

Volumetric and Viscometric Studies of Tetrapropyl Ammonium Iodide in Binary Mixture of N, N-Dimethylformamide and Ethylmethylketone at Different Temperatures

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Abstract: Density (ρ) and Viscosities (η) of tetrapropylammonium iodide (Pr_4NI) in N,N-Dimethylformamide (DMF), ethylmethyl ketone (EMK) and DMF + EMK solvent mixtures containing 0, 20, 40, 60, 80 and 100 mol % of DMF at 298, 308 and 318K have been reported. The experimental values of Density (ρ) and Viscosities (η) were used to calculate the values of the apparent molar volume (ϕ_v), partial molar volume (ϕ_v^0) at infinite dilution. The viscosity data have been analysed in terms A- and B- viscosity coefficients of the Jones Dole equation. Both A- and B coefficients have found to be positive over the entire solvent composition range at all temperatures. The activation parameters have been examined as a function of solvent composition to interpret the solution behaviour of tetrapropyl ammonium bromide (Pr_4NI) in binary mixture of DMF-EMK. The behaviour of these suggests strong ion-solvent interactions in these systems and that Pr_4NI act as structure-maker in EMK+DMF mixed solvents.

I. Introduction

Volumetric and viscometric properties of binary mixtures have been very helpful to obtain information on the solute-solvent interactions and geometrical effects in the systems¹⁻². Experimental results of viscosity measured in large concentration of electrolytes in aqueous solutions and the solvent – solvent interaction are available in the literature³⁻⁴. However, only limited numbers of experimental viscosity data of electrolytes in highly concentrated solution in non-aqueous solvents are available⁵⁻⁷. Solvents like, N,N-dimethylformamide (DMF) and ethylmethylketone (EMK) find a wide range of applications of technological importance, namely as solvent and solubilizing agents in organic synthesis, reaction kinetics and electrochemical studies⁸⁻⁹. A systematic study of the structural and energetic consequences of the interaction between electrolytes and solvent mixtures will enable us to understand how electrolytes exercise thermodynamic and kinetic control over the chemical activities in non-aqueous media. On the basis of this hypothesis the title study has been taken.

In the present study, density (ρ) and viscosity (η) of tetrapropyl ammonium iodide (Pr_4NI) in N,N-dimethylformamide (DMF), ethylmethylketone (EMK) and DMF + EMK mixtures at 298, 308 and 318 K have been measured. Experimental values of ρ and η were used to calculate the apparent molar volume (ϕ_v), limiting apparent molar volume (ϕ_v^0), A- and B- coefficient of Jones-Dole equation¹⁰. The viscosity B-coefficients of given electrolyte at different temperature have also been used to estimate the transition parameters for viscous flow process of the electrolyte in DMF- EMK mixtures. These parameters are the true representatives of the behaviour of ions in a given solution.

II. Materials And Methods

Tetrapropyl ammonium bromide (Pr_4NI) of analytical grade, Fluka, was dried and used as described earlier⁶⁻⁷. Both Solvents, EMK and DMF (extrapure AR grade; S D Fine Chemicals Ltd.) were purified by the methods reported in our previous works^{7,11-12}. Viscosity measurements were carried out as described elsewhere^{6-7,11-12}. Viscosity values were found to be in good agreement with those reported in literature^{7,11-12}. The densities of pure solvent, solvent system and various electrolytic solutions were measured with the help of a sealable type of pycnometer (supplied by M/s. Harsh & Co., Ambala Cantt.) of 20 cm³ capacity).

The viscosities and densities of the above electrolyte in DMF, EMK and DMF+EMK solvent systems were measured at 298,308 and 318K. The overall accuracy of the viscosity and density measurements in this study was estimated to be $\pm 0.2\%$ and $\pm 0.1\%$ respectively.

III. Results And Discussion

Densities and viscosities of tetrapentyl ammonium bromides (Pr_4NI) in N, N-Dimethylformamide (DMF), ethylmethyl ketone (EMK) and DMF – EMK mixtures containing 0, 20, 40, 50, 60, 80 and 100 mol% of DMF in the concentration range (0.02-0.1) mol dm⁻³ at 298, 308 and 318 K. The viscosity data of present solutions were analysed by using the Jones-Dole equation¹⁰:

$$\eta/\eta_0 = \eta_r = 1 + AC^{1/2} + BC \quad \text{-----(1)}$$

arranged in the form of straight line equation as:

$$\Psi = \frac{(\eta_r - 1)}{C^{1/2}} A + BC^{1/2} \quad \text{-----(2)}$$

where η and η_0 respectively, are viscosities of solution and solvent, η_r is relative viscosity of solution, A is Falkenagen Coefficient¹³ and is a measure of ion – ion interactions theoretically. On the other hand, B is empirical and is a function of ion-solvent interactions and C is the molar concentration.

Furthermore, the viscosity data is also examined in the light of the transition state theory of the relative viscosity of various electrolytic solutions proposed by Feaken et al¹⁴.

