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Relative Viscosity and Apparent Molal Volume of N-Methylpropionamide

Solutions at Various Temperatures

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The relative viscosities, η_r 's, of solutions of benzene, pyridine, and NaNO_3 in N-methylpropionamide and apparent molal volumes, ϕ_v 's, of benzene, pyridine, benzoic acid, NaCl , KCl , NaBr , KBr , NaNO_3 , and sodium benzoate in N-methylpropionamide have been determined from 15 to 40°. The results are discussed by comparing the viscosity B coefficients, molal volumes, \bar{V}^0 's, and molal expansibilities, \bar{E}^0 's, for these solutes in water and N-methylpropionamide.

Introduction

Although there have been many studies of the relative viscosity, η_r , and apparent molal volume, ϕ_v , of solutes in aqueous solutions and in low dielectric solvent systems, few studies have been made of these properties in high dielectric solvent systems.¹⁻³ The present paper deals with solutions of nonelectrolytes and electrolytes in N-methylpropionamide (NMP). NMP has a high dielectric constant (176 at 25°)⁴ and is a highly associated liquid.^{4,5} Both electrolytes and nonelectrolytes (polar and nonpolar) are soluble in NMP; thus quite a wide variety of solutes can be studied in this solvent.

Viscosity measurements were made on pure NMP and solutions of benzene, pyridine, and NaNO_3 in NMP at 5° intervals from 15 to 40°. Density measurements were also made for these solutions and also for some other solutions (NaCl , KCl , NaBr , KBr , sodium benzoate, and benzoic acid in NMP). The relative viscosities, η_r 's, apparent molal volumes, ϕ_v 's, and apparent molal expansibilities, ϕ_E 's, were calculated for these solutions.

Experimental Section

The preparation and purification of NMP has been described elsewhere.^{1,6} All the solutes were of reagent grade and were used without further purification. The solutions were all made by weight.

The density measurements were made with a magnetic-float densitometer similar to the one described elsewhere.⁷ The apparatus was calibrated with doubly distilled H_2O from 15 to 40° at 5° intervals. The apparatus reproduced the density of water⁸ to ± 11 ppm over this range. The sensitivity of the densitometer used in this study was less than that obtained recently⁷ because of differences in the magnetic interaction constants, f ($f = 9.5$ g/A for the densitometer used in this study compared with $f = 3.5$ g/A for the recently described apparatus.)⁷

The viscosity measurements were made with Os-

wald-type viscometers calibrated with standard viscosity oil, National Bureau of Standards Oil H, Lot No. 12. No kinetic corrections were made; however, head corrections were made for the thermal expansion of the liquid.

For both calibrations with the National Bureau of Standards Oil H and measurements on pure NMP, correction factors for the viscometer constant, K , were calculated as $1 + (V_s - V)/(\pi R^2 h)$. Here, V_s is the nominal volume of the charge (10 ml) and V is the actual volume based on the weight of the charge and its density at the temperature of the measurement; R is the radius of the lower bulb; and h is the mean difference between the liquid levels during the run. This correction was small and was neglected for the other solutions.

The temperature bath used for the density and viscosity measurements was controlled to $\pm 0.005^\circ$. The bath temperature was set to better than $\pm 0.01^\circ$ with a platinum thermometer and resistance bridge.

Results and Discussion

The viscosity, η^0 , of NMP at various temperatures was calculated from the equation

$$\eta^0 = K d^0 \tau^0 \quad (1)$$

where K is a constant, d^0 is the density, and τ^0 is the flow time of pure NMP. K was determined by cali-

(1) (a) T. B. Hoover, *J. Phys. Chem.*, **68**, 876 (1964); (b) T. B. Hoover, *ibid.*, **68**, 3003 (1964).

(2) L. R. Dawson, R. H. Graves, and P. G. Sears, *J. Amer. Chem. Soc.*, **79**, 298 (1957).

(3) D. Feakins and K. G. Lawrence, *J. Chem. Soc., A*, 212 (1966).

(4) S. J. Bass, W. I. Nathan, R. M. Meighan, and R. H. Cole, *J. Phys. Chem.*, **68**, 509 (1964).

(5) R. Lin and W. Dannhauser, *ibid.*, **67**, 1805 (1963).

