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Apparent Molar Volume and Viscosity of *N*-Ethylpyridinium Iodide in Water

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The apparent molar volume and the viscosities of *N*-ethylpyridinium iodide in water at 25, 30, 35, and 40 °C are reported. The apparent molar volumes decrease with increasing temperature and obey Masson's equation. The high values of ϕ_v° and S_v^* indicate strong ion–ion interactions in water. ϕ_v° is linearly related to temperature. The viscosity data were analyzed by the Jones–Dole equation. The B values indicate greater solvation. The thermodynamic parameters of viscous flow and hydration number are discussed in terms of hydrophobic hydration and solvent-shared ion-pairs.

In our previous paper,[1] the apparent molar volumes and viscosities of *N*-methylpyridinium iodide and its methyl-substituted derivatives were discussed on the basis of hydrophobic hydration and solvent-shared ion-pairs. In this note, we report the apparent molar volume and viscosity of *N*-ethylpyridinium iodide (**1**) in water at 25, 30, 35, and 40 °C (Chart 1).

Experimental

N-Ethylpyridinium iodide (NEPI) was prepared by refluxing pyridine (BDH) and ethyl iodide (Sisco) in ethanol. The product was twice recrystallized from ethanol, vacuum dried, and stored under vacuum in the dark over fused $CaCl_2$. A stock solution was prepared in double-distilled water at (25±0.01) °C and the concentration was computed from the gravimetric estimation of iodide ion as silver iodide.[2] The densities and viscosities were measured as described previously.[3]

Results and Discussion

The Apparent Molar Volume. The apparent molar volume (ϕ_v) of the salt was calculated from the density data using the following equation.

$$\phi_v = \frac{10^3(\rho_0 - \rho)}{C\rho_0} + \frac{M_2}{\rho_0}, \tag{1}$$

where the symbols have their usual meanings. The variation of ϕ_v with $\sqrt{C}$ is shown in Fig. 1 which reveals that the ϕ_v values decrease with increasing temperature. The apparent molar volume of the salt varies with the square root of the molar concentration and obeys Masson's equation[4] Eq. 2 instead of Redlich and Meyer's equations,[5]

$$\phi = \phi_v^\circ + S_v^* \sqrt{C}, \tag{2}$$

where ϕ_v° and S_v^* have their usual meanings. The values of ϕ_v° and S_v^* are given in Table 1. The values of S_v^* increase with increasing temperature and they are positive. With increasing temperature, agitation in the solution increases. Therefore the possibility of ions of opposite charges coming closer is high. The high positive values of S_v^* indicate strong ion–ion interactions which are felt through solvent molecules. This supports the formation of solvent-shared ion-pairs in water as indicated by spectroscopic and ultrasonic absorption measurements.[6] In Fig. 2, the variation of ϕ_v° with T is shown. This can be represented by an empirical equation,

$$\phi_v^\circ(t) = \phi_v^\circ(25) + \alpha(25 - t), \tag{3}$$

where α is a constant having a value of 0.46 in this case. The ϕ_v° values calculated from Eq. 3 agree with the experimental values.

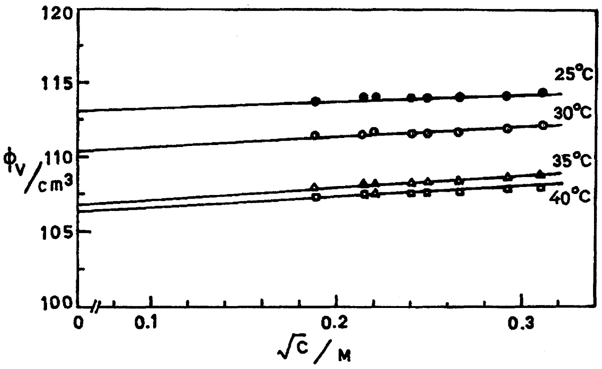

Fig. 1. Variation of ϕ_v with $\sqrt{C}$.

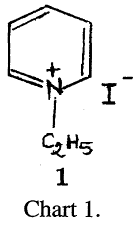

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Chart 1.

Viscosity of Salt Solutions. The viscosity data of the salt at various temperatures are shown graphically in Fig. 3. The figure shows that viscosity is almost linear when plot-

Table 1. The Values of ϕ_V°, S_V^*, A, B, B_+, R_S and n_B of NEPI in Water at Different Temperatures

Temp	ϕ_V°	S_V^*	A	B	B_+	R_S	n_B
°C	$cm^3\,mol^{-1}$	$cm^3\,l^{1/2}mol^{-3/2}$	$dm^3mol^{-1/2}$	dm^3mol^{-1}	dm^3mol^{-1}	Å	
25	113.04	4.592	0.0014	0.1959	0.2644	7.48	17.34
30	110.46	5.537	0.0015	0.1994	0.2589	7.43	16.6
35	107.86	5.904	0.0020	0.2039	0.2574	7.41	16.3
40	106.28	6.273	0.0025	0.2081	0.2490	7.34	15.4

a) standard error of estimate is of the order of 10^{-2} to 10^{-3}. The B_- values of I^- are 25°, −0.0685; 30°, −0.0595; 35°, −0.0535; 40°, −0.0409 $dm^3\,mol^{-1}$.