According to theory, viscosity B-coefficient is given as:

$$B = \frac{\bar{V}_2^0 - \bar{V}_2^*}{1000} + \frac{\bar{V}_2^0 \left[\frac{\Delta G_2^* - \Delta G_2^*}{RT} \right]}{1000} \quad \text{-----(3)}$$

where \bar{V}_1^0 and \bar{V}_2^0 are the partial molar volumes of the solvent and solute respectively, ΔG_1^* and ΔG_2^* are the free energy activation for viscous flow per mole of pure solvent and solute solution respectively.

The free energy activation, ΔG_1^* for viscous flow process per mole of pure solvent system is estimated using Eyring's equation¹⁵:

$$\Delta G_1^* = RT \ln(\eta_0 \bar{V}_1^0) / hN \quad \text{-----(4)}$$

where R, h and N are gas constant, Planck's constant respectively, \bar{V}_1^0 is the molar volume mass of the solvent and T is the absolute temperature.

ΔG_2^* , the free energy activation for viscous flow per mole of pure solvent is derived from equation (3) as:

$$\Delta G_2^* = \Delta G_1^* + \left(\frac{RT}{\bar{V}_1^0} \right) [1000B - (\bar{V}_1^0 - \bar{V}_2^0)] \quad \text{---- (5)}$$

The molar volume \bar{V}_1^0 , of the pure solvent system has been determined from the relation:

$$\bar{V}_1^0 = \frac{x_1 M_1 + x_2 M_2}{\rho_{mixt.}} \quad \text{-----(6)}$$

where x_i refers to the mole fraction of the solvent component i, M_i is the molar mass of the solvent mixture and $\rho_{mixt.}$ is the density of the mixture.

The values of the partial molar volume, \bar{V}_2^0 of solute solution are obtained by the use of least square treatment to the plots of the use of ϕ_v , apparent molar volumes of solution versus $C^{1/2}$ in accordance with Masson's empirical¹⁶:

$$\phi_v = \phi_v^0 + S_v^* + C^{1/2} \quad \text{-----(7)}$$

where ϕ_v^0 ($= \bar{V}_2^0$) is the partial molar volume of the solution and S_v^* is the experimental slope.

The apparent molar volume, ϕ_v is calculated from the density data by using flowing expression:

$$\phi_v = 1000 \frac{(\rho_0 - \rho)}{C \rho_0} + \frac{M_2}{\rho_0} \quad \text{-----(8)}$$

where ρ_0 and ρ are densities of solvent and solution, respectively; C is molar concentration of electrolyte and M_2 is its molecular weight.

The plots of ψ ($= (\eta/\eta_0 - 1)/C^{1/2}$) versus $C^{1/2}$ to be linear over the whole concentration range of studied electrolytes at different solvent composition and temperatures. Jones-Dole viscosity A-and B-coefficient have obtained from these plots by the least square fitting method. Table-1 gives these values for various solvent compositions at 298, 308 and 318 K.

Table -1: Experimentally determined viscosity A(dm^{2/3} mol^{-1/2}) and B(dm³ mol⁻¹) -coefficients of Pr₄NI in DMF -EMK mixtures at different temperatures.

Mole Fraction of DMF												
Temperatures	1.00		0.80		0.60		0.40		0.20		0.00	
	Ax10 ²	B	Ax10 ²	B	Ax10 ²	B	Ax10 ²	B	Ax10 ²	B	Ax10 ²	B
298 K	2.38	1.30	3.13	1.28	4.05	1.27	4.35	1.26	3.48	1.25	3.67	1.24
308 K	3.98	1.21	5.92	1.17	5.15	1.14	6.86	1.11	7.62	1.09	8.14	1.08
318 K	5.24	1.10	7.49	1.06	9.67	1.03	11.57	1.01	13.40	0.98	15.60	0.97

Viscosity A-coefficients in all the cases are found to be positive. Most of the studies in pure and mixed solvents have been reported positive A-coefficient^{36-7,17}. Some authors¹⁸⁻¹⁹ have also reported negative A-coefficients. But it has been suggested that negative A-coefficient have no physical significance²⁰ and may have arisen due to some systematic error in viscosity measurements. Comparing B- values reported in Table-1 for Pr₄NI in DMF and EMK with those reported in literature can check the accuracy of the present viscosity data. The B-coefficients for studied electrolyte are positive, which is common feature for most of the solvents^{6-7,11-12}. The positive B-coefficients value attributed to strong ion-solvent interaction in the system. The positive B-coefficients in the present work, however, show only slight increase with the addition of DMF in DMF+EMK mixtures. This observation fairly consistent with the viscosity studies of Prasad et al²¹ and Baljeet et al⁶ in DMF+H₂O mixtures, Gill et al²² in DMF + Ac mixtures and Baljeet et al⁷ in DMF+EMK mixtures. The present results, therefore, indicate the ideal behavior of DMF + EMK mixtures as suggested in literature^{6-7,22}.

