conductance, m^2 ohm^{-1} mol^{-1}

Registry No. Benzoic acid, 65-85-0.

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Physical Properties of *N*-Methylpyrrolidinone as Functions of Temperature

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The relative permittivity, viscosity, and refractive index of the cyclic amide *N*-methylpyrrolidinone (NMP) were determined at various temperatures ranging from 251 to 353 K. Linear functions were derived to describe the changes in the physical properties with temperature. The values obtained were compared to data available in the literature for NMP and other cyclic amides. The rate of diffusion control, the activation energies of diffusion and viscous flow, and the Kirkwood correlation factor were calculated.

Introduction

The cyclic amide *N*-methylpyrrolidinone (NMP) is an excellent dissociating solvent (*1*, *2*) suitable for use in electrochemistry (*3*), organic synthesis requiring dipolar aprotic media (*4*), and polymer membrane casting (*5*). Our current investigations indicate that NMP is also a good solvent in which to study aromatic radical anions and their electron-transfer reactions using pulse radiolysis (*6*). However, there is an absence of data on the temperature dependence of the physical properties of this solvent except for its density (*7*).

Experimental Section

NMP (Aldrich) was purified by refluxing over calcium hydride for 6 h followed by distillation under vacuum. The solvent was then redistilled under vacuum from freshly prepared sodium–potassium alloy.

Capacitance and conductance measurements were obtained in duplicate at 10^4 Hz using a Wayne Kerr Universal Bridge B221A, AF Signal Generator S121, and Waveform Analyser A321 in conjunction with a glass cell containing platinum electrodes. The temperature of the cell was adjusted by circulating water from a thermostated water bath through the outer glass

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Table I. Experimental Data (Mean Values)

temp, °C	rel permittivity	refractive index	viscosity, 10^3/N s m^{-2}	density, kg m^{-3}
-22			4.021	
-11			3.171	
0			2.572	
2			2.504	1047.0
16			1.927	1034.2
18		1.4704		
20	33.20			
21		1.4692	1.788	
25	32.23	1.4672	1.666	1025.7
27		1.4671		
30	31.80			
31		1.4652	1.525	
34		1.4638	1.469	1020.0
41	30.69		1.328	
43			1.293	1009.0
44		1.4596		
45		1.4590		
47	29.66			
50		1.4569	1.175	
54			1.112	
60	27.93			
65	27.23			
80	25.48			
a	0.13	0.0001	0.007	

[a] Standard deviation of the mean.

jacket. The cell was calibrated over the temperature range by using air and nitrobenzene as standards since their relative permittivities are well known (*8*–*10*). Relative permittivities were calculated as described elsewhere (*11*, *12*). The conductivity of NMP was calculated by using 10^{-3} mol dm^{-3} aqueous KCl solutions to determine the cell constant.

Viscosities were measured in duplicate with a glass capillary U-tube viscometer (made to BS 188) which was calibrated by using the viscosity of water (*10*). The efflux times were all in excess of 300 s so that kinetic energy corrections were negligible.

The densities of NMP at five temperatures between 273 and 323 K were found to agree with published data (*7*) and so values from that more detailed study were used in this work.

Two Abbe refractometers (Bellingham and Stanley) were used to measure the refractive index with reference to the D line of sodium. Readings were taken in duplicate for each refractometer.

Temperatures were measured with thermometers graduated to 0.1 °C. Experimental data were fitted to the appropriate equations by least-squares linear regression analysis with errors quoted as the standard deviation of the mean.

Results

The experimental data for the relative permittivity, refractive index, viscosity, and density of NMP at various temperatures are summarized in Table I. Values for the physical properties of NMP at 298 K calculated from these data are presented in Table II with some of the values available from the literature for comparison. Also included are the corresponding values for the cyclic amides 1,3-dimethyl-2-imidazolidinone (DMI) and 1,3-dimethyl-2-oxohexahydropyrimidine (DMH).

Relative permittivities were determined over the temperature range 293–353 K and the data were analyzed by using

$$\epsilon_r = a/T + b \tag{1}$$

Values of relative permittivity determined in this investigation are in good agreement with published values (*3*, *13*) and the constants *a* and *b* are given in Table III.

The refractive index was measured over the temperature range 291–323 K and the experimental data were fitted to eq 2, and the values obtained for *c* and *d* are given in Table III.

$$\ln n_D = c/T + d \tag{2}$$

The refractive index of 1.4674 at 298 K is in good agreement with those determined elsewhere (*3*, *7*, *13*).

Viscosity data over the temperature range 251–327 K were corrected for density changes and then fitted to

$$\ln \eta = x/T + y \tag{3}$$

Again good agreement was found with a known value (*13*) at 298 K. The activation energy of viscous flow was calculated from

$$E_{vis} = \frac{R\,d(\ln \eta)}{d\left(\frac{1}{T}\right)} \tag{4}$$

and the value given in Table II indicates that NMP is a non-associated liquid. The values of E_{vis} for the *N*,*N*-dimethyl-substituted amides fall within the range 12.5–21 kJ mol^{-1}, indicating slight association. By substituting the viscosity into the Stokes–Einstein equation

$$k_{diff} = 8000RT/3\eta \tag{5}$$

the diffusion-controlled rate constant at various temperatures is obtained. An Arrhenius plot gave the activation energy, E_{act}, and the *A* factor given in Table II. The corresponding values were calculated for DMI and DMH by using the data in ref *14*.

