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Apparent Molar Volume and Viscosity of *N*-Methylpyridinium Iodide and Its Methyl-Substituted Derivatives in Water

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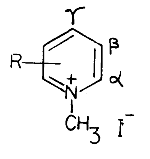
The apparent molar volume and the viscosities of *N*-methylpyridinium iodide and its methyl derivatives in water at 25, 30, 35, and 40 °C are reported. The apparent molar volumes obey Masson's equation. The ϕ_V° and S_V^* values indicate strong ion–ion interaction in water. ϕ_V° is linearly related to temperature. The relative viscosity data of these salts obey Jones–Dole and Vand equations well. The A and B values of Jones–Dole equation and Q values of Vand equation suggest greater solvation in case of NMPI and the β-CH$_3$ salt and greater ion–ion interaction in case of α-CH$_3$ and γ-CH$_3$ salts. The data have been discussed in terms of hydrophobic hydration and solvent shared ion pairs. The free energy of activation for viscous flow are almost equal for these salts. The importance of *A*, *B*, *B*+, and *Q* to the study of the solvent structure is discussed.

N-Methylpyridinium iodide (NMPI) is formed from pyridine and methyl iodide in the form of an ionic compound. It possesses a charge-transfer band which has been thoroughly studied by Kosower[1] and Ray.[2] The formation of ion pairs of NMPI in 90% and 100% ethanol and acetone was reported by Hemmes,[3] Jong-Gi Lee[4] and co-workers from the thermodynamic and kinetic studies. Bagchi[5] has studied the effect of added NaI on the thermodynamic and spectral properties of NMPI in mixed solvents. The transition energy (E_T) and *Z*-values of the CT band have been calculated for *N*-alkylpyridinium iodides in mixed aqueous solvents by Bagchi.[6] In this paper we report the apparent molar volume and viscosity of *N*-methylpyridinium iodides (**1**) in water at various temperatures.



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NMPR$^+$I$^-$: R=H, CH$_3$ at α, β, and γ positions.
When R=H the salt is NMPI. Short abbreviations for the salts are H, α, β, and γ.

Experimental

All the iodide salts were prepared by refluxing pure pyridine (BDH) and picolines (Sisco) which were redistilled previously under vacuum, with methyl iodide (Sisco) in ethanol. The salts were recrystallized twice from ethanol, vacuum dried and then stored under vacuum in dark over fused CaCl$_2$. The stock solutions of these salts were prepared at (25±0.01) °C and standardized by gravimetric estimation for iodide ion as silver iodide.[7] Solutions of lower concentrations were prepared by dilution of the stock solution after being thermostated at (25±0.01) °C. Doubly distilled water was used for all the measurements. The densities were measured in a double capillary pycnometer (50 cm^3 capacity) and viscosities were measured in an Ostwald viscometer having a flow time of 400 S for 10 cm^3 water as described in our previous paper.[8] All the density and viscosity measurements were carried out in duplicate at 25, 30, 35, and 40 °C.

Results and Discussion

The Apparent Molar Volume: The apparent molar volume ϕ_v of the salts were calculated from the density data by using the following equation.

$$\phi_v = \frac{10^3(\rho_o - \rho)}{C\rho_o} + \frac{M_2}{\rho_o} \tag{1}$$

where ρ_o and ρ are the densities of water and salt solutions having concentration C molar respectively and M_2 is the molecular mass of the solute. The apparent molar volumes of these salts vary with square root of the molar concentration and obey Masson's equation.[9]

$$\phi_v = \phi_V^\circ + S_V^* \sqrt{C} \tag{2}$$

where ϕ_V° is the apparent molar volume at infinite dilution and S_V^* is the experimental slope identified as ion–ion interaction term which depends on the nature of the electrolyte. The values of ϕ_V° and S_V^* are given in Table 1. In Fig. 1, the variation of ϕ_V° with $\sqrt{C}$ for

