In the present investigations, the thermodynamic and transport properties of multicomponent solutions have been studied. This thesis consists of four chapters. The first chapter is entitled as "General Introduction", second chapter as "Partial molal volumes of multicomponent systems", third chapter as "E.M.F. studies of copper sulphate in urea + water systems" and fourth chapter as "Coupled transport processes through sintered disc impregnated with cellulose acetate".

The first chapter of the thesis gives a brief introduction to the thermodynamic and transport properties of multicomponent systems.

The second chapter represents the molal volume studies of strong and weak electrolyte multicomponent systems. Densities have been determined at different concentrations for the following multicomponent systems:

i) \( \text{NH}_4\text{Cl}-\text{NH}_4\text{Br}-\text{H}_2\text{O} \)

ii) \( \text{NH}_4\text{Cl}-\text{NH}_4\text{NO}_3-\text{H}_2\text{O} \)

iii) \( \text{CH}_3\text{COONH}_4-\text{NH}_4\text{Cl}-\text{H}_2\text{O} \)

iv) \( \text{CH}_3\text{COONH}_4-\text{NH}_4\text{Br}-\text{H}_2\text{O} \)

v) \( \text{CH}_3\text{COONH}_4-\text{NH}_4\text{NO}_3-\text{H}_2\text{O} \)

The density data have been used to evaluate the apparent molal volume, \( \bar{\varphi}_v \), for the above systems by the use of the following expression:
\[ \phi_v = \frac{1000(d^0 - d)}{md} + \frac{M}{d} \]  

(S.1)

where \( d \) is the density of the solution, \( d^0 \) is the density of the solvent, \( m \) is the molality of the solution and \( M \) is the molecular weight of the solute. The apparent molal volume, thus calculated vary linearly with \( m \). From the linear plots, the apparent molal volume at infinite dilution, \( \phi_v^0 \), and the experimental slope, \( S_v \), have been calculated. The information regarding ion-ion and ion-solvent interactions has been obtained from the magnitude of experimental slope, \( S_v \), and apparent molal volume at infinite dilution, \( \phi_v^0 \).

The mean apparent molal volume, \( \phi_v \), for all the systems have been determined by using the density data with the help of following expression:

\[ \phi_v = \frac{1000(d^0 - d)}{mTd} + \frac{M_T}{d} \]  

(S.2)

where \( d \) is the density of the solution and \( d^0 \) is the density of pure water. \( m_T \) is the total molality of the solution and \( M_T \) is the mean molecular weight.

The mean apparent molal volumes, \( \phi_v \), have also been calculated for all the systems by using Young's rule.

\[ \phi_v^{(\text{cal.})} = \sum_i d_i \phi_v(i) \]  

(S.3)
where \( V_i(t) \) is the molal volume of the component \( i \) in pure water at \( m_T \) and \( Y_i = m_i/m_T \) is the molal weighing factor. The \( \Phi_i \) (cal.) values thus calculated have been compared with \( \Phi_i \) (obs.) values obtained by using relation (S.2). The difference between \( \Phi_i \) (cal.) and \( \Phi_i \) (obs.) values is the excess molal volume and is related to the volume change caused by the mixing of ammonium salts.

The third chapter gives an account of the thermodynamic functions of transfer and activity coefficients of copper sulphate in different urea + water mixtures at different temperatures from e.m.f. measurements. The cell used is represented as:

\[
\text{Cu-Hg/CuSO}_4(\text{m}), \text{urea + water mixtures/Hg}_2\text{SO}_4(\text{s})/\text{Hg}
\]

Standard molal potentials of the cell have been determined from Hitchcock type equation:

\[
E^0 = E + k \log m - k \cdot \frac{AZ^+Z^-I^+}{1 + BaO} = E^0_m - kB'I^+ \tag{S.4}
\]

\( E^0_m \) values have been estimated from the extrapolation to \( I = 0 \) of the linear plots between \( E^0 \) and \( I \). \( E^0_m \) values have been fitted by the method of least squares to the following equation:

\[
E^0_m = a - b(T - 298.15) - c(T - 298.15)^2 \tag{S.5}
\]
where $T$ is the temperature in K and $a$, $b$ and $c$ are empirical constants.

The values of mean activity coefficients, $\gamma^+_\pm$, for the various solutions have been evaluated from the relation:

$$E = E^o_m - k \log m \gamma^+_\pm$$

It has been observed that in a particular solvent, activity coefficient constantly decreases with the increase of concentration of $\text{CuSO}_4$ up to concentration range $< 0.05 \text{ m}$. This decrease in the activity coefficient may be attributed to the increase of ion-ion interactions with the increase of $\text{CuSO}_4$ concentration in a particular solvent. However, at higher concentration ($\geq 0.05 \text{ m}$), the activity coefficient increases with the increase of the concentration of $\text{CuSO}_4$ thereby indicating that solute-solvent interactions dominate over ion-ion interactions.