(6) G. R. Leader and J. F. Gormley, *J. Amer. Chem. Soc.*, **73**, 5731 (1951).

(7) F. J. Millero, *Rev. Sci. Instrum.*, **38**, 1441 (1967).

(8) L. W. Tilton and J. K. Taylor, *J. Res. Nat. Bur. Stand.*, **18**, 205 (1937).

brating the viscometers with Oil H. The average η^0 and d^0 of NMP at various temperatures are given in Table I. The average deviation of η^0 over this range was ± 0.001 to ± 0.004 cP. The η^0 results agree very well with the values obtained by Hoover^{1b} at various temperatures. The density values listed in Table I are those taken from the recent measurements of Malmberg and Hoover.⁹ These density values are lower than those reported earlier,^{1a} owing to the presence of water in the NMP used in the earlier work.

Table I: Density and Viscosity of N-Methylpropionamide at Various Temperatures

Temp, °C	Density, g/ml	Viscosity, cP
15	0.93855	6.994
20	0.93452	6.016
25	0.93050	5.215
30	0.92650	4.554
35	0.92250	4.001
40	0.91850	3.533

The relative viscosity, η_r , for the various solutions was calculated from the equation

$$\eta_r = \frac{\eta}{\eta^0} = \frac{d\tau}{d^0\tau^0} \quad (2)$$

where η , d , and τ are the viscosity, density, and flow time for the solution. The η_r 's for benzene and pyridine solutions at various concentrations (c is the number of moles per liter of solution) were fit to equations of the form

$$\eta_r = 1 + A'c + B'c^2 + C'c^3 \quad (3)$$

The constants for the equations at various temperatures are given in Table II. The average deviations between the experimental and the calculated η_r 's were 0.005 and 0.002 for the benzene and pyridine NMP solutions, respectively. However, the results from different series of solutions differ by as much as ± 0.05 . Reproducibility for the benzene solutions at high concentrations and at high temperatures was difficult, owing to the volatility of benzene.

The η_r for the NaNO_3 solutions in NMP was fitted to a Jones-Dole-type equation

$$\eta_r = 1 + A\sqrt{c} + Bc \quad (4)$$

The constants for these equations at various temperatures are given in Table III. The average deviations between the experimental and calculated η_r 's were ± 0.005 for a given experiment; however, the results from different series of solutions differ by as much as ± 0.01 . The standard deviations for A were between 0.02 and 0.05 (l./mol)^{1/2} at the various temperatures, and the standard deviations for B were between 0.06

Table II: Constants for the η_r Equation for Benzene and Pyridine in NMP at Various Temperatures^a

Temp, °C	Benzene (0.14–2.8 M) ^b			Pyridine (0.27–4.10 M)		
	$-A'$, l./mol	$10^2B'$, (l./mol) ²	$10^2C'$, (l./ mol) ³	$-A'$, l./mol	$10^2B'$, (l./ mol) ²	$10^2C'$, (l./mol) ³
15	0.2231	8.10	-1.80	0.2404	3.22	0.19
20	0.1485	-0.60	0.44	0.2297	3.14	0.21
25	0.1283	-2.69	0.98	0.2216	3.04	0.22
30	0.3683	-471	0.63	0.2163	2.98	0.22
35	0.3829	-488	0.66	0.2011	2.77	0.18
40	0.3859	-476	0.64	0.1932	2.35	0.17

^a The constants given in this table were determined from one set of experiments by a least-squares best-fit method with the aid of an IBM 1401 computer. The root-mean-square fit was 0.005 for benzene-NMP and 0.002 for pyridine-NMP solutions. The constants are given to enough significant figures to comply with this precision; however, the constants probably have larger uncertainties (since the η_r from a different series varied by as much as ± 0.05).⁹ ^b The constants at 30, 35, and 40° are only valid over the concentration range from 0.1 to 0.5 M; thus they should not be used outside this concentration range. It was impossible to work at higher concentrations at these temperatures, owing to the volatility of the benzene-NMP solutions.