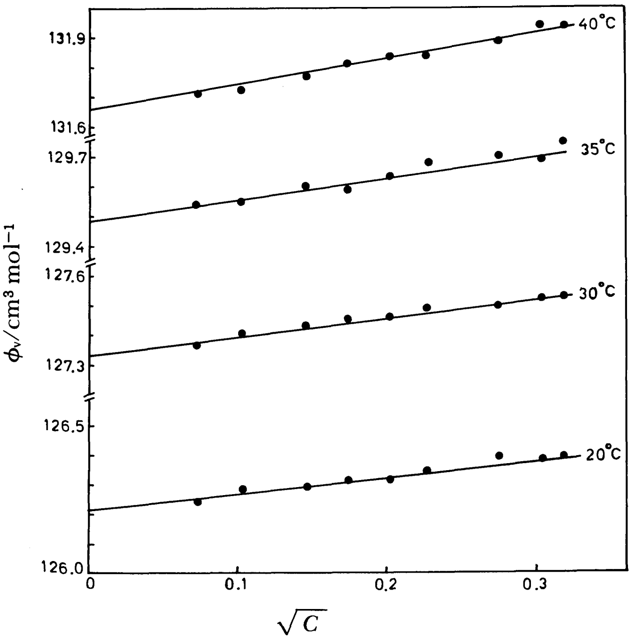

Fig. 1. Plot of ϕ_v against $\sqrt{C}$ of NMPI.

Table 1. The Values of ϕ_V° and S_V^* of Compounds **1** at Different Temperatures

Compound (R)	$T/^\circ C$	$\phi_V^\circ/cm^3\ mol^{-1}$	S_V^*	a
			$cm^3\ l^{1/2}\ mol^{-3/2}$	$cm^3\ mol^{-1}\ K$
H	25	126.21	0.587	0.387
	30	127.34	0.606	
	35	129.47	0.810	
	40	131.63	0.979	
α-CH_3	25	140.49	0.807	0.206
	30	141.77	1.049	
	35	142.53	1.082	
	40	143.30	1.222	
β-CH_3	25	140.53	0.644	0.215
	30	141.64	0.707	
	35	142.72	0.826	
	40	143.35	0.997	
γ-CH_3	25	140.79	0.782	0.167
	30	141.82	1.114	
	35	142.27	1.185	
	40	143.25	1.260	

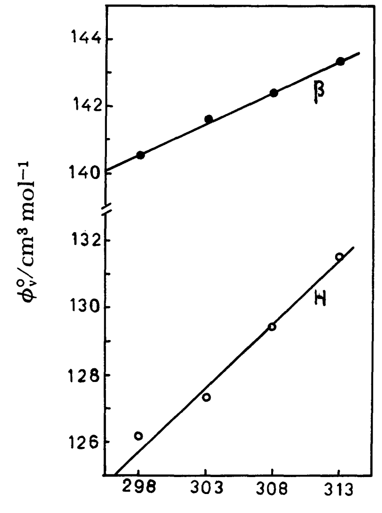

Fig. 2. Plot of ϕ_V° against T for NMPI and β salts.

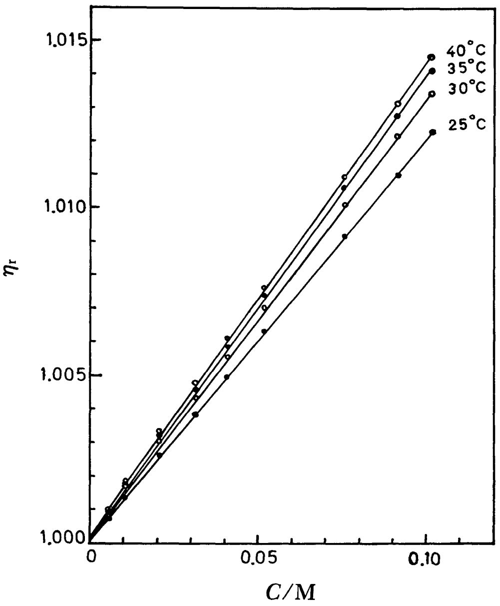

Fig. 3. Plot of η_r against C of NMPI.

