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 (Bu₄NB₄Ph₄), sodium tetraphenyl boride (NaB₄Ph₄), tetraropropylammonium 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 308 K 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 Bₐ ionic coefficients using Bu₄NB₄Ph₄ assumptions. The Bₐ values of tetraalkynammonium ions are found to be positive. Partial molal volumes (\(\bar{\nu}_m\)) 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 composition

Viscosity studies of electrolytic solutions in mixed solvent systems is one of the most fundamental transport properties that play a vital role in understanding the solution behavior of the electrolytes.

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 Bₐ values on the Bu₄NB₄Ph₄ assumptions. The ionic Bₐ values of Pr₄NI, Bu₄NI, Pen₄NI, NaB₄Ph₄, Ph₃B⁺, Na⁺ and I⁻ 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. Acetone (Ac) of 99.5% purity (BDH,AR) was dried over 4Å molecular sieves and distilled. Sodium tetraphenylboride (NaB₄Ph₄) from E. Merck, tetraropropylammonium iodide (Pr₄NI), tetrabutyl ammonium iodide (Bu₄NI) and tetraropropylammonium iodide (Pen₄NI) all from Fluka, were dried and used as described earlier. Tetrabutylammonium tetraphenylboride (Bu₄NB₄Ph₄) was synthesized by the method reported in literature. The purity of sample was checked by determining its melting point (224°C). Viscosity measurements were carried out as described elsewhere. Viscosity values were found to be in good agreement with those reported in literature. 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 electrolytes at different temperature were measured at 298 and 308 K. 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 Bu₄NB₄Ph₄, Pr₄NI, Bu₄NI, Pen₄NI and NaB₄Ph₄ 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 Bu₄NB₄Ph₄, NaB₄Ph₄ and Bu₄NI and (0.10-0.50) mol dm⁻³ for Pr₄NI and Pen₄NI at 298 and 308 K. The viscosity data of present solutions were analysed by using the Jones-Dole equation.
\[ \eta/\eta_o = \eta_1 + AC^{1/2} + BC \]

arranged in the form of straight line equation as:
\[ \Psi = \frac{(\eta_t - 1)}{C^{1/2}} A + BC^{1/2} \]

-(2)

where \( \eta \) and \( \eta_o \), respectively, are viscosities of solution and solvent, \( \eta_t \) is relative viscosity of solution, A is Falkenagen Coefficient\(^7\) 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\(^8\).

According to theory, viscosity B-coefficient is given as:
\[ B = \frac{\nabla_1^o - \nabla_2^o}{1000} + \frac{\nabla_1^o [\Delta G_1^o + \Delta G_2^o]}{1000RT} \]

--------(3)

where \( \nabla_1^o \) and \( \nabla_2^o \) are the partial molar volumes of the solvent and solute respectively, \( \Delta G_1^o \) and \( \Delta G_2^o \) are the free energy activation for viscous flow per mole of pure solvent and solute solution respectively.

The free energy activation, \( \Delta G_1^o \), for viscous flow process per mole of pure solvent system is estimated using Erying’s equation\(^10\):
\[ \Delta G_1^o = RT \ln(\eta_1^o) + hN \]

---------(4)

where R, h and N are gas constant, Planck’s constant respectively, \( \eta_1^o \) is the molar volume mass of the solvent and T is the absolute temperature.

\( \Delta G_2^o \), the free energy activation for viscous flow per mole of pure solvent is derived from equation (3) as:
\[ \Delta G_2^o = \Delta G_1^o + \left(\frac{RT}{\nabla_1^o}\right)\left[1000B - \left(\nabla_1^o - \nabla_2^o\right)\right] \]

---------(5)

The molar volume \( \nabla_1^o \), of the pure solvent system has been determined from the relation:
\[ \nabla_1^o = \frac{z_1^o M_1 + z_2^o M_2}{\rho_{mix}} \]

-------------------(6)

where \( z_i \) refers to the mole fraction of the solvent component i, \( M_i \) is the molar mass of the solvent mixture and \( \rho_{mix} \) is the density of the mixture.

