A Study of Activation Parameters for Viscous Flow Process of Tetraalkyl Ammonium Salts in Binary Mixture of Dimethylsulphoxide and Acetone

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Abstract: Viscosities and densities of tetrabutylammonium tetraphenyl boride (Bu₄NBPh₄), sodium tetraphenyl boride (NaBPh₄), tetrapropylammonium iodide (Pr₄NI), tetrabutylammonium iodide (Bu₄NI) and tetrapentylammonium iodide (Pen₄NI) in Dimethylsulphoxide (DMSO) and Dimethylsulphoxide + Acetone solvent mixtures containing 50,60,70,80,90 and 100 mol % of DMSO at 298 and 308K have been reported. The viscosity data have been analysed in terms of 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 B-coefficients have been resolved into B_± ionic coefficients using Bu₄NBPh₄ assumptions. The B_± values of tetraalkylammonium ions are found to be positive. Partial molal volumes (\overline{V}_2°) 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 tetraalkyl ammonium salts in binary mixture of Dimethylsulphoxide and Acetone.

I. Introduction:

During recent years, there has been an increasing interest in the study of transport properties of electrolytes in mixed solvents because the use of mixed solvent enables one to study the nature of ion-ion and ion-solvent interactions under varied conditions simply by changing the solvent composition¹⁻⁶.

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.⁷

The present investigation reports the viscosity studies of some tetraalkylammonium salts in Dimethylsulphoxide (DMSO) and Dimethylsulphoxide(DMSO)-Acetone(Ac) mixtures at 298 and 308 K. The viscosity B-coefficients of these salts have been determined and resolved into ionic B_{\pm} values on the Bu_4NBPh_4 assumptions. The ionic B_{\pm} -values Pr_4N^+ , Pen_4N^+ , Ph_4B^- , Na^+ and Γ at different temperatures have been evaluated and discussed.

The viscosity B-coefficients of these electrolytes at different temperature have also been used to estimate the activation parameters for viscous flow process of these electrolytes in aforementioned mixtures. The activation parameters are true representative of the behaviour of ions in a given solution.

II. Experimental:

Dimethyl sulphoxide (extra pure, Sisco Research Laboratories Pvt. Ltd., Mumbai) was kept over Cao and distilled^{8,9} Acetone (Ac) of 99.5% purity (BDH,AR) was dried over 4Å molecular sieves and distilled^{9,10}. Sodium tetraphenylbrodie (NaBPh₄) from E. Merck, tetrapropylammonium iodide (Pr₄NI), tetrabutyl ammonium iodide (Bu₄NI) and tetrapentylammonium iodide (Pen₄NI) all from Fluka, were dried and used as described earlier ^{11,12}. Tetrabutylammonium tetrapheylboride (Bu₄NBPh₄) was synthesized by the method reported in literature ^{11,12}. The purity of sample was checked by determining its melting point ($224^{\circ}c$)^{11,12}. Viscosity measurements were carried out as described elsewhere^{1,11-13}. Viscosity values were found to be good agreement with those reported in literature^{8,12,14,15}. 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 cm³ capacity).

The viscosities and densities of the above electrolytes in DMSO and DMSO +Ac solvent systems were measured at 298 and 308 K. 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 Bu_4NBPh_4 , Pr_4NI , Bu_4NI , Pen_4NI and $NaBPh_4$ have been measured in DMSO and DMSO + Ac mixtures containing 100,90,80,70,60 and 50 mol% of DMSO in the concentration range (0.10-0.50) mol dm⁻³ for Bu_4NBPh_4 , $NaBPh_4$ and Bu_4NI and (0.10-0.50) mol dm⁻³ for Pr_4NI and Pen_4NI at 298 and 308 K. The viscosity data of present solutions were analysed by using the Jones-Dole equation¹⁶:

-----(1)

 $\eta/\eta_{o} = \eta_{r} = 1 + AC^{1/2} + BC$

arranged in the form of straight line equation as:

 $\Psi = \frac{(\eta_r - 1)}{C^{1/2}} \mathbf{A} + \mathbf{B} \mathbf{C}^{1/2}$ -----

-(2)

where η and η_o respectively, are viscosities of solution and solvent, η_r is relative viscosity of solution, A is Falkenagen Coefficient¹⁷ 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^{18} .