Since the dipole moment of NMP is known to be 1.364 × 10^{-29} C m (*15*) the Kirkwood correlation factor *g* was calculated by using equation 6 (*16*), which is in a form suitable for SI units.

$$g = \frac{\epsilon_0(\epsilon_r - \epsilon_\infty)(2\epsilon_r + \epsilon_\infty)9MkT}{\epsilon_r(\epsilon_\infty + 2)^2 N\rho\mu_0^2} \tag{6}$$

A value of $g = 1.00$ indicates a normal polar liquid. Values above this indicate neighboring dipoles are parallel with respect to each other whereas a value less than this indicates antiparallel alignment. Although the value of *g* for NMP is slightly lower than this and those for DMI and DMH are slightly higher,

Table II. Physical Properties of Cyclic Amides at 298 K

	NMP			
	this work	lit.	DMI[a]	DMH[a]
rel permittivity	32.46	32.0[b]	37.64	36.14
refractive index	1.4674	1.468[b]	1.4707	1.4881
viscosity, N s m^{-2}	1.686 × 10^{-3}	1.67 × 10^{-3} [b]	1.944 × 10^{-3}	2.934 × 10^{-3}
E_{vis}, kJ mol^{-1}	11.47 ± 0.05		13.72	16.89
density, kg m^{-3}	1025.7	1025.8[c]	1051.9	1059.5
conductivity, S m^{-1}	1.19 × 10^{-9}	(1–2) × 10^{-10} [d]	(1–7) × 10^{-10}	4.73 × 10^{-10}
kirkwood factor	0.92		1.20	1.17
k_{diff}, dm^3 mol^{-1} s^{-1}	3.93 × 10^9		3.39 × 10^9 [e]	2.24 × 10^9 [e]
E_{act}, kJ mol^{-1}	13.88 ± 0.37		15.80[e]	18.65[e]
log *A*, dm^3 mol^{-1} s^{-1}	12.03 ± 0.07		12.30[e]	12.62[e]

[a] Reference *14*. [b] Reference *13*. [c] Reference *7*. [d] Reference *2*. [e] Calculated from data in ref *14*.

Table III. Calculated Constants for Eq 1-3

a, K	12968 ± 95	d	0.2927 ± 0.0009
b	−11.058 ± 0.312	x, K	1379.33 ± 6.43
c, K	27.066 ± 0.240	y	−11.014 ± 0.012

all three solvents are probably best considered to be normal polar liquids.

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Glossary

a, b	constants in eq 1, a has units of K
c, d	constants in eq 2, c has units of K
x, y	constants in eq 3, x has units of K
g	Kirkwood correlation factor
k	Boltzmann constant, J K^{-1}
k_{diff}	diffusion-controlled rate constant, dm^3 mol^{-1} s^{-1}
n_{D}	refractive index
A	Arrhenius A factor, dm^3 mol^{-1} s^{-1}
E_{act}	activation energy, kJ mol^{-1}
E_{vis}	activation energy of viscous flow, kJ mol^{-1}
M	molar mass, kg mol^{-1}
N	Avogadro number, mol^{-1}
R	gas constant, J mol^{-1} K^{-1}
T	temperature, K
ϵ_r	relative permittivity
ϵ_∞	high-frequency relative permittivity (= 1.1 × n_{D}^2)
ϵ_0	permittivity of vacuum, C^2 N^{-1} m^{-2}
η	viscosity, N s m^{-2}
μ_0	dipole moment, C m
ρ	density, kg m^{-3}

Conductivity is in units of S m^{-1} (1 siemen = 1 mho)

Registry No. NMP, 872-50-4.

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Enthalpies of Solution of Butanes in Water from 5 to 45 °C

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The enthalpies of solution of *n*-butane and isobutane (2-methylpropane) have been determined by direct calorimetry over a range of 0–45 °C. The temperature dependence of the enthalpies of solution allows accurate determination of the heat capacity change for the solution process as a function of temperature. A simple two-energy-state model of water molecules in the first solvation shell, developed to account for the heat capacity properties of small hydrocarbons in solution, has been found to predict the heat capacity changes upon solution for *n*-butane and isobutane as well.

Introduction

In previous papers, an extensive study of the heats of solution of methane (*1*) and ethane and propane (*2*) over as wide a temperature range as is currently experimentally practical was made. This work has now been extended to *n*-butane and isobutane with the purpose of obtaining precise energetic data about larger gaseous hydrocarbon solutes by direct calorimetry, in order that a critical comparison with van't Hoff studies (*3*) can be made. These results have also been of great value in further testing the generality of the simple two-state model of water molecules in the first solvation shell, which predicts, for hydrophobic solutes, abnormally large values for the heat capacities, which decrease with increasing temperature. The theoretical basis of the model and its application to other compounds are discussed in detail elsewhere (*1*, *2*, *4*).

Table I. Enthalpy of Solution of *n*-Butane in Water from 0 to 45 °C

temp, K	$\Delta H°$ ± 2σ, kJ mol^{-1}	no. of determinations
273.25	−35.68 ± 0.22	3
278.15	−33.62 ± 0.43	5
283.15	−31.60 ± 0.31	5
288.15	−29.26 ± 0.18	5
293.15	−27.38 ± 0.34	4
298.15[a]	−25.92 ± 0.17	11
303.15	−23.67 ± 0.17	4
308.15	−22.15 ± 0.17	6
313.15	−20.15 ± 0.17	5
318.15	−17.81 ± 0.15	4

[a] Reference *13*.

Experimental Section

The microcalorimeter and its method of operation have been described previously (*5*). *n*-Butane (Scientific Gas Products)

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