NMPI at these temperatures is shown. Examination of Table 1 and Fig. 1 reveals that for each salt both ϕ_V° and S_V^* increase with increase in temperature. The S_V^* values of NMPI and β-CH_3 salts are less than those of α-CH_3 and γ-CH_3 salts. The order of S_V^* is "$H<\beta<\gamma<\alpha$ at 25 °C". The increase of ϕ_V° for NMPI and β-CH_3 salts at 25 °C with temperature is shown in Fig. 2 which indicates that it can be represented by an empirical equation

$$\phi_V^\circ(t) = \phi_V^\circ(25) + a(t - 25) \tag{3}$$

where 'a' is a constant independent of the concentration of the salt and the temperature. The values of 'a' for these salts are given in Table 1. The calculated ϕ_V° values by Eq. 3 agree well with the experimental values. The ϕ_V° values of the salts are higher than that of water. Therefore the positive and high values of ϕ_V° indicate[10] that in solution the motion of the ions $NMPR^+$ and I^- are not restricted. The S_V^* values are positive and indicate strong ion-ion interaction between these two ions which supports the formation of solvent shared ion pairs[1-5] reported in case of NMPI.

Viscosity of Salt Solutions: The viscosity data of these salts are presented in Figs. 3—6. The relative viscosity η_r of these salt solutions is almost linear with C. Therefore the data can be best represented by

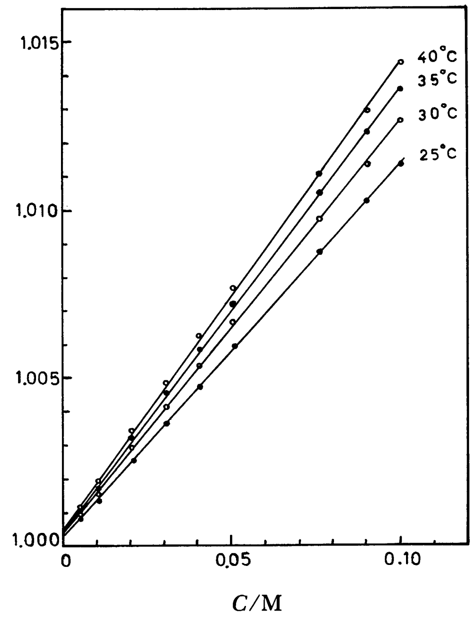

Fig. 4. Plot of η_r against C of NMPCH$_3^+$(α)I$^-$.

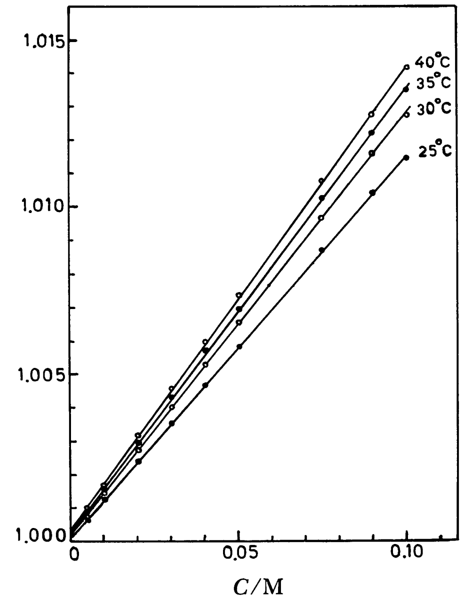

Fig. 5. Plot of η_r against C of NMPCH$_3^+$(β)I$^-$.

Jones–Dole[11] equation,

$$\eta_r = 1 + AC^{1/2} + BC \tag{4}$$

where A deals with ion–ion interaction and B deals with ion–solvent interaction and to the size and shape of the ion, the nature of the electrolyte, and the temperature of measurement. This equation is solved by the method of least squares and the values of the parameters are set out in Table 2. The values of A for NMPI and β-CH$_3$ salts are less than those of α-CH$_3$ and γ-CH$_3$ salts. But the B coefficient of these salts are in the order H>β>γ>α. Both A and B values increase with temperature. The ions NMPR$^+$ and I$^-$ are supposed to be surrounded by a seath of water molecules. As the temperature rises, the disorder in the water structure increases and this results in the greater interaction between these two ions to form solvent-shared ion pairs in water.

