Density and Viscosity of Tetrakethyl Ammonium Iodide in Binary Mixture of N, N-imethylformamide and Ethylmethylketone at Different Temperatures.

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Abstract: Density (ρ) and Viscosities (η) of tetrakethylammonium iodide (Pen₄NI) 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 experimental values of Density (ρ) and Viscosities (η) were used to calculate the values of the apparent molar volume (ϕₐ), partial molar volume (ϕₚ), 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 activation parameters have been examined as a function of solvent composition to interpret the solution behaviour of tetraketyl ammonium bromide (Pen₄NI) in binary mixture of DMF-EMK. The behaviour of these suggests strong ion-solvent interactions in these systems and that Pen₄NI act as structure-maker in EMK+DMF mixed solvents.

Keywords: Density, viscosity, apparent molar volume, partial volume, B-coefficients, tetrakethylammonium iodide, DMF and EMK

1. Introduction

The density is one of the key thermodynamic properties of electrolyte solutions and belongs with an equilibrium property, while the viscosity is one of the key transport properties of electrolyte solutions and belongs with a dynamic state property. Both of them rein dispensable basic data to engineering design and process optimization. Knowledge of viscometric studies in binary solvent system is useful for engineering design of new applications. Viscosities are important physic-chemical parameters widely studied in aqueous, aqueous-organic, and others. The density and viscosity are important basic data used in chemical engineering designs, solution theory, and molecular thermodynamics. Physicochemical processes of electrolyte solutions are of considerable interest due their importance in numerous industrial processes. Extensive experimental viscosity data are available for mixed-solvent system. In mixed solvent electrolyte solutions, viscosity is affected by the concentration of electrolytes but also by the composition of the solvent. Even the viscosity of solvent mixtures may show a complex behavior and change significantly with composition. The knowledge of Physico-chemical properties of liquid mixtures of two or more components are of theoretical and industrial importance due to their wide range of applicability as solvent media in various physic-chemical process.

In the present study, density (ρ) and viscosity (η) of tetrakethyl ammonium iodide (Pen₄NI) in N,N-dimethylformamide (DMF), ethylmethylketone (EMK) and DMF+EMK mixtures at 298, 308 and 318 K have been measured. Experimental values of ρ and η were used to calculate the apparent molar volume (ϕₐ), limiting apparent molar volume (ϕₚ), A- and B- coefficient of Jones-Dole equation. 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.

2. Materials and Methods

Tetrakethyl ammonium bromide (Pen₄NI) of analytical grade, Fluka, was dried and used as described earlier. Both Solvents, EMK and DMF (extra pure AR grade; S D Fine Chemicals Ltd.) were purify by the methods reported in our previous works. Viscosity measurements were carried out as described elsewhere. Viscosity values were found to be good agreement with those reported in literature. 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 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.

3. Results and Discussion

Densities and viscosities of tetrakethyl ammonium bromides (Pen₄NI) 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:

\[ \frac{\eta}{\eta_0} = 1 + AC^{1/2} + BC \]

arranged in the form of straight line equation as:

\[ \Psi = \frac{[\eta/\eta_0 - 1]}{C^{1/2}} A + BC^{1/2} \]

where \( A \) and \( B \) are characteristic parameters for the given electrolyte and \( C \) is concentration.

The overall accuracy of the viscosity and density measurements in this study was estimated to be ± 0.2% and ± 0.1% respectively.
where $\eta$ and $\eta_0$ respectively, are viscosities of solution and solvent, $\eta_i$ is relative viscosity of solution, A is Falkenagen Coefficient 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. According to theory, viscosity B-coefficient is given as:

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\rho_m}{1000} \left[ \frac{\Delta G^v_1 - \Delta G^v_2}{RT} \right] \quad ------(3)$$

where $\bar{V}_1^0$ and $\bar{V}_2^0$ are the partial molar volumes of the solvent and solute respectively, $\Delta G^v_1$ and $\Delta G^v_2$ are the free energy activation for viscous flow per mole of pure solvent and solute solution respectively. The free energy activation, $\Delta G^v_1$ for viscous flow process per mole of pure solvent system is estimated using Eyring’s equation:

$$\Delta G^v_1 = RT \ln(\eta \bar{V}_1^0 / \eta N) \quad ------(4)$$

where $R$, $h$ and $N$ are gas constant, Planck’s constant respectively, and $\bar{V}_1^0$ is the molar volume mass of the solvent and T is the absolute temperature.

$\Delta G^v_2$, the free energy activation for viscous flow per mole of pure solvent is derived from equation (3) as:

$$\Delta G^v_2 = \Delta G^v_1 + \left( \frac{RT}{\eta^2} \right) \left[ 1000B - \left( \bar{V}_1^0 - \bar{V}_2^0 \right) \right] \quad ------(5)$$

The molar volume $\bar{V}_2^0$, of the pure solvent system has been determined from the relation:

$$\bar{V}_2^0 = \frac{x_1M_1 + x_2M_2}{\rho_{mixt}} \quad ------(6)$$

where $x_i$ refers to the molar 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:

$$\phi_v = \frac{\phi_v^0 + S \psi + C^{1/2}}{12} \quad ------(7)$$

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

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

$$\phi_v = \frac{4900(\eta - \eta_0)}{\rho_0} + \frac{M_2}{\rho_0} \quad ------(8)$$