It is clear from Table-1 that viscosity B- coefficients for the given electrolyte decrease with decrease in Temperature. This is found to be consistent with the works reported in literature^{6-7,17}.

The activation parameters for viscous flow process, like ΔH*, TΔS* and ΔG₂* obtained for Pr₄NI in DMF + EMK mixtures at 298, 308 and 318 K are summarized in Table-2 and Table-3.

Table-2 Free energy of activation, ΔG₁* (kJ mol⁻¹) and apparent molar volume, \bar{V}_1° (dm³ mol⁻¹) for DMF, EMK and DMF+EMK mixtures at different temperatures

Temperatures						
X _{DMF}	298K		308K		318K	
	\bar{V}_1°	ΔG ₁ *	\bar{V}_1°	ΔG ₁ *	\bar{V}_1°	ΔG ₁ *
1.00	77.4	23.9	79.0	24.4	78.2	25.0
0.80	79.8	23.6	81.5	24.1	80.6	24.6
0.60	82.2	23.4	84.1	23.9	83.1	24.3
0.40	84.7	23.1	86.8	23.5	85.7	24.0
0.20	87.4	22.8	89.7	23.2	88.5	23.6
0.00	90.2	22.5	92.9	23.0	91.4	23.4

Table 3- Activation parameters, \bar{V}_2° (dm³ mol⁻¹), ΔG₂* (kJ mol⁻¹), TΔS* (kJ mol⁻¹) and ΔH* (kJ mol⁻¹) for Pr₄NI in DMF, EMK and DMF+ EMK mixtures at different temperatures.

Temperatures												
X _{DMF}	298K				303K				308K			
	\bar{V}_2°	ΔG ₂ *	TΔS*	ΔH*	\bar{V}_2°	ΔG ₂ *	TΔS*	ΔH*	\bar{V}_2°	ΔG ₂ *	TΔS*	ΔH*
1.00	290.2	67.2	47.7	114.9	291.6	65.2	49.3	114.5	292.8	64.0	50.9	114.9
0.80	289.9	64.6	53.6	118.2	290.8	62.9	55.4	118.3	292.3	61.0	57.2	118.2
0.60	289.7	62.5	59.6	122.1	290.4	60.5	61.6	122.1	291.7	58.5	63.6	122.1
0.40	289.6	60.5	65.6	126.1	290.1	58.3	67.8	126.1	290.2	56.1	70.0	126.1
0.20	289.0	58.7	71.52	130.22	289.9	56.3	73.9	130.2	290.1	54.0	76.3	130.3
0.00	287.5	57.4	77.5	134.9	288.4	54.9	80.1	135.0	289.1	52.2	82.7	134.9

$\phi_v^\circ (= \bar{V}_2^\circ)$ is a measure of ion-solvent interaction. It is evident from the table-3 that \bar{V}_2° values are large positive for Pr₄NI in EMK+DMF mixtures, suggesting the presence of strong ion-solvent interactions. Small decrease in \bar{V}_2° as the amount of EMK in the solution indicates the decreasing trend of ion-solvent interaction.

The present solvent system possesses ideal structure²³ as explained above. However, ΔG₂* > ΔG₁* for present electrolyte over the entire composition ranges suggest some structure making effect of this electrolyte. In fact, Feakens et al¹⁴ have shown that ΔG₂* > ΔG₁* for electrolytes that are structure makers. This is found to be consistent not only with the fact that the B coefficients for Pr₄NI in dipolar-aprotic solvents^{6-7,22}, but also the fact that ΔG₂* decreases with rise in temperature. Similarly, the decrease in ΔG₂* with addition of EMK manifests the reduction in dipolar association of DMF^{6-7,24} on account of inter molecules interactions between

DMF and EMK. Similar argument must hold well in respect of ΔS^* values. The ΔS^* values increase almost linearly with the increase in EMK concentration in DMF+EMK mixtures at 298, 308 and 318K. Moreover, the relative magnitude of positive ΔH^* and ΔS^* for Pr_4NI in DMF+EMK mixtures suggest that the transition state is associated with bond breaking and decrease in order, however small it may be.

The data further reveal that ΔH^* and ΔS^* values for given salt decrease almost regularly with the addition of DMF in the mixture over the entire solvent composition range. Scrutiny of activation parameters for Pr_4NI in DMF+ EMK system further reveals that a comparable amount of structure is disrupted in the viscous flow process by Pr_4N^+ ions, as the relative magnitude of ΔH^* and ΔS^* values for this salt is observed to be independent of solvent composition. This is found to be consistent with the experimental fact that (i) Pr_4N^+ ions, due to their larger size and small surface charge density is weakly solvated in this system and (ii) that there is no significant structural consequence of intermolecular interactions between the solvent components due to their dipolar aprotic natures. The experimental evidences as reported by Baljeet⁶⁻⁷ Parker²³ and Gill²⁵ substantiate both these facts.

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