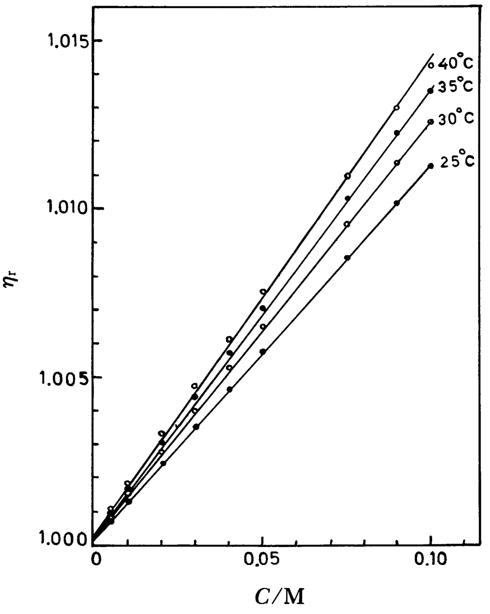

Fig. 6. Plot of η_r against C of NMPCH$_3^+$(γ)I$^-$.

The viscosity B coefficient can be separated into $B_\pm$ coefficients as

$$B = B_+ + B_-. \tag{5}$$

Since the B_- values for I$^-$ are known[12] the B_+ values for NMPR$^+$ ions can be found out. These ionic B_+ values are set out in Table 2. The iodide ion is a known structure-breaker of water, but the high values of B_+ coefficients for NMPR$^+$ ions indicate that these ions are structure-promoter of water, which may be due to hydrophobic hydration.[13] The order of B_+ for these ions is H>β>γ>α. In Figs. 7 and 8 the behavior of B and B_+ with temperature is shown. The positive values of dB/dT indicate that these salts as a whole are water-structure-breaking and the negative values of dB_+/dT indicate that the ions NMPR$^+$ are water-structure-making.[14] The dB_+/dT values are given in Table 2 and these are in order of H<β<α<γ.

The behavior of these salts can be tested well by Vand[15] equation

$$\ln \eta_r = \frac{2.5C\bar{V}}{1 - QC\bar{V}} \tag{6}$$

which on rearrangement leads to

$$\frac{1}{\ln \eta_r} = \frac{0.4}{C\bar{V}} - 0.4Q \tag{7}$$

Table 2. Values of A, B, B_+ of Compounds **1** at Different Temperatures

Compound (R)	T/°C	A / $\mathrm{dm^{3/2}\,mol^{-1/2}}$	B / $\mathrm{dm^3\,mol^{-1}}$	B_+ / $\mathrm{dm^3\,mol^{-1}}$	$\frac{-\mathrm{d}B_+}{\mathrm{d}T} \times 10^3$
H	25	0.0014	0.1159	0.1844	0.40
	30	0.0031	0.1227	0.1822	
	35	0.0038	0.1269	0.1804	
	40	0.0043	0.1295	0.1785	
α-CH_3	25	0.0028	0.1041	0.1726	0.067
	30	0.0040	0.1127	0.1722	
	35	0.0052	0.1184	0.1719	
	40	0.0063	0.1226	0.1716	
β-CH_3	25	0.0012	0.1109	0.1794	0.12
	30	0.0027	0.1192	0.1787	
	35	0.0032	0.1246	0.1781	
	40	0.0040	0.1286	0.1776	
γ-CH_3	25	0.0025	0.1046	0.1731	0.047
	30	0.0038	0.1133	0.1728	
	35	0.0050	0.1191	0.1726	
	40	0.0061	0.1234	0.1724	

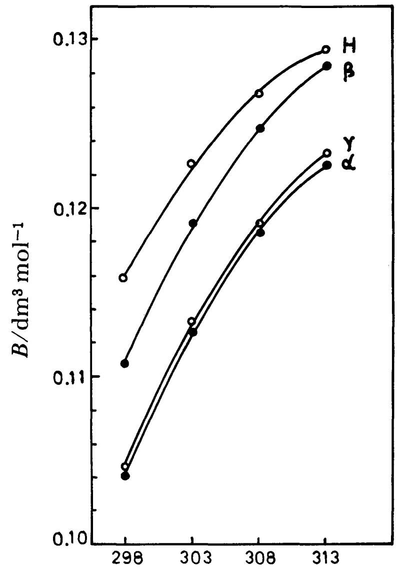

Fig. 7. Variation of B against T.