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 $\psi = \left( \eta/\eta_0 - 1 \right) / C^{1/2}$ 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>
<thead>
<tr>
<th>Table 1: Experimentally determined viscosity A(dm$^{3}$/mol$^{1/2}$) and B(dm$^{3}$/mol$^{-1}$) -coefficients of Pen$_4$NI in DMF - EMK mixtures at different temperatures.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole Fraction of DMF</td>
</tr>
<tr>
<td>Temperatures</td>
</tr>
<tr>
<td>-------------</td>
</tr>
<tr>
<td>Ax$10^{-3}$</td>
</tr>
<tr>
<td>298 K</td>
</tr>
<tr>
<td>308 K</td>
</tr>
<tr>
<td>318 K</td>
</tr>
</tbody>
</table>

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. Some authors have also reported negative A-coefficients. But it has been suggested that negative A-coefficient have no physical significance and may have arisen due to some systematic error in viscosity measurements. Comparing B- values reported in Table 1 for Pen$_4$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. 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 and Baljeet et al in DMF+H$_2$O mixtures, Gill.
et al\textsuperscript{19} in DMF + Ac mixtures and Baljeet et al\textsuperscript{5} in DMF+EMK mixtures.

The present results, therefore, indicate the ideal behavior of DMF + EMK mixtures as suggested in literature\textsuperscript{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 literature\textsuperscript{18}.

Table 2: Free energy of activation, $\Delta G^\circ_2$ (kJ mol$^{-1}$) and apparent molar volume, $\bar{V}_1^\circ$ (dm$^3$ mol$^{-1}$) for DMF, EMK and DMF+EMK mixtures at different temperatures

<table>
<thead>
<tr>
<th>$X_{DMF}$</th>
<th>298K</th>
<th>308K</th>
<th>318K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{V}_1^\circ$</td>
<td>$\Delta G^\circ_2$</td>
<td>$\bar{V}_1^\circ$</td>
</tr>
<tr>
<td>1.00</td>
<td>77.4</td>
<td>23.9</td>
<td>79.0</td>
</tr>
<tr>
<td>0.80</td>
<td>79.8</td>
<td>23.6</td>
<td>81.5</td>
</tr>
<tr>
<td>0.60</td>
<td>82.2</td>
<td>23.4</td>
<td>84.1</td>
</tr>
<tr>
<td>0.40</td>
<td>84.7</td>
<td>23.1</td>
<td>86.8</td>
</tr>
<tr>
<td>0.20</td>
<td>87.4</td>
<td>22.8</td>
<td>89.7</td>
</tr>
<tr>
<td>0.00</td>
<td>90.2</td>
<td>22.5</td>
<td>92.9</td>
</tr>
</tbody>
</table>

Table 3- Activation parameters, $\bar{V}_2^\circ$ (dm$^3$ mol$^{-1}$), $\Delta G^\circ_2$ (kJ mol$^{-1}$), $T\Delta S^\circ$ (k J mol$^{-1}$) and $\Delta H^\circ$ (kJ mol$^{-1}$) for Pen$_4$NI in DMF, EMK and DMF+ EMK mixtures at different temperatures.

<table>
<thead>
<tr>
<th>$X_{DMF}$</th>
<th>298K</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{V}_2^\circ$</td>
<td>$\Delta G^\circ_2$</td>
<td>$T\Delta S^\circ$</td>
</tr>
<tr>
<td>1.00</td>
<td>439.2</td>
<td>77.1</td>
<td>41.7</td>
</tr>
<tr>
<td>0.80</td>
<td>436.3</td>
<td>74.4</td>
<td>53.6</td>
</tr>
<tr>
<td>0.60</td>
<td>435.3</td>
<td>72.4</td>
<td>65.6</td>
</tr>
<tr>
<td>0.40</td>
<td>433.3</td>
<td>70.2</td>
<td>68.5</td>
</tr>
<tr>
<td>0.20</td>
<td>429.1</td>
<td>68.0</td>
<td>77.5</td>
</tr>
<tr>
<td>0.00</td>
<td>427.1</td>
<td>65.9</td>
<td>80.5</td>
</tr>
</tbody>
</table>

$\phi^\circ$ ($\bar{V}_2^\circ$) 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$_4$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\textsuperscript{20} as explained above. However, $\Delta G^\circ_2 > \Delta G^\circ_1$ for present electrolyte over the entire composition ranges suggest some structure making effect of this electrolyte. In fact, Feakens et al\textsuperscript{18} have shown that $\Delta G^\circ_2 > \Delta G^\circ_1$ for electrolytes that are structure makers. This is found to be consistent not only with the fact that the B coefficients for Pen$_4$NI in dipolar-aprotic solvents\textsuperscript{3,5,18,22}, but also the fact that $\Delta G^\circ_2$ decreases with rise in temperature. Similarly, the decrease in $\Delta G^\circ_2$ with addition of EMK manifests the reduction in dipolar association of DMF\textsuperscript{5,13} on account of inter molecules interactions between DMF and EMK. Similar argument must hold well in respect of $T\Delta S^\circ$ values. The $T\Delta S^\circ$ values increase almost linearly with the increase in DMF concentration in DMF+EMK mixtures at 298, 308 and 318K. Moreover, the relative magnitude of positive $\Delta H^\circ$ and $T\Delta S^\circ$ for Pen$_4$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 $\Delta H^\circ$ and $T\Delta S^\circ$ 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$_4$NI in DMF+EMK system further reveals that a comparable amount of structure is disrupted in the viscous flow process by Pen$_4$N$^+$ ions, as the relative magnitude of $\Delta H^\circ$ and $T\Delta S^\circ$ 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$_4$N$^+$ 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\textsuperscript{3,4} Parker\textsuperscript{20} and Gill\textsuperscript{23} substantiate both these facts.

References