Table III: Constants for the η_r Equation for NaNO_3 in NMP at Various Temperatures^a

Temp, °C	NaNO_3 (0.05–0.5 M)	
	$-A$, (l./mol) ^{1/2}	B , l./mol
15	0.021	1.296 (1.085) ^b
20	0.039	1.277 (1.099)
25	0.034	1.243 (1.053)
30	0.049	1.234 (1.034)
35	0.029	1.204 (1.009)
40	0.069	1.182 (0.973)

^a The A and B constants were determined from one set of experiments by a least-squares best-fit method with the aid of an IBM 1401 computer. Although the root-mean-square deviation of this proposed fit was 0.005, the uncertainties in the A and B constants are larger (± 0.02 – 0.06 (l./mol)^{1/2} for A and ± 0.06 – 0.12 l./mol for B), based on measurements of other salts in NMR. (See ref 9 and J. V. Botscheller and W. G. Bourdieu, National Bureau of Standards unpublished data.) ^b These values of B were calculated by using the estimated theoretical value of A (approximately 0.008 (l./mol)^{1/2}) and adding an additional term Dc^2 to eq 4. The theoretical value of A was determined from the Fuoss approximate relation $A = \beta/80\Lambda^0$, where β is the electrophoretic term in the conductance limiting law ($\beta = 82.486/\eta(DT)^{1/2}$): R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publisher, New York, N. Y., 1959, p 234.

and 0.12 l./mol.⁹ A better fit of the data for the NaNO_3 -NMP solutions was obtained by estimating the theoretical value of A and by adding the Dc^2 term to eq 4. This reduces the B values by about 25% (values in parentheses in Table III) and reduces the standard deviations of the B values to 0.01–0.06 l./mol.⁹

(9) C. G. Malmberg and T. B. Hoover, personal communication.

Benzene and pyridine both decrease the viscosity of NMP presumably by breaking down the solvent structure. Pyridine has the greater structure-breaking effect, although benzene has a lower absolute viscosity (both solutes have similar molar volumes in the pure state). Pyridine is apparently able to break down the structure of NMP by dilution and also by formation of terminal hydrogen bonds with NMP. The viscosity B coefficients for NaNO_3 in NMP and its change with temperature is of the same order of magnitude as KCl in NMP.^{1a} Owing to their large uncertainty, the values for A listed in Table III cannot be compared with their estimated theoretical value.⁹ A few measurements were made on NaBr solutions in NMP at one concentration and B was estimated by assuming that A was zero. Values of $B = 2.19$ l./mol at 15° and $B = 2.04$ l./mol at 25° were calculated for NaBr . These large B coefficients in NMP and NMF (N-methylformamide) have been discussed elsewhere.³ If one assumes that the B coefficient is proportional to the molal volume, \bar{V}^0 , one might expect B to increase by the same order of magnitude as \bar{V}^0 when comparing NMP with water. \bar{V}^0 for NaNO_3 increases by 41% when transferred from water to NMP, while B increases by 2900%. This difference cannot be explained by electrostriction, since the electrostriction differences between NMP and water are in the opposite order (*i.e.*, $\bar{V}^0(\text{elect})$ in water $>$ $\bar{V}^0(\text{elect})$ in NMP). Another possible explanation for the large B coefficients (*i.e.*, structure-forming ability of salts in NMP) may be due to the formation of intimate ion pairs across the linear hydrogen bonds. When one compares the η_r of NaNO_3 in NMP with that in water on a mole basis (1 m NaNO_3 in NMP is equivalent to 5 m NaNO_3 in H_2O), the effect of NaNO_3 is not as great. For example, $\eta_r = 1.57$ for 5 m NaNO_3 in H_2O ¹⁰ and $\eta_r = 2.34$ for 1 m NaNO_3 in NMP (a 49% increase). The change of B and V^0 with increasing temperature are both negative for salts in NMP. This parallelism does not exist in H_2O because of the ability of some ions or salts to have structure-breaking or structure-making effects.

The apparent energy of activation of viscous flow, ΔE , given by the equation

$$\frac{\Delta E}{R} = \frac{\partial \ln \eta}{\partial 1/T} \quad (5)$$

has been calculated for these solutions, and the results at 25° at various concentrations are shown in Figure 1. Benzene and pyridine both decrease ΔE , while NaNO_3 increases ΔE . The effects of these solutes on ΔE conform with the previous discussion.