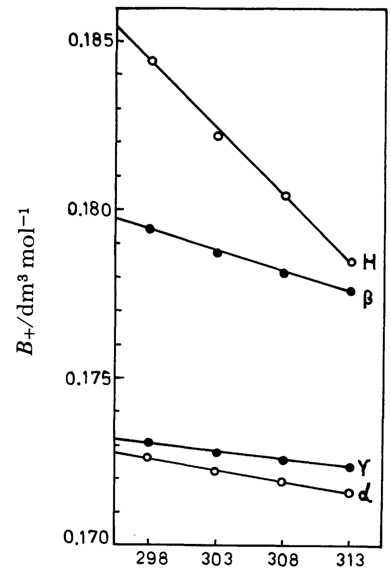

Fig. 8. Variation of B_+ against T.

where $\bar{V}$ is the rigid molar volume of the salt in solution and Q is the interaction parameter dealing with mutual interference between the spheres and with their Brownian motion. Equation 7 was solved by the method of least squares and the values of $\bar{V}$ and Q, thus obtained, are set out in Table 3. The values of Q indicate the order as $H<\beta<\gamma<\alpha$.

The values of A, B_+, and Q indicate that both NMPI and β-CH_3 salts are more solvated than α-CH_3 and γ-CH_3 salts whereas the ion–ion interaction between $NMPR^+$ and I^- to form ion pairs for α-CH_3 and γ-CH_3 salts are greater than those of NMPI and β-CH_3 salts. This is perhaps due to the partial neutralization of the positive charge in the pyridinium ion by the electron-donating methyl groups at α and γ positions which results in the less solvation of the pyridinium ion and greater ion–ion interaction between $NMPR^+$ and I^- ions of these two salts.

Free Energy of Activation for Viscous Flow: Feakins[16)] derived an equation to calculate the free energy of activation of viscous flow, $\Delta\mu_2^{\circ\mp}$ for electrolytic solutions using the B and ϕ_v° values as,

$$\Delta\mu_2^{\circ\mp} = \Delta\mu_1^{\circ\mp} + \frac{RT}{\bar{V}_1^\circ}\left[10^3B - (\bar{V}_1^\circ - \bar{V}_2^\circ)\right] \qquad (8)$$

where $\bar{V}_1^\circ$ and $\bar{V}_2^\circ$ (equal to ϕ_v° at infinite dilution) are

Table 3. Values of $\bar{V}$ and Q of Vand Equation

Compound (R)	T/°C	$\bar{V}$ / dm^3 mol^{-1}	Q
H	25	0.0533	45.69
	30	0.0669	72.76
	35	0.0726	77.86
	40	0.0766	80.81
α-CH$_3$	25	0.0574	86.75
	30	0.0676	92.43
	35	0.0767	97.65
	40	0.0847	100.73
β-CH$_3$	25	0.0514	45.73
	30	0.0636	73.49
	35	0.0687	76.10
	40	0.0751	82.43
γ-CH$_3$	25	0.0566	86.49
	30	0.0678	97.25
	35	0.0773	103.27
	40	0.0857	107.73

the partial molar volumes of the solvent and solute respectively at infinite dilution and $\Delta\mu_1^{\circ\neq}$ and $\Delta\mu_2^{\circ\neq}$ are the contributions per mole of solvent and solute to the free energy of activation for viscous flow. The values of $\Delta\mu_2^{\circ\neq}$ have been calculated for these salts at 25 °C for 0.1 M solution which are found to be 40.03, 40.38, 41.31, and 40.49 kJ mol^{-1} for NMPI, α, β, and γ salts respectively. The variation of $\Delta\mu_2^{\circ\neq}$ for those salts are not that significant and hardly contribute to the structure of the solvent system. Therefore the S_V^*, B_+, and Q parameters play a dominant role to know the type of interaction taking place between NMPR$^+$ and I$^-$ ions and the hydrophobic hydration between NMPR$^+$ and water.

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