



where  $\eta$  and  $\eta_0$  respectively, are viscosities of solution and solvent,  $\eta_r$  is relative viscosity of solution, A is Falkenagen Coefficient<sup>11</sup> 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.<sup>6</sup>. According to theory, viscosity B-coefficient is given as:

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0 \left[ \frac{\Delta G_2^* - \Delta G_1^*}{RT} \right]}{1000} \quad \text{-----(3)}$$

where  $\bar{V}_1^0$  and  $\bar{V}_2^0$  are the partial molar volumes of the solvent and solute respectively,  $\Delta G_1^*$  and  $\Delta G_2^*$  are the free energy activation for viscous flow per mole of pure solvent and solute solution respectively. The free energy activation,  $\Delta G_1^*$  for viscous flow process per mole of pure solvent system is estimated using Eyring's equation<sup>12</sup>:

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

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.

$\Delta G_2^*$ , 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  $\phi_v$ , apparent molar volumes of solution versus  $C^{1/2}$  in accordance with Masson's empirical<sup>13</sup>:

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

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

The apparent molar volume,  $\phi_v$  is calculated from the density data by using following expression:

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

where  $\rho_0$  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  $\psi (= (\eta/\eta_0 - 1)/C^{1/2})$  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<sup>2/3</sup> mol<sup>-1/2</sup>) and B(dm<sup>3</sup> mol<sup>-1</sup>) -coefficients of Pen<sub>4</sub>Ni 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 <sup>2</sup>	B	Ax10 <sup>2</sup>	B	Ax10 <sup>2</sup>	B	Ax10 <sup>2</sup>	B	Ax10 <sup>2</sup>	B	Ax10 <sup>2</sup>	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<sup>3-5,14</sup>. Some authors<sup>15-16</sup> have also reported negative A-coefficients. But it has been suggested that negative A-coefficient have no physical significance<sup>17</sup> and may have arisen due to some systematic error in viscosity measurements. Comparing B- values reported in Table 1 for Pen<sub>4</sub>Ni 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<sup>3-5</sup>. 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<sup>18</sup> and Baljeet et al<sup>3</sup> in DMF+H<sub>2</sub>O mixtures, Gill

et al<sup>19</sup> in DMF + Ac mixtures and Baljeet et al<sup>5</sup> in DMF+EMK mixtures.

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

The activation parameters for viscous flow process, like  $\Delta H^*$ ,  $T\Delta S^*$  and  $\Delta G_2^*$  obtained for Pen<sub>4</sub>Ni in DMF + EMK mixtures at 298, 308 and 318 K are summarized in Table-2 and Table-3.

**Table 2:** Free energy of activation,  $\Delta G_1^*$  (kJ mol<sup>-1</sup>) and apparent molar volume,  $\bar{V}_1^\circ$  (dm<sup>3</sup> mol<sup>-1</sup>) for DMF, EMK and DMF+EMK mixtures at different temperatures

X <sub>DMF</sub>	Temperatures					
	298K		308K		318K	
	$\bar{V}_1^\circ$	$\Delta G_1^*$	$\bar{V}_1^\circ$	$\Delta G_1^*$	$\bar{V}_1^\circ$	$\Delta G_1^*$
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,  $\bar{V}_2^\circ$  (dm<sup>3</sup> mol<sup>-1</sup>),  $\Delta G_2^*$  (kJ mol<sup>-1</sup>),  $T\Delta S^*$  (kJ mol<sup>-1</sup>) and  $\Delta H^*$  (kJ mol<sup>-1</sup>) for Pen<sub>4</sub>Ni in DMF, EMK and DMF+ EMK mixtures at different temperatures.**

X <sub>DMF</sub>	Temperatures											
	298K				303K				308K			
	$\bar{V}_2^\circ$	$\Delta G_2^*$	$T\Delta S^*$	$\Delta H^*$	$\bar{V}_2^\circ$	$\Delta G_2^*$	$T\Delta S^*$	$\Delta H^*$	$\bar{V}_2^\circ$	$\Delta G_2^*$	$T\Delta S^*$	$\Delta H^*$
1.00	439.2	77.1	41.7	118.8	444.9	76.1	43.1	119.2	450.2	74.3	44.5	118.8
0.80	436.3	74.4	53.6	128.0	444.5	72.8	55.4	128.2	447.4	70.9	57.2	128.1
0.60	435.3	72.4	65.6	138.0	440.6	70.1	67.8	137.9	444.1	68.0	70.0	138.0
0.40	433.3	70.2	68.5	138.7	438.9	67.2	70.8	138.0	443.4	65.6	73.1	138.7
0.20	429.1	68.0	77.5	145.5	436.5	64.9	80.1	145.0	441.7	62.9	82.7	145.6
0.00	427.1	65.9	80.5	146.4	434.2	62.9	83.2	146.1	439.7	60.9	85.9	146.8

$\phi_v^\circ (= \bar{V}_2^\circ)$  is a measure of ion-solvent interaction. It is evident from the table-3 that  $\bar{V}_2^\circ$  values are large positive for Pen<sub>4</sub>Ni in EMK+DMF mixtures, suggesting the presence of strong ion-solvent interactions. Small decrease in  $\bar{V}_2^\circ$  as the amount of EMK in the solution indicates the decreasing trend of ion-solvent interaction. The present solvent system possesses ideal structure<sup>20</sup> 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<sup>6</sup> 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 Pen<sub>4</sub>Ni in dipolar-aprotic solvents<sup>3-5,21,22</sup>, but also the fact that  $\Delta G_2^*$  decreases with rise in temperature. Similarly, the decrease in  $\Delta G_2^*$  with addition of EMK manifests the reduction in dipolar association of DMF<sup>5,23</sup> 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  $\Delta H^*$  and  $T\Delta S^*$  for Pen<sub>4</sub>Ni 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  $\Delta H^*$  and  $T\Delta S^*$  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 Pen<sub>4</sub>Ni in DMF+ EMK system further reveals that a comparable amount of structure is disrupted in the viscous flow process by Pen<sub>4</sub>N<sup>+</sup> ions, as the relative magnitude of  $\Delta H^*$  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) Pen<sub>4</sub>N<sup>+</sup> 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<sup>3-4</sup> Parker<sup>20</sup> and Gill<sup>24</sup> substantiate both these facts.

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