The values of the partial molar volume, \( \nabla_2^o \) of solute solution are obtained by the use of least square treatment to the plots of the use of \( \phi \), apparent molar volumes of solution versus C\(^{1/2}\) in accordance with Masson’s empirical\(^5\):
\[ \phi_1^o = \phi_2^o + S_2^o + C^{1/2} \]

---------(6)

where \( \phi_2^o \) (\( = \nabla_2^o \)) is the partial molar volume of the solution and \( S_2^o \) is the experimental slope.

The apparent molar volume, \( \phi \), is calculated from the density data by using flowing expression:
\[ \phi_1 = 1000 \left(\frac{\rho_t - \rho}{\rho_0 - \rho}\right) + \frac{M_2}{\rho_0} \]

---------(7)

where \( \rho_t \) and \( \rho \) are densities of solvent and solution, respectively, C is molar concentration of electrolyte and M\(_2\) is its molecular weight.

The plots of \( \Psi = (\eta/\eta_o) - 1/C^{1/2} \) 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.

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

<table>
<thead>
<tr>
<th>Salt</th>
<th>Mole Fraction of DMSO</th>
<th>Temperature 298 K.</th>
<th>0.10</th>
<th>0.08</th>
<th>0.07</th>
<th>0.10</th>
<th>0.08</th>
<th>0.07</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.00</td>
<td>Ax10(^3) B</td>
<td>Ax10(^3) B</td>
<td>Ax10(^3) B</td>
<td>Ax10(^3) B</td>
<td>Ax10(^3) B</td>
<td>Ax10(^3) B</td>
<td>Ax10(^3) B</td>
</tr>
<tr>
<td>BuNBPh(_6)</td>
<td>8.48</td>
<td>1.44</td>
<td>12.38</td>
<td>1.43</td>
<td>16.07</td>
<td>1.43</td>
<td>16.63</td>
<td>1.43</td>
</tr>
<tr>
<td>NaBPh(_4)</td>
<td>0.59</td>
<td>1.35</td>
<td>1.70</td>
<td>1.35</td>
<td>4.93</td>
<td>1.36</td>
<td>5.95</td>
<td>1.36</td>
</tr>
<tr>
<td>PrNJ</td>
<td>0.10</td>
<td>0.81</td>
<td>1.20</td>
<td>0.82</td>
<td>1.80</td>
<td>0.82</td>
<td>3.32</td>
<td>0.82</td>
</tr>
<tr>
<td>BuNJ</td>
<td>0.08</td>
<td>0.94</td>
<td>0.11</td>
<td>0.94</td>
<td>0.94</td>
<td>0.95</td>
<td>2.32</td>
<td>0.95</td>
</tr>
<tr>
<td>PenNJ</td>
<td>1.06</td>
<td>1.09</td>
<td>12.90</td>
<td>1.09</td>
<td>15.39</td>
<td>1.10</td>
<td>16.37</td>
<td>1.09</td>
</tr>
<tr>
<td>Temperature 308 K.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BuNBPh(_6)</td>
<td>1.22</td>
<td>1.32</td>
<td>3.05</td>
<td>1.32</td>
<td>4.57</td>
<td>1.32</td>
<td>5.59</td>
<td>1.32</td>
</tr>
<tr>
<td>NaBPh(_4)</td>
<td>3.46</td>
<td>1.22</td>
<td>5.51</td>
<td>1.22</td>
<td>6.76</td>
<td>1.23</td>
<td>8.23</td>
<td>1.21</td>
</tr>
<tr>
<td>PrNJ</td>
<td>0.14</td>
<td>0.70</td>
<td>1.31</td>
<td>0.71</td>
<td>2.52</td>
<td>0.72</td>
<td>3.94</td>
<td>0.72</td>
</tr>
<tr>
<td>BuNJ</td>
<td>1.04</td>
<td>0.85</td>
<td>2.03</td>
<td>0.86</td>
<td>3.16</td>
<td>0.86</td>
<td>4.27</td>
<td>0.86</td>
</tr>
<tr>
<td>PenNJ</td>
<td>7.42</td>
<td>0.93</td>
<td>9.72</td>
<td>0.92</td>
<td>10.97</td>
<td>0.93</td>
<td>11.60</td>
<td>0.92</td>
</tr>
</tbody>
</table>