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

$$B = \frac{\overline{v}_{1}^{o} - \overline{v}_{2}^{o}}{1000} + \frac{\overline{v}_{1}^{o} \left[\frac{\Delta G_{2}^{o} - \Delta G_{1}^{o}}{RT}\right]}{1000} - \dots \dots (3)$$

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 equation¹⁹:

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:

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

$$\overline{V}_{1}^{0} = \frac{x_{1}M_{1} + x_{2}M_{2}}{\rho_{\text{mixt}}} \qquad -----(6)$$

where x_i refers to the mole fraction of the solvent component i, M_i is the molar mass of the solvent mixture and ρ_{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_1} apparent molar volumes of solution versus $C^{1/2}$ in accordance with Masson's emperical²⁰:

$$\phi_{V} = \phi_{V}^{0} + S_{V}^{*} + C^{1/2}$$
------(6)
where $\phi_{V}^{0} \left(= \overline{V}_{2}^{0}\right)$ 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:

$$\phi_{\rm V} = 1000 \frac{(\rho_{\rm o} - \rho)}{c\rho_{\rm o}} + \frac{M_2}{\rho_{\rm o}} ---(7)$$

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 and 308 K.

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

Mole Fraction	DMSO											
Salt	1.00		0.90		0.80		0.70		0.60		0.50	
	$Ax10^2$	В										
Temperature 298 K.												
Bu_4NBPh_4	8.48	1.44	12.38	1.43	16.07	1.43	16.63	1.43	17.74	1.44	20.97	1.44
NaBPh ₄	0.59	1.35	1.70	1.35	4.93	1.36	5.95	1.36	6.07	1.35	8.47	1.35
Pr ₄ NI	0.10	0.81	1.20	0.82	1.80	0.82	3.32	0.82	5.27	0.82	7.47	0.81
Bu ₄ NI	0.08	0.94	0.11	0.94	0.94	0.95	2.32	0.95	2.84	0.95	0.48	0.95
Pen ₄ NI	10.64	1.09	12.90	1.09	15.39	1.10	16.37	1.09	17.21	1.09	18.34	1.10
Temperature 308 K.												
Bu ₄ NBPh ₄	1.22	1.32	3.05	1.32	4.57	1.32	5.59	1.32	7.11	1.31	8.82	1.31
NaBPh ₄	3.46	1.22	5.51	1.22	6.76	1.23	8.23	1.21	9.66	1.20	1.04	1.20
Pr ₄ NI	0.14	0.70	1.31	0.71	2.52	0.72	3.94	0.72	4.81	0.72	5.70	0.72
Bu ₄ NI	1.04	0.85	2.03	0.86	3.16	0.86	4.27	0.86	5.28	0.86	6.55	0.86
Pen ₄ NI	7.42	0.93	9.72	0.92	10.97	0.93	11.60	0.92	12.96	0.92	15.22	0.91

Viscosity A-coefficients in all the cases are found to be positive. Most of the studies in pure and mixed solvents have been positive^{1,13, 21, 22}. The B-coefficients for all studied electrolytes are large and positive which is common feature for most of the non-aqueous solvents^{1,13, 23,24}. The positive B-coefficients value attributed to strong ion-solvent interaction in the system. From Table 1, it is clear that viscosity B-coefficients for all the salts decrease with rise in temperature. This found to be consistent with the work reported in literature^{13,21}. However, it is observed that B values for tatraalkylammonium salts in DMSO and DMSO + Ac mixtures follow the order: $Pr_4NI < Bu_4NI < Pen_4NI$ indicating that B- values are higher for tetraalkylammonium salt having larger cation. This may be attributed to greater electrostatic ion-solvent interaction and resistance to the movement of ion due to large size of cation. The same kind of behavior has been reported in literature¹³.

IONIC B_± VALUES OF DMSO + AC MIXTURES:

The viscosity B-coefficients values of electrolytes were resolved into ionic B_{\pm} - coefficients by method reported by Gill and Sharma²⁴ involving the following equation:

This method has been found applicable in many recent studies in binary mixtures of non-aqueous dipolar aprotic solvents^{1,13,23,24}.