The densities of the pyridine and benzene NMP solutions at various temperatures were fit to equations of the form

$$d = d^0 + Em + Fm^2 + Gm^3 \quad (6)$$

where d^0 is the density of pure NMP, m is the molality,

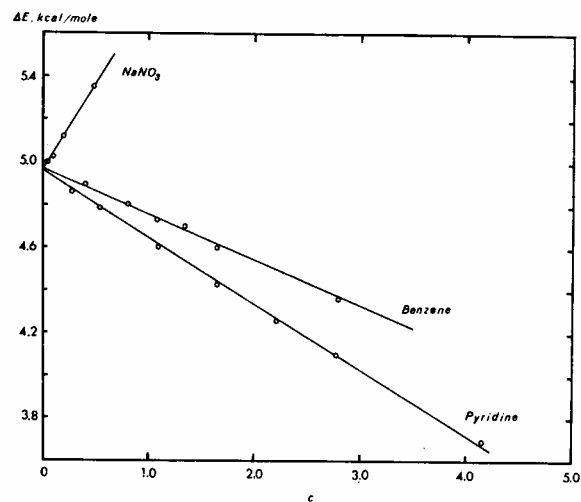


Figure 1. Apparent energy of activation for viscous flow, ΔE , for various solutes in NMP vs. molarity, c , at 25° .

Table IV: Constants for the Density Equation for Benzene, Pyridine, and NaNO_3 in NMP^a at Various Temperatures^a

Temp, °C	10^3E	10^3F	10^3G	Av dev, g/ml
Pyridine in NMP (0.29–6.65 m)				
15	5.721	−1.279	0.190	±0.0001
20	5.793	−1.423	0.220	±0.0002
25	5.515	−8.857	0.074	±0.0003
30	5.756	−1.515	0.240	±0.0002
35	5.656	−1.488	0.238	±0.0002
40	5.497	−1.122	0.145	±0.0002
Benzene in NMP (0.14–3.98 m)				
15	−2.992	−0.0735	−0.109	±0.0004
20	−2.732	−0.215	0.455	±0.0005
25	−2.737	−0.248	0.477	±0.0004
NaNO_3 in NMP (0.05–0.5 m)				
15	−1.086	50.60	−5.970	±0.00000
20	−1.221	50.80	−5.748	±0.00001
25	−0.722	49.09	−4.148	±0.00002
30	−1.146	50.73	−5.533	±0.00002
35	−1.021	50.28	−5.107	±0.00003
40	−1.055	50.23	−4.684	±0.00003

^a Determined by a least-squares best-fit method with the aid of an IBM 1401 computer. The units for the constants E , F , and G are as follows: for the benzene, pyridine, and NMP solutions, the units are, respectively, g/ml(kg of H_2O /mol), g/ml(kg of H_2O /mol)², and g/ml(kg of H_2O /mol)³; for the NaNO_3 -NMP solutions, the units are, respectively, g/ml(kg of H_2O /mol)^{1/2}, g/ml(kg of H_2O /mol), and g/ml(kg of H_2O /mol)^{3/2}.

and E , F , and G are constants. The density of NaNO_3 was fit to similar equations, except for replacing m by \sqrt{m} . The constants for these equations are given in Table IV, which also includes the average deviations between the measured and calculated densities.

(10) R. H. Stokes and R. Mills, "The International Encyclopedia of Physical Chemistry and Chemical Physics," Vol. 3, Pergamon Press Inc., New York, N. Y., 1965, Topic 16.

The apparent molal volumes, ϕ_v 's, were calculated from the density data of the solutes studied in this paper (and also the unpublished data of Botscheller and Borduin¹¹) from the equation

$$\phi_v = \frac{1000(d^0 - d)}{d^0 dm} + \frac{M}{d} \quad (7)$$

The infinite dilution values, $\phi_v^0 \equiv \bar{V}^0$, were calculated from the equation

$$\phi_v = \phi_v^0 + S_v c \quad (8)$$

for the nonelectrolytes and c was replaced by \sqrt{c} for the salts. Figures 2 and 3 show ϕ_v vs. c or \sqrt{c} for some of the solutes at 25°. Table V gives \bar{V}^0 and S_v for pyridine, benzene, and NaNO₃ solutions of NMP at various temperatures. Table VI gives \bar{V}^0 and the average apparent molal expansibilities at infinite dilution, $\phi_E^0 \equiv \bar{E}^0$, for all the solutes studied at 25°.

