Viscosity and thermodynamic studies of interaction in concentrated aqueous mixed electrolyte solutions

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Viscosities and densities of solutions of electrolytes at different molalities have been measured at 298.15 K. The values of apparent molal volume, \( \phi \), relative viscosity \( (\eta_{rel}) \) and free energy of activation \( \Delta \mu \) have been deduced from density and viscosity data. Results show that (i) these are short range and weak interactions in these systems, (ii) ions such as Na\(^+\), K\(^+\), Mg\(^2+\), Ba\(^2+\), NO\(_3\), SO\(_4\), CH\(_3\)COO\(^-\), and Cl\(^-\) are structure makers in water in the order Na\(^+\) > Mg\(^2+\) > K\(^+\) > Ba\(^2+\) > Cl\(^-\) > CH\(_3\)COO\(^-\) > NO\(_3\) > SO\(_4\)^-. The studies of thermodynamic properties of aqueous solutions at 298.15 K. The density and viscosity of concentrated mixed solutions have been measured with the help of pyknometer and Ostwald type viscometer. The density and viscosity of these solutions were measured at the same temperature by calibrated way using thermostatic—bath. The density and viscosity data were found to be accurate within ± 0.1 g m\(^{-3}\) and ± 0.1 g m\(^{-3}\) s\(^{-1}\) respectively.

The apparent molal volume, \( \phi \), has been calculated from equation (1)

\[
\phi_v = \left(1000/m \rho^0\right)(\rho^0/\rho) + \dot{M}/\rho^0 \quad \ldots (1)
\]

where, \( \rho \) and \( \rho^0 \) are the densities of solutions and solvent respectively and \( m \) is the molality of the solutions. \( \dot{M} \) is the effective molecular weight of the solution given by

\[
\dot{M} = n_1M_1 + n_2M_2 + n_3M_3/n_1 + n_2 + n_3 \quad \ldots (2)
\]

\[
\eta_{rel} = \eta/\eta^0 = 1 + Am^{1/2} + Bm \quad \ldots (3)
\]

where, \( \eta_{rel} \) is the relative viscosity of electrolytic solutions. A and B are the Falkenhagen\(^5\) and Jones-Dole coefficients respectively.

The free energy of activation per mole of solvent and solution were measured with the help of Eqs (4) and (5) respectively.

\[
\Delta \mu_{1}^{0+} = RT\ln(\eta^0/\dot{\eta}_0)/hN \quad \ldots (4)
\]

\[
\Delta \mu_{2}^{0+} = (RT/\dot{\eta}_0^{0+})1000B - \left(\dot{\eta}_0 - \dot{\eta}_0^0\right) \quad \ldots (5)
\]

where, \( h \) is the Planck constant, \( N \) is the Avagadro's number and \( R \) is the gas constant.

Results and discussion

The density, viscosity, relative viscosity and other parameters of the aqueous solutions of ternary systems (KCI + NaCl + CH\(_3\)COOK; NaNO\(_3\) + KNO\(_3\) + CH\(_3\)COONa; CH\(_3\)COONa + CH\(_3\)COOK + NaCl; MgSO\(_4\) + Na\(_2\)SO\(_4\) + KCl; MgCl\(_2\) + BaCl\(_2\) + NaNO\(_3\); Na\(_2\)SO\(_4\) + NaNO\(_3\) + CH\(_3\)COOK; NaCl + NaNO\(_3\) + MgSO\(_4\)) at different molalities (0.00 + 0.00 + 0.5; 0.05 + 0.05 + 0.4; 0.05 + 0.4; 0.1 + 0.1 + 0.3; 0.15 + 0.15 + 0.2 and 0.2 + 0.2 + 0.1) \( m \) have been measured at
298.15 K and recorded in Tables 1 and 2.

The apparent molal volume, \( \phi_v \), were calculated from Eq. (1). The values of apparent molal volumes of these ternary systems at different compositions are recorded in Table 1. The plots of \( \phi_v \) against \( \sqrt{m} \) for such systems are found to be linear. Partial molal volume, as a measure of ion-solvent interactions, has been worked out with the help of apparent molal volume, at infinite dilutions by Masson\(^7\),

\[
\phi_v = \phi_0^\circ + S_v \sqrt{m} \quad \ldots \quad (6)
\]