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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.15,21 However, it is observed that B values for tetraalkylammonium salts in DMSO and DMSO + Ac mixtures follow the order: Pr₅NI < Bu₄NI < Pen₅NI 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 literature.13

**IONIC B VALUES OF DMSO + AC MIXTURES:**

The viscosity B-coefficients values of electrolytes were resolved into ionic B±-coefficients by method reported by Gill and Sharma24 involving the following equation:

\[
\begin{align*}
\text{B Ph₄B}^- + \text{B Bu₄N}^+ & = \text{B Bu₄NBPh₄}^- \\
\text{B Bu₄B}^- + \text{B Bu₄N}^+ & = \text{B Bu₄N}^+ + \text{B Bu₄N}^+ \\
\end{align*}
\]

This method has been found applicable in many recent studies in binary mixtures of non-aqueous dipolar aprotic solvents.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 Bu₄N¹ and Ph₄B ions, and B values of Pr₅NI, Bu₄NI, Pen₅NI and NaBPh₄, B± values for all other ions i.e. Pr₅N¹, Pen₅N¹, Na⁺ and I⁻ have been calculated on the basis of additivity relationship. The calculated B± values for Pr₅N¹, Bu₄N¹, Pen₅N¹, Na⁺ , I⁻ and Ph₄B⁻ 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.

<table>
<thead>
<tr>
<th>Mole Fraction of DMSO</th>
<th>Ion</th>
<th>0.00</th>
<th>0.05</th>
<th>0.10</th>
<th>0.20</th>
<th>0.30</th>
<th>0.50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature 298 K.</td>
<td>Pr₅N¹</td>
<td>0.52</td>
<td>0.65</td>
<td>0.79</td>
<td>0.59</td>
<td>0.67</td>
<td>0.73</td>
</tr>
<tr>
<td>Bu₄N¹</td>
<td>0.90</td>
<td>0.79</td>
<td>0.79</td>
<td>0.79</td>
<td>0.79</td>
<td>0.79</td>
<td>0.79</td>
</tr>
<tr>
<td>Pen₅N¹</td>
<td>0.80</td>
<td>0.79</td>
<td>0.79</td>
<td>0.79</td>
<td>0.79</td>
<td>0.79</td>
<td>0.79</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
</tr>
<tr>
<td>I⁻</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
</tbody>
</table>

| Temperature 308 K.     | Pr₅N¹ | 0.44 | 0.59 | 0.67 | 0.73 | 0.49 | 0.26 |
| Bu₄N¹                 | 0.44 | 0.59 | 0.67 | 0.73 | 0.50 | 0.27 | 0.27 |
| Pen₅N¹                | 0.44 | 0.59 | 0.67 | 0.73 | 0.48 | 0.27 | 0.27 |
| Na⁺                   | 0.44 | 0.59 | 0.67 | 0.73 | 0.48 | 0.27 | 0.27 |
| I⁻                    | 0.44 | 0.59 | 0.67 | 0.73 | 0.48 | 0.27 | 0.27 |

The B± values of tetraalkylammonium cations in DMSO at 298 K increasing in the order:

Pr₅N¹ > Bu₄N¹ > Pen₅N¹

0.80 > 0.65 > 0.52

this shows that B± values for these ions with the increases of tetraalkylammonium cation.