Table V: Molal Volume at Infinite Dilution, \bar{V}^0 , and the Limiting Slope, S_v , for Benzene, Pyridine, and NaNO₃ at Various Temperatures^a

Temp, °C	Benzene		Pyridine		NaNO ₃	
	\bar{V}^0 , ml/mol	S_v	\bar{V}^0 , ml/mol	S_v	\bar{V}^0 , ml/mol	S_v
15	87.4	~0	29.0	1.7	40.6	-2.7
20	87.7	~0	30.9	3.5	40.3	-3.0
25	88.1	~0	31.3	3.6	39.6	-2.0
30	89.2	~0	32.1	3.0	40.1	-3.2
35	88.9	~0	33.2	3.5	39.9	-2.7
40	90.3	~0	34.3	3.2	39.7	-3.4

^a The average deviations of \bar{V}^0 for benzene, pyridine, and NaNO₃ are ± 0.7 , ± 0.5 , and ± 0.3 ml/mol, respectively.

Table VI: Molal Volume, \bar{V}^0 , and Molal Expansibility, \bar{E}^0 , at Infinite Dilution for Various Solutes in NMP at 25°

Solute	\bar{V}^0 , ml/mol	\bar{E}^0 , ml/mol deg
Benzene	88.1	0.09
Pyridine	31.3	0.18
NaNO ₃	39.6	-0.04
NaCl	30.7	-0.06
KCl	35.5	-0.07
NaBr	35.8	-0.05
KBr	40.9	-0.04
NaOBz	103.6	...
HOBz	100.2	...
Av dev ± 0.3 -0.8		Av dev ± 0.01 -0.04

The limiting slope for the salts in NMP, S_v , cannot be compared with the theoretical Debye-Hückel limiting slope, because the change of the dielectric constant with pressure and the compressibility of NMP are not known. The limiting slope¹² is equal to $S_v = kw^{1/2}$, where $w = 1/2 \sum (\nu_i Z_i^2)$ and $k = 2N^2 e^3 (2\pi/1000RT)^{1/2}$

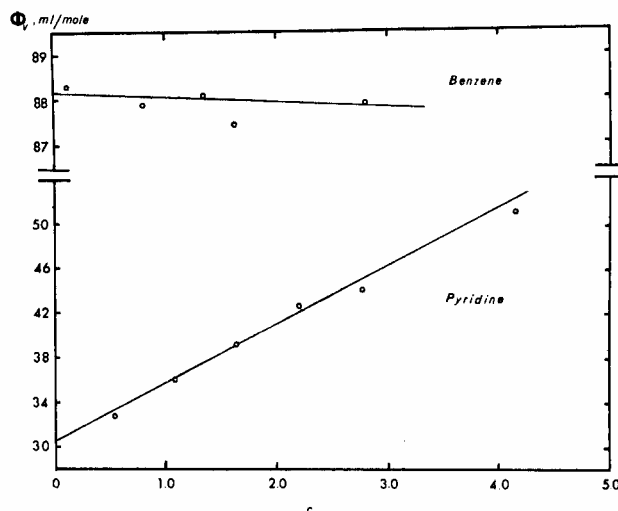


Figure 2. Apparent molal volumes, ϕ_v , of benzene and pyridine in NMP in various concentrations, c , (molar units) at 25°.

$\epsilon^{-1/2}(d \ln \epsilon/dp - \beta/3)$, where N is Avogadro's number; ϵ and β are the dielectric constant and the compressibility of the solvent, respectively; and the other terms have their usual meaning. If one compares the S_v values in methanol (15.77 at 25°)¹³ and water (1.86 at 25°)¹² as a function of ϵ , it is not surprising that the value is negative in NMP solutions.