In the present studies B – values of Bu₄NBPh₄ in DMSO and DMSO + Ac have been split into BPh₄B⁻ & BBu₄N⁺ values using equation (8) and (9). From the calculated B_± values of Bu₄N⁺ and Ph₄B⁻ ions, and B values of Pr₄NI, Bu₄NI, Pen₄NI and NaBPh₄, B_± values for all other ions i.e. Pr₄N⁺, Pen₄N⁺, Na⁺ and I⁻ have been calculated on the basis of additivity relationship. The calculated B_± values for Pr_4N^+ , Bu_4N^+ , Pen_4N^+ , Na^+ , I^- and Ph_4B^- at temperatures 298 and 308 K are given in table-2.

 Table-2: Experimentally determined B± -values of various ions in DMSO-Ac mixtures at different temperatures.

Mole Fracti	on of DMSO					
Ion	1.00	0.90	0.80	0.70	0.60	0.50
Temperatur	e 298 K.					
Pr_4N^+	0.52	0.52	0.51	0.51	0.52	0.51
Bu_4N^+	0.65	0.64	0.64	0.64	0.65	0.65
Pen_4N^+	0.80	0.79	0.79	0.78	0.78	0.80
Ph_4B^-	0.79	0.79	0.79	0.79	0.79	0.79
Na^+	0.56	0.56	0.57	0.57	0.56	0.56
Ľ	0.29	0.30	0.31	0.31	0.30	0.30
Temperatur	e 308 K.					
Pr_4N^+	0.44	0.44	0.45	0.45	0.45	0.45
Bu_4N^+	0.59	0.59	0.59	0.59	0.59	0.59
Pen_4N^+	0.67	0.65	0.66	0.65	0.65	0.64
Ph ₄ B ⁻	0.73	0.73	0.73	0.73	0.72	0.72
Na^+	0.49	0.49	0.50	0.48	0.48	0.48
I.	0.26	0.27	0.27	0.27	0.27	0.27

The B_+ values of tertraalkylammonium cations in DMSO at 298 K increasing in the order:

 $\frac{\text{Pen}_{4}\text{N}^{+} > \text{Bu}_{4}\text{N}^{+} > \text{Pr}_{4}\text{N}^{+}}{0.80} > 0.65$

this shows that B_+ values for these ions with the increases of tertraalkylammonium cation. For anions, B_- values have been found in the order: $Ph_4B^- > I_-$ The similar types of order has been reported in DMSO+ dioxane mixtures ²⁵ and EMK +DMF mixtures ¹³

Variations Of $B_{\pm}\text{-}Coefficients$ And Solvation Behaviour:

The solvation behaviour of ions with the help of viscosity measurement can be expressed in terms of variations of B_{\pm} - coefficients of an ions as a function of composition of mixtures. A linear change in B_{\pm} - coefficients of an ions with the change of solvent composition generally is interpreted in terms of no preferential solvation of the ions 267,27 . On the other hand, a non-linear behaviour of B_{\pm} values is refer to the preferential solvation of the ion under consideration 24 .

In the present investigation, it is found that B_{\pm} values for Pr_4N^+ , Bu_4N^+ , Pen_4N^+ , Na^+ , Γ and Ph_4B^- remains practically constant over the entire solvent composition range at 298 and 308K as shown in the table-2. However in view of pure solvation of tertraalkylammonium ions in dipolar aprotic solvents due to their large size and small surface charge density²⁴, The change in B_+ values can be attributed to the size of solvent molecules. Since the molecules size of DMSO is ca ~ 118.41Å³ and that of acetone is ca ~ 118.45Å³, the B_{\pm}

data reported in the table-2 reflects the weak preferential solvation of these ions by DMSO. This observation is found to be consistent at both the temperature.

From these viscosity results, it is calculated that Pr_4N^+ , Bu_4N^+ , Pen_4N^+ , Na^+ , I^- and Ph_4B^- show weak solvation DMSO. The poor solvation effect of these ions with DMSO in DMSO+Ac solvent system is further substantiated from the temperature dependence of B_{\pm} values is observed as temperature is increased.

Activation Parameters For Viscous Flow:

The energies of activation of viscous flow ΔG_1^* and ΔG_2^* obtained for Bu₄NBPh₄, Pr₄NI, Bu₄NI, Pen₄NI and NaBPh₄ in DMSO +Ac mixtures at 298 and 308 K are summarized in Table 3 and Table 4.