The partial molal volume, \( \phi_0^\circ \) and the experimental slopes \( S_v \) of the ternary systems are pre-

| Table 1—Density (\( \rho \)), viscosity (\( \eta \)), relative viscosity (\( \eta_{rel} \)), and apparent molal volume (\( \phi_v \)) of various systems in concentrated aqueous solutions at 298.15\( K \) |
|----------------|----------|----------|----------|
| Molality (\( m \)) | Density (\( \rho \)) \( 10^3 \space \text{kg.m}^{-3} \) | Viscosity (\( \eta \)) \( 10^3 \space \text{kg.m.s}^{-1} \) | Apparent molal volume (\( \phi_v \)) \( 10^6 \space \text{m}^3.\text{mol}^{-1} \) |
| \( m \) | \( f^0 = 0.9971 \) | \( \eta^0 = 0.8512 \) | |
| KCl + NaCl + CH\(_3\)COOK | 1.017 | 0.2406 | 85.21 |
| NaNO\(_3\) + KNO\(_3\) + NaAc | 1.015 | 0.1543 | 125.69 |
| NaCl + Na\(_2\)NO\(_3\) + MgSO\(_4\) | 1.023 | 0.1357 | 143.6 |
| NaAc + KAc + NaCl | 1.019 | 0.3292 | 107.49 |
| MgSO\(_4\) + Na\(_2\)SO\(_4\) + KCl | 1.02 | 0.2927 | 109.51 |
| MgCl\(_2\) + BaCl\(_2\) + NaNO\(_3\) | 1.017 | 0.5499 | 201.31 |

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represented in Table 2. The positive values of $\phi_i$ indicate greater solute-solvent interactions for these ternary systems. They behave as structure makers. The slopes $S_v$ are found to be positive for these systems (NaNO$_3$ + KNO$_3$ + CH$_3$COONa; CH$_3$COONa + CH$_3$COOK + NaCl and NaCl + NaNO$_3$ + MgSO$_4$) which indicates strong ion interaction and more complex ion formation. In the case of these systems (KCl + NaCl + CH$_3$COOK; MgSO$_4$ + Na$_2$SO$_4$ + KCl; MgCl$_2$ + BaCl$_2$ + NaNO$_3$ and Na$_2$SO$_4$ + NaNO$_3$ + CH$_3$COOK) the values of $S_v$ are negative which indicate weak ion-ion interaction and less complex ion formation.

Viscosity and relative viscosity of various systems at different compositions in aqueous solutions are reported in Table 1. The values of A and B are determined by the least squares method. A and B coefficients of mixed electrolytes are obtained, as intercept and slope of the linear plots of $[\eta/\eta_0] - (1/\eta)$ versus $1/\eta$. The B-coefficients for respective ternary systems in aqueous solutions are found to be positive in some systems and negative in others. It is also known as a measure of order or disorder induced by the ions or solutes into the solvent. The B-coefficient are found to be positive in the case of systems NaNO$_3$ + KNO$_3$ + CH$_3$COONa and CH$_2$COONa + CH$_3$COOK + NaCl which indicates strong ion-solvent or solute-solvent interaction. They behave as structure makers. The negative values of B-coefficient are indicating weak ion-solvent interaction in the case of systems KCl + NaCl + CH$_3$COOK; NaCl + NaNO$_3$ + MgSO$_4$; MgSO$_4$ + Na$_2$SO$_4$ + KCl; MgCl$_2$ + BaCl$_2$ + NaNO$_3$ and NaNO$_3$ + Na$_2$SO$_4$ + CH$_3$COOK. They behave as structure breakers. The values of A are found to be small and negative in the case of these respective ternary systems in aqueous solutions which indicate the presence of weak ion-ion interactions.

The values of $\Delta \mu_{0^+}^i$ and $\Delta \mu_{0^+}^i$ parameter have been calculated by using relations (4) and (5) are recorded in Table 2 for these respective ternary systems. The values of $\Delta \nu_{0^+}^i$ do not change in the present case. The free energy of activation of solutes $\Delta \mu_{0^+}^i$ is determined by the B-coefficient and $\left(\mu_0 - \mu_2\right)$ term for all the ternary systems in aqueous solutions are recorded in Table 2. The values of $\Delta \mu_{0^+}^i$ for respective systems, NaNO$_3$ + KNO$_3$ + CH$_3$COONa and CH$_3$COONa + CH$_3$COOK + NaCl, are greater than $\Delta \mu_{0^+}^i$ showing the behaviour as structure maker. The values of $\Delta \mu_{0^+}^i$ for all the systems are less than $\Delta \mu_{0^+}^i$. They behave as structure breakers. The positive value of $\Delta \mu_{0^+}^i$ shows that formation of transition state is less favoured in the presence of these systems, meaning thereby that the formation of transition state is accompanied by the breaking and distortion of the intermolecular bonds.

**References**