The ϕ_v and ϕ_E of benzene in NMP are independent of concentration and are approximately equal to the values of pure benzene (88.8 ml/mol and 0.100 ml/mol deg, respectively, at 25°).¹⁴ These results indicate that there is little or no solute-solvent interaction between benzene and NMP. The \bar{V}^0 of pyridine in NMP is smaller than the molar volume of pure pyridine (80.5 ml/mol at 25°)¹⁴ and also smaller than \bar{V}^0 of pyridine in H₂O (78.0 ml/mol at 25°).¹⁵ These results indicate that the solute-solvent interactions between pyridine and NMP are very large and not electrostatic in nature. These facts support the earlier postulation that pyridine breaks down the structure of NMP by forming terminal hydrogen bonds which decrease the volume. S_v is positive, since the effect of pyridine in decreasing the volume of NMP (or breaking down the linear hydrogen bonds) is less important as more is added. The ϕ_E is positive, since at higher temperatures there is less structure in NMP to break down.

The additivity of \bar{V}^0 for salts in NMP can be shown by comparing the differences between the salt pairs, $\bar{V}^0(\text{KCl}) - \bar{V}^0(\text{NaCl})$, $\bar{V}^0(\text{KBr}) - \bar{V}^0(\text{NaBr})$, $\bar{V}^0(\text{NaBr}) -$

(11) J. V. Botscheller and W. G. Borduin, National Bureau of Standards, unpublished data.

(12) O. Redlich, *J. Phys. Chem.*, **67**, 469 (1963).

(13) J. Padova and I. Abrahamer, *ibid.*, **71**, 2112 (1967).

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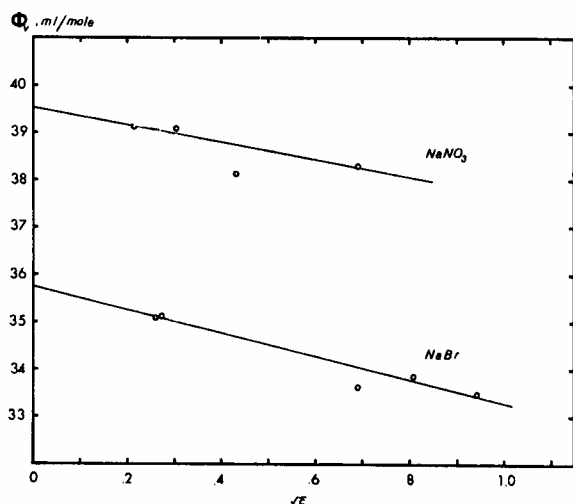


Figure 3. Apparent molal volumes, ϕ_v , of NaNO_3 and NaBr in NMP vs. \sqrt{c} at 25°.

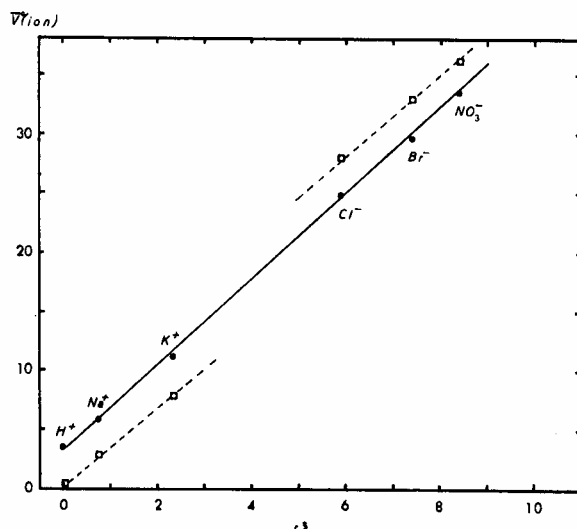


Figure 4. Ionic molal volume, $\bar{V}^0(\text{ion})$ for various ions in NMP vs. r^3 at 25° for two different values of H^+ : dotted lines, $\bar{V}^0(H^+) = 0$; solid line, $\bar{V}^0(H^+) = 3.4$ ml/mol.