Table-3 Free energy of activation, $\Delta G_1^*(kJ \text{ mol}^{-1})$ and apparent molar volume, $\overline{V}_1^o(dm^3 \text{ mol}^{-1})$ for DMSO and DMSO+Ac mixtures at different temperatures.

Temperatures				
	298K		308K	
X _{DMSO}	\overline{V}_{1}^{o}	ΔG_1^*	\overline{V}_{1}^{o}	ΔG_1^*
1.00	71.32	48.78	71.98	50.22
0.90	71.54	48.22	72.21	49.41
0.80	71.68	47.74	72.40	48.96
0.70	71.86	47.22	72.62	48.48
0.60	72.02	46.70	72.84	47.99
0.50	72.26	46.30	73.12	47.58

Table-4 Free energy of activation, $\Delta G_2^*(kJ \text{ mol}^{-1})$ and apparent molar volume, $\overline{V}_2^0(dm^3 \text{ mol}^{-1})$ for DMSO and DMSO+Ac mixtures at different temperatures.

remperatures				
	298K		308K	
X _{DMSO}	\overline{V}_{2}^{o}	ΔG_2^*	\overline{V}_{2}^{o}	ΔG_2^*
Bu ₄ NBPh ₄	-		-	
1.00	491.23	113.39	498.86	112.35
0.90	497.67	112.50	501.06	111.42
0.80	503.98	112.10	508.47	111.07
0.70	508.82	111.59	513.69	110.59
0.60	514.86	111.47	519.74	109.76
0.50	520.84	111.06	523.68	109.23
NaBPh ₄				
1.00	292.30	103.36	295.56	101.56
0.90	291.74	102.60	294.68	100.56
0.80	291.12	102.33	294.06	100.31
0.70	290.58	101.65	293.62	98.94
0.60	289.88	100.23	293.15	97.93
0.50	289.26	100.03	292.26	97.28
Pr ₄ NI				
1.00	297.85	84.16	282.25	82.59
0.90	276.09	83.70	278.56	81.90
0.80	272.57	83.02	274.36	81.57
0.70	268.64	82.28	271.77	80.89
0.60	264.89	81.54	268.46	80.17
0.50	260.32	80.52	265.55	79.53
Bu ₄ NI				
1.00	322.18	90.15	324.18	89.42
0.90	319.08	89.34	320.56	88.51
0.80	316.23	89.02	318.34	88.07
0.70	314.08	88.32	315.89	87.38
0.60	312.24	87.64	313.60	86.69
0.50	310.32	87.04	311.15	86.03
Pen ₄ NI				
1.00	365.49	96.87	370.02	93.98
0.90	362.00	96.02	368.03	92.52
0.80	359.39	85.70	366.19	92.11
0.70	357.84	94.66	364.57	91.21
0.60	354.87	93.93	362.38	90.50
0.50	352.94	93.64	360.56	89.51

The present solvent system processes ideal structure ²⁸ as explained above. However, $\Delta G^*_2 > \Delta G^*_1$ for all electrolytes over the entire composition ranges suggest some structure making effect of these electrolytes. In fact, Feakens et al¹⁸ 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 all electrolytes in dipolar aprotic solvents ^{1,24}, but also the fact that ΔG^*_2 decreases with rise in temperature. Similarly, the decrease in ΔG^*_2 with addition of Ac manifests the reduction in dipolar association of DMSO^{1, 29} on account of inter molecules interactions between DMSO and Ac.

It is, however, interesting to observe that for Pr_4NI , Bu_4NI , ΔG^*_2 values for these electrolytes decreases in the order: $Pr_4NI < Bu_4NI < Pen_4NI$ over the entire solvent composition range at 298 and 308K. The different behaviour of these tertraalkylammonium salts must be attributed to their hydrocarbon chain length since the contribution due to Γ -ions is not significantly different²⁸.

It is also observed that ΔG_2^* for Bu₄NBPh₄ and NaBPh₄ decrease almost linearly with the increase in the concentration of Ac in the DMSO + Ac mixtures. Moreover, ΔG_2^* tends to increase with increasing the amount of DMSO in the solution. This suggests that the process of viscous flow becomes difficult as the content of DMSO in the solution Increases. This may be attributed to the strong ion-solvent interaction in the solution. Thus, the behavior of ΔG_2^* suggest that strong ion- solvent interaction exists in the salts + mixed solvent systems. It may be noted that for these salts in the present solvent systems ($\Delta G_2^* - \Delta G_1^*$) > 0. This is due to the fact that Bu₄NBPh₄ and NaBPh₄ in DMSO+Ac Mixtures behave as structure-makers. A similar conclusion is reported in literatures^{2,30}.

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References:

- [1]. Patial B S, Chauhan S, Chauhan M S & Syal V K, Ind. J. of Chem., <u>41A</u>(2002)2039.
- [2]. Alli A, Nain A K, Kumar N & Ibrahim M, Proc. Ind. Acd. Sci (Chem.Sci.), <u>114(5)</u>(2002)495.
- [3]. Anwar Ali, Sabir S & Tariq M, Acta Physico-Chemical Sinica, 23(1)(2007)79.
- [4]. Fedeles Anca, Ciocirlan O & Iulian O, Rev. Roum. Chim, <u>56(5)</u>(2011)571.
- [5]. Shaikh M, Shafique M, Agrawal B R & Faroogui M, Rasayan J Chem., <u>4(1)</u>(2011)172.
- [6]. Jha I S, Koirala R P & Adhikari D, Bibechana,<u>6</u>(2010)9.
- [7]. Feakens D, Freementle J & Lawrence K G, J. Chem. Soc. Faraday Trans 1,7(1974)795.
- [8]. Syal V K, Chauhan S & Chauhan M S, Z. Phys. Chem.(NF), <u>49</u>(1988)159.
- [9]. Syal V K, Chauhan S & Kumari U, Ind. J. Pure & Appl. Phys., <u>43</u>(2005)844.
- [10]. Reddick J A, Burger W B & Sankano T K, Tecknique in Chemistry Vol.II 4th edition(John Wiley, N.Y., 1986).
- [11]. Syal V K, Patial B S & Chauhan S, Acoust. Lett., <u>23</u>(2000)137.
- [12]. Syal V K, Patial B & Chauhan S, Ind. J. Pure and Appl. Phys.,<u>37(1999)</u>366.
- [13]. Syal V K, Bist P and Chauhan M S, Proc. Nat. Acad. Sci., India, <u>67A</u>(1977)1.
- [14]. Syal V K, Chauhan S, Katoch A & Chauhan M S, Czech. Chem. Commun., <u>56</u>(1991)803.
- [15]. Chauhan S, Syal V K & Chauhan M S, Ind. J. Pure and Appl. Phys., 32(1994)186.
- [16]. Jone G & Dole M, J. Am. Chem. Soc., <u>51</u>(1929)2950.
- [17]. Falkenhagen H & Dole M, Phys. Z., <u>30</u>(1929)611; Falkenhagen H and Vernon E L, Phys. Z.<u>33</u>(1932)140.
- [18]. Feakins D, Freemantle D J & Lawrennce K G, J. Chem. Soc., Faraday Trans 1, 70(1974)795.
- [19]. Glasston S, Laider K J & Erying H, The Theory Process (Mcgraw-Hill,NewYork)(1941)477.
- [20]. Masson D O, Philos. Mag.8(1929)218.
- [21]. Gill D S & Singh B, J. Chem.Soc. Faraday Trans.1,<u>84</u>(1988)4417.
- [22]. Jauhar S P, Banait J S, Guruya P S & Narula S P, Ind. J. Chem., 19A(1980)797.
- [23]. Gill D S & Chauhan M S, Z. Phys. Chem.(N.F.),<u>140</u>(1984)149.
- [24]. Gill D S & A N Sharma, J. Chem. Soc. Faraday Trans.1,78(1982)475.
- [25]. Syal V K, Bisht P & Ranowt P C, Collect. Czech. Chem. Commun.,56(1991)1813.
- [26]. Gill D S & Cheema J S, Z. Phys. Chem.(N.F.),<u>134</u>(1983)205.
- [27]. Syal V K, Chauhan S & Chauhan M S, Ind. J. Chem., <u>29A</u>(1990)693.
- [28]. Parker A J, Chem. Rev., <u>69</u>(1969)1; Quart. Rev., <u>16</u>(1962)163.
- [29]. Choi Y S, Huh Y D & Bonner O D, Spectrochem. Acta Part A, <u>41</u>(1985)1127.
- [30]. Kannappan A N & Rajendran V, Ind. J. Phys., <u>B66</u> (1992)135.