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A Study Of Activation Parameters For Viscous Flow Process Of Tetrabutyl Ammonium Iodide In Binary Mixture Of N,N-Dimethylformamide And Ethylmethylketone At Different Temperatures.

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ABSTRACT:
Viscosities and densities of tetrabutylammonium iodide (Bu_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 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. Partial molal volumes ($\overline{V}_2^o$) have also been calculated which have been used along with B- values to calculate the activation parameters for viscous flow process electrolytic solution. The activation parameters have been examined as a function of solvent composition to interpret the solution behaviour of tetraethyl ammonium bromide (Bu_4NI) in binary mixture of DMF-EMK. The behaviuor of these suggests strong ion-solvent interactions in these systems and that Bu_4NI act as structure-maker in EMK+DMF mixed solvents.

I. INTRODUCTION

Studies on the behavior of ions in mixed water + non-aqueous solvents have received a lot of attention in the recent past[1-2]. However, similar studies of electrolytes in non-aqueous solvents are scare in the literature. Precise data on electrolytes in mixed solvents find applications in many industrial processes, as they provide a wide choice of solutions with appropriate properties[3-5]. Viscosity studies of electrolytic solutions in mixed solvent system is one of the most fundamental transport properties that play a vital role in understanding the solution behavior of the electrolytes[6]. An attempt has been made to investigate the ion-solvent interactions of tetrabutyl ammonium iodide (Bu_4NI)in N,N-dimethylformamide (DMF) and ethylmethylketone (EMK) mixtures. It is found that the character of molecular interaction considerably influences the solvation of ions. Thus, DMF+EMK mixed solvents would be interesting media for the study of ion-solvent and solvent – solvent interactions of Bu_4NI. The present investigation reports the viscosity studies of tetraethyl ammonium bromides (Bu_4NI) in N, N-Dimethylformamide (DMF), ethylmethyl ketone (EMK) and DMF + EMK mixtures at 298, 308 and 318 K. Studies of viscosity of ionic solutions are of great help in characterizing the structure and properties of solutions. The viscosity B-coefficients of this salt in the given mixture are analysed in terms of ion-solvent interactions. 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

Tetraethyl ammonium bromide (Bu_4NI) of analytical grade, Fluka, was dried and used as described earlier[3-5]. Solvent DMF (extrapure AR grade; S D Fine Chemicals Ltd.) was purify methods reported in our previous works[3-5,7]. Viscosity measurements were carried out as described elsewhere[8-9]. Viscosity values were found to be good agreement with those reported in literature[8-9,10]. The densities of pure solvent, solvent system and various electrolytic solutions were measurement with the help of a sealable type of pycnometer (supplied by M/s. Harsh & Co., Ambala Cantt.) of 20 cm^3 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 ± 0.2% and ± 0.1% respectively.

III. RESULTS AND DISCUSSION

Densities and viscosities of tetraethyl ammonium bromides (Bu_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 equation[11]:

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

arranged in the form of straight line equation as:

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

where η and η_o respectively, are viscosities of solution and solvent, η_r is relative viscosity of solution, A is Falkenagen Coefficient[12] 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 al[6].

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

$$B = \frac{\overline{V}_1^o - \overline{V}_2^o}{1000} + \frac{\overline{V}_1^o\left[\frac{\Delta G_2^* - \Delta G_1^*}{RT}\right]}{1000} \qquad \text{-------(3)}$$

where $\overline{V}_1^o$ and $\overline{V}_2^o$ 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 Erying's equation[13]:

$$\Delta G^*_1 = RT \ln(\eta_o \overline{V}_1^o)/hN \qquad \text{------(4)}$$

where R, h and N are gas constant, Planck's constant respectively, $\overline{V}_1^o$ 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:

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

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

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

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, $\overline{V}\,{}_2^0$ 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 emperical[14]:

$$\phi_V = \phi_V^o + S_V^* + C^{1/2} \qquad \text{--------(7)}$$

where $\phi_V^o \left(= \overline{V}_2^o\right)$ 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:

$$\phi_V = 1000\frac{(\rho_o - \rho)}{C\rho_o} + \frac{M_2}{\rho_o} \qquad \text{--------(8)}$$

Where ρ_o 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 (= $(\eta/\eta_o - 1)/C^{1/2}$) 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 (dm^3 mol^{-1}) -coefficients of Bu_4NI in DMF -EMK mixtures at different temperatures.

Temperatures	Mole Fraction of DMF 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	1.16	1.22	1.33	1.19	1.57	1.17	2.40	1.16	3.25	1.15	3.63	1.14
308 K	1.47	1.14	2.15	1.10	3.24	1.07	6.86	1.05	1.00	1.03	8.14	1.02
318 K	3.29	1.04	9.53	1.01	9.97	0.98	1.38	0.96	1.42	0.95	1.45	0.94

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[3-5,15]. Some authers[2,16] have also reported negative A-coefficients. But it has been suggested that negative A-coefficient have no physical significance[17] and may have arisen due to some systematic error in viscosity measurements. Comparing B- values reported in Table 1 for Bu_4NI 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[3-5,17-18]. 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 al[18] and Baljeet et al[3] in DMF+H_2O mixtures, Gill et al[19] in DMF + Ac mixtures and Baljeet et al[5] in DMF+EMK mixtures.

The present results, therefore, indicate the ideal behavior of DMF + EMK mixtures as suggested in literature[3-5,18,19].

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 litrature[18].

The activation parameters for viscous flow process, like ΔH^*, $T\Delta S^*$ and ΔG_2^* obtained for Bu_4NI in DMF + EMK mixtures at 298,308 and 318 K are summarized in Table 2 and Table 3.

Table-2 Free energy of activation, ΔG_1^* (kJ mol^{-1}) and apparent molar volume, $\overline{V}_1^o$ (dm^3 mol^{-1}) for DMF, EMK and DMF+EMK mixtures at different temperatures.

X_{DMF}	Temperatures 298K $\overline{V}_1^o$	ΔG_1^*	308K $\overline{V}_1^o$	ΔG_1^*	318K $\overline{V}_1^o$	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, $\overline{V}_2^o$ (dm^3 mol^{-1}), ΔG_2^* (k J mol^{-1}), $T\Delta S^*$ (k J mol^{-1}) and ΔH^* (k J mol^{-1}) for Bu_4NI in DMF, EMK and DMF+ EMK mixtures at different temperatures.

X_{DMF}	Temperatures 298K $\overline{V}_2^o$	ΔG_2^*	$T\Delta S^*$	ΔH^*	303K $\overline{V}_2^o$	ΔG_2^*	$T\Delta S^*$	ΔH^*	308K $\overline{V}_2^o$	ΔG_2^*	$T\Delta S^*$	ΔH^*
1.00	364.4	72.3	41.7	114.0	368.2	71.1	43.1	114.2	371.3	69.6	44.5	114.1
0.80	362.2	69.3	44.7	114.0	364.5	68.1	46.2	114.3	369.5	66.7	47.7	114.4
0.60	360.1	67.1	47.7	114.8 1	362.4	65.5	49.3	114.8	367.2	64.0	50.9	114.9
0.40	356.8	65.0	50.7	115.7	358.1	63.0	52.4	115.4	362.9	61.7	54.1	115.8
0.20	354.2	63.1	53.6	116.7	354.6	61.2	55.4	116.4	361.1	59.6	57.2	116.2
0.00	351.7	61.3	56.6	117.9	353.3	59.3	58.5	117.8	358.0	57.6	60.4	118.0

The present solvent system possesses ideal structure[20] as explained above. However, $\Delta G^*_2 > \Delta G^*_1$ for present electrolyte over the entire composition ranges suggest some structure making effect of this electrolyte. In fact, Feakens et al[6] have shown that $\Delta G^*_2 > \Delta G^*_1$ for electrolytes that are structure makers. This is found to be consistent not only with the fact that the B coefficients for Bu_4NI in dipolar-aprotic solvents [3-5,21,22], but also the fact that ΔG^*_2 decreases with rise in temperature. Similarly, the decrease in ΔG^*_2 with addition of DMF manifests the reduction in dipolar association of DMF[5, 23] on account of inter molecules interactions between DMF and EMK. Similar argument must hold well in respect of $T\Delta S^*$ values. The $T\Delta S^*$ values increase almost linearity with the increase in DMF concentration in DMF+EMK mixtures at 298, 308 and 318K. Moreover, the relative magnitude of positive ΔH^* and $T\Delta S^*$ for Bu_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 $T\Delta S^*$ values for given salt decrease1 almost regularly with the addition of DMF in the mixture over the entire solvent composition range. Scrutiny of activation parameters for Bu_4NI in DMF+ EMK system further reveals that a comparable amount of structure is disrupted in the viscous flow process by Bu_4N^+ ions, as the relative magnitude of ΔH^* and $T\Delta S^*$ values for this salt is observed to be independent of solvent composition. This is found to be consistent with the experimental fact that (i) Bu_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 Baljeet[3-4] Parker[20] and Gill[24] substantiate both these facts.

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