For anions, B± values have been found in the order: Ph₄B⁻ > I⁻. The similar types of order has been reported in DMSO+ dioxane mixtures and EMK +DMF mixtures.24

**Variations Of B±-Coefficients And Solvation Behaviour:**

The solvation behaviour of ions with the help of viscosity measurement can be expressed in terms of variations of B±-coefficients of an ions as a function of composition of mixtures. A linear change in B±-coefficients of an ions with the change of solvent composition generally is interpreted in terms of no preferential solvation of the ions.26,27 On the other hand, a non-linear behaviour of B± values is refer to the preferential solvation of the ion under consideration.24

In the present investigation, it is found that B± values for Pr₅N¹, Bu₄N¹, Pen₅N¹, Na⁺, I⁻ and Ph₄B⁻ 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 tetraalkylammonium ions in dipolar aprotic solvents due to their large size and small surface charge density.24 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±...
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 Pr₄N⁺, Bu₄N⁺, Pen₄N⁺, Na⁺, I⁻ and Ph₃B⁻ 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 $B_2$ values is observed as temperature is increased.

**Activation Parameters For Viscous Flow:**

The energies of activation of viscous flow $\Delta G_1^*$ and $\Delta G_2^*$ 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, $\Delta G_1^*(kJ mol^{-1})$ and apparent molar volume, $\tilde{V}_1(dm^3 mol^{-1})$ for DMSO and DMSO+Ac mixtures at different temperatures.

<table>
<thead>
<tr>
<th>X_DMSO</th>
<th>298K</th>
<th>308K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta G_1^*$</td>
<td>$\Delta G_2^*$</td>
</tr>
<tr>
<td>1.00</td>
<td>491.23</td>
<td>498.86</td>
</tr>
<tr>
<td>0.90</td>
<td>497.67</td>
<td>501.06</td>
</tr>
<tr>
<td>0.80</td>
<td>503.98</td>
<td>508.47</td>
</tr>
<tr>
<td>0.70</td>
<td>508.82</td>
<td>513.69</td>
</tr>
<tr>
<td>0.60</td>
<td>514.86</td>
<td>519.74</td>
</tr>
<tr>
<td>0.50</td>
<td>520.84</td>
<td>523.68</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>X_DMSO</th>
<th>298K</th>
<th>308K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta G_2^*$</td>
<td>$\tilde{V}_2$</td>
</tr>
<tr>
<td>1.00</td>
<td>491.23</td>
<td>498.86</td>
</tr>
<tr>
<td>0.90</td>
<td>497.67</td>
<td>501.06</td>
</tr>
<tr>
<td>0.80</td>
<td>503.98</td>
<td>508.47</td>
</tr>
<tr>
<td>0.70</td>
<td>508.82</td>
<td>513.69</td>
</tr>
<tr>
<td>0.60</td>
<td>514.86</td>
<td>519.74</td>
</tr>
<tr>
<td>0.50</td>
<td>520.84</td>
<td>523.68</td>
</tr>
</tbody>
</table>

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 al 18 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 1,2,4, but also the fact that $\Delta G_2^*$ decreases with rise in temperature. Similarly, the decrease in $\Delta G_2^*$ with addition of Ac manifests the reduction in dipolar association of DMSO1,2,4 on account of inter molecules interactions between DMSO and Ac.
It is, however, interesting to observe that for Pr\(_2\)NI, Bu\(_2\)NI, \(\Delta G^{*}\) values for these electrolytes decreases in the order: Pr\(_2\)NI < Bu\(_2\)NI < Pen\(_2\)NI over the entire solvent composition range at 298 and 308K. The different behaviour of these tetraalkylammonium salts must be attributed to their hydrocarbon chain length since the contribution due to I - ions is not significantly different\(^{28}\).

It is also observed that \(\Delta G^{*}\) for Bu\(_4\)NBPh\(_4\) and NaBPh\(_4\) decrease almost linearly with the increase in the concentration of Ac in the DMSO + Ac mixtures. Moreover, \(\Delta G^{*}\) 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 \(\Delta G^{*}\) 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 (\(\Delta G^{*} - \Delta G^{*1}\)) > 0 .This is due to the fact that Bu\(_4\)NBPh\(_4\) and NaBPh\(_4\) in DMSO+Ac Mixtures behave as structure-makers. A similar conclusion is reported in literatures\(^{30}\).

Acknowledgement:
The author thanks University Grant Commission, New Delhi for the sanction of Minor Research Project.

References: