A Study Of Activation Parameters For Viscous Flow Process Of Tetraethyl Ammonium Bromide In Binary Mixture Of N,N-Dimethylformamide And Water

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Abstract: *Viscosities and densities of tetraethylammonium boride (Et_4NBr) in N,N-Dimethylformamide (DMF), Water (H_2O) and DMF + H_2O solvent mixtures containing 0, 20, 40, 60, 80 and 100 mol % of DMF at 298, 303 and 308K 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 (Et_4NBr) in binary mixture of DMF-water.*

I. Introduction

The study of transport properties of electrolytic solutions gives useful information regarding ion-solvent interaction[1-5]. 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].

The present investigation reports the viscosity studies of tetraethyl ammonium bromides (Et_4NBr) in N, N-Dimethylformamide (DMF), Water (H_2O) and DMF –H_2O mixtures at 298, 303 and 308 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- H_2O mixtures.

II. Materials And Methods

Tetraethyl ammonium bromide (Et_4NBr) of analytical grade, Fluka, was dried and used as described earlier[1-2]. Solvent DMF (extrapure AR grade; S D Fine Chemicals Ltd.) was purify methods reported in our previous works[1-2,7]. 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, H_2O and DMF+H_2O solvent systems were measured at 298,303 and 308K. 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 (Et4NBr) in N, N-Dimethylformamide (DMF), Water(H_2O) and DMF –H_2O mixtures containing 0, 20, 40, 50, 60, 80 and 100 mol% of DMF in the concentration range (0.01-0.22) mol dm^{-3} at 298. 303 and 308 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]:

$$\phi_V = \phi_V^o + S_V^* + C^{1/2} \qquad \text{-----(6)}$$

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:

$$\phi_V = 1000 \frac{(\rho_o - \rho)}{C \rho_o} + \frac{M_2}{\rho_o} \qquad \text{---(7)}$$

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, 303 and 308 K.

Table -1: Experimentally determined viscosity A(dm$^{2/3}$ mol$^{-1/2}$) and B(dm^3 mol^{-1}) -coefficients in DMF -Water 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	3.74	0.63	2.65	0.54	2.11	0.43	2.11	0.37	1.92	0.35	0.45	0.35
303 K	2.98	0.61	2.62	0.53	3.98	0.42	1.72	0.36	2.23	0.35	3.03	0.34
308 K	1.02	0.60	1.98	0.51	2.63	0.41	1.26	0.34	0.78	0.35	0.56	0.32

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[1-2,15]. Some authers[1,16] 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 Et$_4$NBr in DMF and H$_2$O 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[1-2,17-18].

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+H_2O mixtures. This observation fairly consistent with the viscosity studies of Prasad et al[18] in DMF+H_2O mixtures, Gill et al[19] in DMF + Ac mixtures and Baljeet et al[2] in DMF+EMK mixtures.

The present results, therefore, indicate the ideal behavior of DMF+H_2O mixtures as suggested in literature[2,18,19].

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 Et_4NBr in DMF + H_2O mixtures at 298,303 and 308 K are summarized in Table 3 and Table 4.

Table-3 Free energy of activation, ΔG_1^* (kJ mol⁻¹) and apparent molar volume, $\overline{V}_1^o$ (dm³ mol⁻¹) for DMF, H_2O and DMF+H_2O mixtures at different temperatures.

	Temperatures					
	298K		303K		308K	
X_{DMF}	$\overline{V}_1^o$	ΔG_1^*	$\overline{V}_1^o$	ΔG_1^*	$\overline{V}_1^o$	ΔG_1^*
1.00	77.39	12.5	77.77	12.6	78.12	12.6
0.80	64.96	12.8	65.63	12.8	65.70	12.8
0.60	52.74	13.2	52.95	13.1	53.21	13.1
0.40	40.69	13.4	40.89	13.3	41.09	13.1
0.20	29.16	12.8	29.28	12.6	29.39	12.5
0.00	18.07	9.16	18.10	9.03	18.13	8.91

Table 4- Activation parameters, $\overline{V}_2^o$ (dm³ mol⁻¹), ΔG_2^* (k J mol⁻¹), $T\Delta S^*$ (k J mol⁻¹) and ΔH^* (k J mol⁻¹) for Et_4NBr in DMF, H_2O and DMF+H_2O mixtures at different temperatures.

	Temperatures											
	298K				303K				308K			
X_{DMF}	$\overline{V}_2^o$	ΔG_2^*	$T\Delta S^*$	ΔH^*	$\overline{V}_2^o$	ΔG_2^*	$T\Delta S^*$	ΔH^*	$\overline{V}_2^o$	ΔG_2^*	$T\Delta S^*$	ΔH^*
1.00	152	35.1	26.82	61.92	157	34.8	27.27	62.07	160	34.2	27.72	61.92
0.80	163	38.1	29.80	67.9	163	37.1	30.30	67.40	165	36.7	30.8	67.50
0.60	160	39.4	38.74	78.14	163	38.5	39.39	77.89	166	37.9	40.04	77.94
0.40	165	43.9	47.68	91.58	168	43.1	48.48	91.58	171	42.3	48.28	90.58
0.20	168	56.2	50.66	106.86	168	55.2	51.51	106.71	171	54.5	52.36	106.86
0.00	175	78.9	56.62	135.52	175	77.4	57.57	134.97	175	77.2	58.52	135.72

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 Et_4NBr in dipolar aprotic solvents [1-2,21], 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[2, 22] on account of inter molecules interactions between DMF and H_2O. 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+H_2O mixtures at 298, 303 and 308K. Moreover, the relative magnitude of positive ΔH^* and $T\Delta S^*$ for Et_4NBr in DMF+H_2O 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 Et_4NBr in DMF+ H_2O system further reveals that a comparable amount of structure is disrupted in the viscous flow process by Et_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) Et_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 Parker[20] and Gill[23] substantiate both these facts.

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