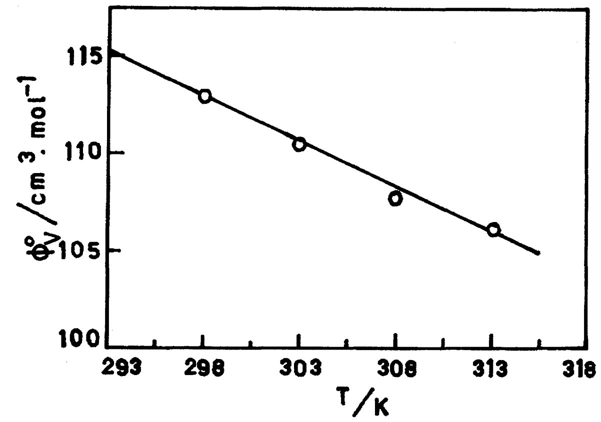

Fig. 2. Variation of ϕ_V° with T.

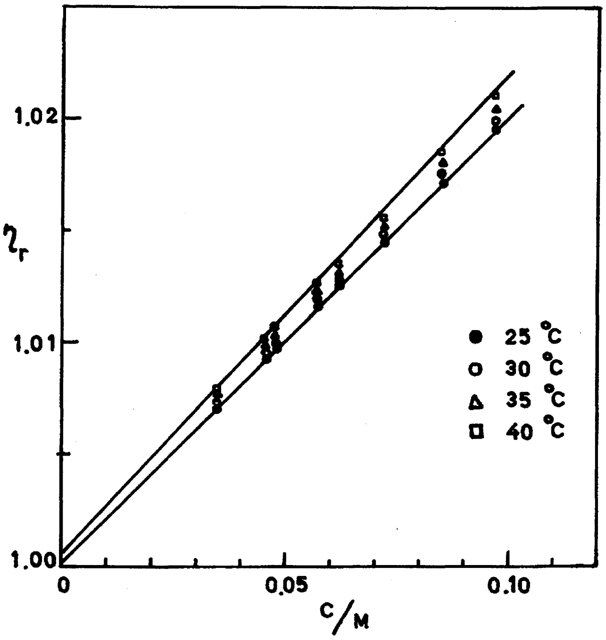

Fig. 3. Variation of η_r with C.

ted against concentration C at these temperatures. Therefore the data can be best represented by the semiquantitative Jones–Dole equation,[7)]

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

where A and B have their usual meanings. This equation is solved by the least squares method and the values of the parameters are given in Table 1. Both A and B values increase with increasing temperature which indicates greater ion–ion and ion–solvent interactions respectively.

The viscosity B coefficient can be separated into $B_\pm$ coefficients[8)] as

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

Using known values of B_- for I^- (Table 1), the B_+ values of NEP^+ can be calculated and are given in Table 1. The B_+ values decrease and the B values of the salt increase with increasing temperature. In Fig. 4, both B and B_+ are plotted as a function of temperature. It is seen from the figure that dB/dT is positive which indicates that the salt as a whole is water-structure-breaking, whereas negative values of dB_+/dT indicate that the NEP^+ ion is water-structure-making.[9)] The high values of B_+ and the negative value of dB_+/dT for NEP^+ indicate that NEP^+ ion is a structure-promotor of water due to hydrophobic hydration.[10)]

Thermodynamic Parameters of Viscous Flow. Treating the flow of a liquid as a rate process,[11)] the following method was adopted to calculate ΔG^*, ΔH^*, and ΔS^* for viscous flow of NEPI solutions at 25 °C. ΔH^* was calculated by the method of Nightingale and Benck[12)] in combination with the Jones–Dole[7)] equation.

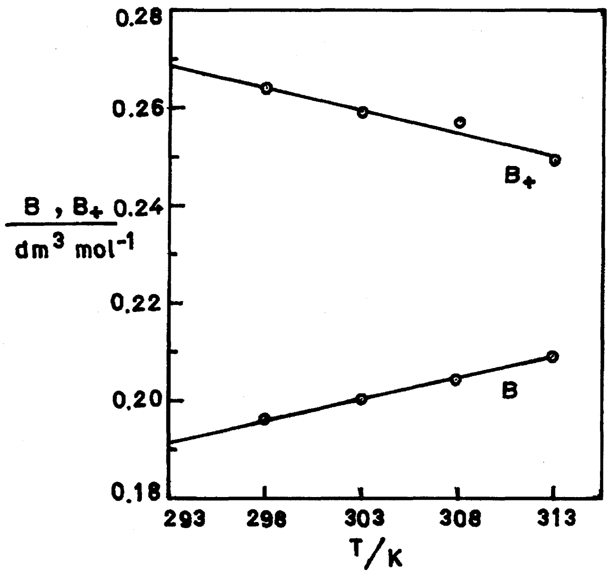

Fig. 4. Variation of B, B_+ with T.

$$\Delta H_1^* = R\frac{\mathrm{d}\ln \eta_0}{\mathrm{d}(1/T)} + \frac{R}{1+BC} \times \frac{\mathrm{d}(1+BC)}{\mathrm{d}(1/T)}. \tag{6}$$

The free energies of viscous flow for water and water+ electrolyte solutions were calculated by the method of Miller and Doran[13] with some modification. We represent the free energies of viscous flow by

$$\Delta G_0^* = RT\ln \eta_0 \overline{V}_0/hN, \tag{7}$$

$$\Delta G_1^* = RT\ln \eta_1 \overline{V}_1/hN. \tag{8}$$

The subscripts 0 and 1 refer to water and salt solution, respectively. $\overline{V}_1$ is the molar volume of the hole in the liquid and the other symbols are well-known. Equations 7 and 8 can be combined as

$$\ln \frac{\eta_1}{\eta_0} = \ln \eta_r = \frac{\Delta G_1^* - \Delta G_0^*}{RT} - \ln \frac{\overline{V}_1}{\overline{V}_0}. \tag{9}$$

Since ΔG_0^* is known, ΔG_1^* can be calculated from a plot of ln η_r vs. 1/*T*. The entropy of activation, ΔS_1^*, for viscous flow is calculated from

$$\Delta G_1^* = \Delta H_1^* - T\Delta S_1^*. \tag{10}$$

The values of the thermodynamic parameters of viscous flow calculated by the above equations were found to be $\Delta G_1^*=9.08$ kJ mol^{-1}, $\Delta H_1^*=16.70$ kJ mol^{-1}, and $\Delta S_1^*=25.56$ J K^{-1} mol^{-1}. The corresponding values of the parameters for water[12] are $\Delta G_0^*=9.16$ kJ mol^{-1}, $\Delta H_0^*=16.77$ kJ mol^{-1}, and $\Delta S_0^*=25.52$ J K^{-1} mol^{-1}. The values of water and the electrolyte solution are so close that no conclusion can be drawn but one can qualitatively say that there is an increase in the disorder in the solution.

Hydration Number. The ionic molar volume $\overline{V}_\pm$ is related to the ion $B_\pm$ coefficient[14] by comparing the Jones–Dole equation with that of Einstein[15] as

$$B_\pm = 2.5\overline{V}_\pm = 2.5\frac{4}{3}\Pi\frac{R_S^3 N}{1000}, \tag{11}$$

where R_S is identified as the Stokes radii. For an ion with a firm layer of water molecules in it's co-sphere it behaves as a rigid system because of strong interactions between the ion and water dipoles. On the basis of this, $\overline{V}_\pm$ can be expressed as

$$\overline{V}_\pm = \overline{V}_{\mathrm{ion}}^\circ + n_B \overline{V}_0^\circ. \tag{12}$$

Therefore, the hydration number n_B is given by

$$n_B = \frac{\overline{V}_\pm - \overline{V}_{\mathrm{ion}}^\circ}{\overline{V}_0^\circ}, \tag{13}$$

where $\overline{V}_0^\circ$ is the molar volume of a water molecule (18.016 cm^3) and $\overline{V}_{\mathrm{ion}}^\circ$=volume of NEP$^+$=$(4/3)\Pi r^3$, which also represents the van der Waals volume. The radius *r* of NEP$^+$ was calculated from the bond distances[16] as

$$\begin{aligned} r &= \text{Bond distances of (C–H} + \text{C}_{\text{(apex)}}\text{–N} \\ &\quad + \text{N–C} + \text{C–C} + \text{C–H)}/2 \\ &= (1.084+2.695+2.426+1.541+1.07)/2 \\ &= 3.908\ \text{Å}. \end{aligned}$$

The Stokes radii and the hydration numbers calculated by Eqs. 11 and 13 are included in Table 1. As expected, both R_S and n_B decrease with increasing temperature. The values of R_B and n_B indicate that the NEP$^+$ ion is strongly hydrated and is surrounded by a firm layer of water molecules. This conclusively proves that the NEP$^+$ ion is a water-structure-maker.

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