$\bar{V}^0(\text{NaCl})$, and $\bar{V}^0(\text{KBr}) - \bar{V}^0(\text{KCl})$. From these differences one obtains, $\bar{V}^0(\text{K}-\text{Na}) = 4.8, 5.1$ ml/mol and $\bar{V}^0(\text{Br}-\text{Cl}) = 5.1, 5.4$ ml/mol. The division of $\bar{V}^0(\text{salt})$ in NMP into its ionic components can be made by the method for calculating $\bar{V}^0(\text{ion})$ in H_2O used by Mukerjee.¹⁶ As a first approximation, $\bar{V}^0(H^+)$ was equated to zero (or $\bar{V}^0(\text{HOBz}) = \bar{V}^0(\text{OBz}^-)$); the values of $\bar{V}^0(\text{ion})$ based on this division were then plotted vs. r^3 (the crystal radius).¹⁶ $\bar{V}^0(H^+)$ was then adjusted until the best fit for both cations and anions was obtained. Table VII gives $\bar{V}^0(\text{ion})$ based on a value of $\bar{V}^0(H^+) = 3.4$ ml/mol and $\bar{V}^0(\text{ion})$ in H_2O .^{16,17} Figure 4 shows the plot of $\bar{V}^0(\text{ion})$, from Table VII, vs. r^3 , from which $\bar{V}^0(\text{ion})$ of other monovalent ions in NMP can be estimated, $\bar{V}^0(\text{ion}) = 4.28r^3 + 3.4$ ml/mol. The slope of $\bar{V}^0(\text{ion})$ vs. r^3 is larger than the theoretical values of

Table VII: Molal Volume of Ions, $\bar{V}^0(\text{ion})$, in NMP and H_2O and $\Delta\bar{V}^0(\text{trans})$ from H_2O to NMP at 25°

Ion	Crystal radius, ^{16,17} Å	$\bar{V}^0(\text{ion})$, ml/mol		$\Delta\bar{V}^0(\text{trans})$ (H_2O -NMP), ml/mol
		NMP	H_2O ^{16,17}	
H^+	...	3.4	-4.5	7.9
Na^+	0.95	6.0	-5.7	11.9
K^+	1.33	11.1	4.5	6.6
Cl^-	1.81	24.7	22.3	2.4
Br^-	1.95	29.8	29.2	0.6
NO_3^-	2.03	33.6	33.6	0
OBz^-	...	97.7

2.52, and $\bar{V}^0(H^+)$ is positive, apparently due to the radius of an ion in solution being larger than the crystal radius (since void space effects in NMP should be smaller than those in H_2O).^{18,19} Further work must be done on other salts to prove this postulation.

The volume of transfer of an ion from water to NMP, $\Delta\bar{V}^0(\text{trans})$, Table VII, can be attributed to the differences in electrostriction or solute-solvent interactions, since the intrinsic volume of an ion in NMP and H_2O should be nearly equal. The electrostriction volume, $\bar{V}^0(\text{elect})$, is generally taken to be proportional to Z^2/r , where Z is the charge.¹⁶⁻²⁰ Thus $\Delta\bar{V}^0(\text{trans})$ from H_2O to NMP would be expected to be proportional to $Z^2/r(A'' - B'')$, where A'' and B'' are constants related to ϵ and $d \ln \epsilon/dP$ of H_2O and NMP, respectively. Figure 5 shows a plot of $\Delta\bar{V}^0(\text{trans})$ vs. $1/r$ taken from Table VII. This plot indicates that if $r > 2.22$ Å $\Delta\bar{V}^0(\text{trans})$ is very small (~ 0) or the electrostriction for monovalent ions with $r > 2.22$ Å is very small in H_2O . If one assumes the electrostriction, $\bar{V}^0(\text{elect})$, in NMP is small, the maximum value for the constant A'' for H_2O in the equation $\bar{V}^0(\text{elect}) = A''Z^2/r$ is 11, compared with a theoretical value of 6 obtained by Benson and Copeland²¹ and an empirical value of 8 obtained by Mukerjee.¹⁶ The value for the constant B'' in NMP (3-5) could be used to estimate $(d \ln \epsilon/dP)$ in NMP; however, until more work is done for divalent and trivalent salts in NMP this estimation may be meaningless.

The molal expansibilities, ϕ_E 's, of the various solutes in NMP were calculated from $d\phi_v/dT$, and the average infinite dilution values, $\phi_E^0 \equiv \bar{E}^0$, are given in Table VI. The \bar{E}^0 of salts in NMP is negative (similar to other solvents, e.g., MeOH),²² while values in H_2O are posi-

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(17) L. A. Dunn, *Trans. Faraday Soc.*, **62**, 2348 (1966).

(18) L. G. Hepler, *J. Phys. Chem.*, **61**, 1426 (1957).

(19) B. E. Conway, R. E. Verrall, and J. E. Desnoyers, *Z. Phys. Chem. (Leipzig)*, **230**, 157 (1965).

(20) E. Glueckauf, *Trans. Faraday Soc.*, **61**, 914 (1965).

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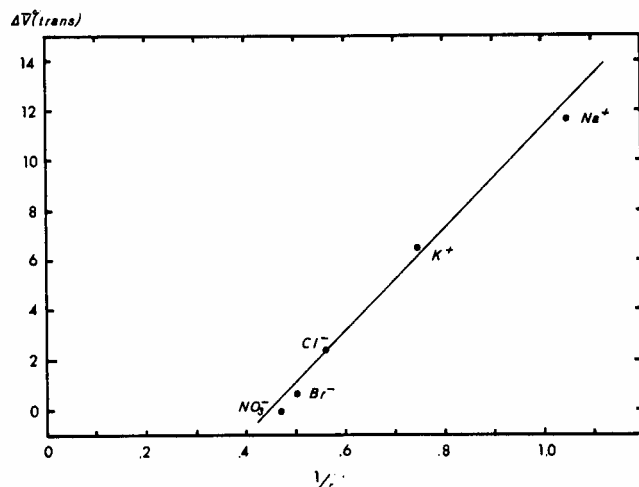


Figure 5. The change in volume in transfer of an ion, $\Delta \bar{V}^0$ (trans), from H_2O to NMP vs. $1/r$ at 25° .

tive.^{22,23} These results indicate that the positive values of $\bar{E}^0(\text{salt})$ in H_2O are related to the ability of the salt to change the structure of water over and above normal electrostriction.

A few measurements¹¹ were made on the density of mixed pairs of salts in NMP at 25° . (See Table VIII).

Table VIII: The Mean Apparent Molal Volume, Φ , of Salt Mixtures in NMP

Mixture	Φ , ml/mol		% error
	Measd	Calcd	
0.0956 <i>m</i> NaOBz + 0.0950 <i>m</i> NaCl	65.3	67.3	3.1
0.0274 <i>m</i> KCl + 0.0275 <i>m</i> NaBr	38.8	35.7	7.9
0.0153 <i>m</i> KCl + 0.0150 <i>m</i> NaBr	41.9	35.7	14.7

The mean apparent molal volume, Φ , of such a mixture can be calculated from the equation

$$\Phi = \frac{V - 11.48 \bar{V}^0(\text{NMP})}{m_1 + m_2} \quad (9)$$

where V is the volume of solution containing 1000 g of NMP, $\bar{V}^0(\text{NMP})$ is the molar volume of pure NMP, and m_1 and m_2 are the molalities of the two electrolytes. This equation can be rewritten as

$$\Phi = \frac{1}{m_1 + m_2} \left(\frac{1000 + m_1 M_1 + m_2 M_2}{d} - \frac{1000}{d^0} \right) \quad (10)$$

where M_1 and M_2 are the molecular weights of the two electrolytes, d is the density of the solution, and d^0 is the density of NMP. Young and Smith²⁴ have shown that their mixture rule

$$\Phi = \frac{m_1 \phi_1 + m_2 \phi_2}{m_1 + m_2} \quad (11)$$

accurately represents the data of Wirth for KCl–NaCl,²⁵ KBr–NaCl,²⁵ and NaClO_4 – HClO_4 ²⁶ mixtures in aqueous solutions. ϕ_1 and ϕ_2 are the molal volumes for the salts in pure NMP at ionic strength corresponding to $m_1 + m_2$. The results of this comparison for the different pairs is shown in Table VIII. The per cent error is larger than the results in H_2O ; however, this may be due to the uncertainties in the density data.

In conclusion, this preliminary study of solutes in NMP has shown how the η_r and \bar{V}^0 can be used to obtain a better understanding of solute–solvent interactions in a high dielectric solvent system.

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