The free energy changes, $\Delta G^o_t$, accompanying the transfer of one mole of the electrolyte from the standard state in water to the mixed solvents were evaluated on the mole fraction scale using the relation:

$$\Delta G^o_t = 2F \left[ (n^o_m)_{\text{S}} - (n^o_m)_{\text{W}} \right] - 2 \times 2.3026 \text{ RT} \log \left( \frac{c_s}{c_w} \right) \quad (E.6)$$
The corresponding entropy changes were calculated by using the relation:

\[ \Delta S_t^0 = F(b_s - b_w) + 2F(T - 298.15)(c_s - c_w) + 2 \times 2.3026 \times R \log \left( \frac{M_s}{M_w} \right) \]  

(S.7)

The corresponding enthalpy changes have been evaluated by the equation:

\[ \Delta H_t^0 = \Delta G_t^0 + T \Delta S_t^0 \]  

(S.8)

The standard Gibbs free energies of transfer, \( \Delta G_t^0 \), have been observed to become more and more positive with the increase of urea content in the medium. The positive values of \( \Delta G_t^0 \) indicate that copper sulphate has more affinity for water than for urea + water mixtures. Therefore, the transfer of copper sulphate from water to urea + water mixtures is not a spontaneous process with the solute in the standard state in either medium.

The values of \( \Delta S_t^0 \) and \( \Delta H_t^0 \) changes from positive to negative with the increase of urea content in the medium. This suggests that tendency of order created by copper sulphate in urea + water mixtures is less than in pure water at lower concentration of urea. However, this tendency of order becomes
more in urea + water mixtures than in pure water at higher concentration of urea. This shows re-introduction of some order in urea + water mixtures at higher concentration of urea.

The $\Delta G^0_t$ values have been split up into two parts, a non-electrostatic or chemical contribution, $\Delta G^0_{t, ch}$, and an electrostatic contribution, $\Delta G^0_{t, el}$, which has been calculated from the Born equation:

$$\Delta G^0_{t, el} = \frac{Ne^2}{2} \left[ \frac{1}{D_s} - \frac{1}{D_w} \right] \left[ \frac{1}{r^+} + \frac{1}{r^-} \right]$$ (8.9)

The electrostatic contribution of the entropy of transfer has been obtained by the relation:

$$\Delta S^0_{t, el} = -\frac{Ne^2}{2} \left[ \frac{1}{D_w} \frac{d \ln D_w}{dT} - \frac{1}{D_s} \frac{d \ln D_s}{dT} \right] \left[ \frac{1}{r^+} + \frac{1}{r^-} \right]$$ (8.10)

The electrostatic contribution of the enthalpy of transfer can then be calculated by the equation:

$$\Delta H^0_{t, el} = \Delta G^0_{t, el} + T \Delta S^0_{t, el}$$ (8.11)

The chemical contributions of the free energy of transfer, $\Delta G^0_{t, ch}$, entropy of transfer, $\Delta S^0_{t, ch}$, and enthalpy of transfer, $\Delta H^0_{t, ch}$, have been obtained by subtracting the
respective electrostatic values from the molal quantities. It has been found that $\Delta G^0_{t,\text{ch}}$ is increasingly positive in all urea + water mixtures. This indicates that transfer of copper sulphate from water to urea + water mixtures is not favoured as far as chemical interactions are concerned. This suggests that all urea + water mixtures are less basic than pure water. The electrostatic part $\Delta G^0_{t,\text{el}}$ is increasingly negative in all urea + water mixtures. However, the chemical contribution predominates over electrostatic contribution and hence making the transfer process unfavourable. The electrostatic part of the enthalpy and entropy change has been found to be positive whereas the chemical part of these quantities is positive only at lower concentration of urea content. This has been attributed to the re-introduction of some order in urea + water mixtures at higher urea content.

The fourth chapter describes the electro-kinetic effects viz., electro-osmosis, electro-osmotic, pressure difference, streaming potential and streaming current for the transport of the solutions of multicomponent ammonium salt solutions at 30°C across a pyrex sintered disc ($G_2$) impregnated with cellulose acetate. The estimation of phenomenological coefficients have been carried out by the use of following equations:
where \( I \) and \( J \) represent the electric current and volume flow while \( \Delta \phi \) and \( \Delta P \) are the electric potential difference and pressure difference respectively. \( L_{ij} \) are the phenomenological coefficients. The values of phenomenological coefficients \( L_{21} \) and \( L_{22} \) have been determined from electro-osmotic data by using equation (S.13). It has been found that the phenomenological coefficient \( L_{22} \) varies with \( \Delta \phi \). This shows that equation (S.13) is not obeyed in case of multicomponent ammonium salt solutions. In order to account for the variation of \( L_{22} \) with \( \Delta \phi \), the equation for \( J \) was modified as:

\[
J = L_{21} \Delta \phi + L_{22} \Delta P + L_\phi \Delta \phi \Delta P
\]  

(S.14)

It was found that this modified equation (S.14) holds good for all the systems studied and the values of phenomenological coefficients \( L_{22} \) and \( L_\phi \) have been determined for all the systems by using equation (S.14). The values of phenomenological coefficients \( L_{11} \) and \( L_{21} \) have been determined from streaming potential data by using equation (S.12).

The comparison of the values of cross-phenomenological coefficients \( L_{12} \) and \( L_{21} \) proved the validity of Onsager's
reciprocity relation:

\[ L_{12} = L_{21} \]  \hspace{1cm} (8.15)

The efficiencies of energy conversion for the two reciprocal phenomena, i.e. electro-osmosis and streaming potential have been estimated from the following relation relations:

\[ E_e = \frac{J \Delta P}{(\Delta \phi)^2/R} \]  \hspace{1cm} (S.16)

\[ E_s = \frac{J \Delta P}{(\Delta \phi)^2/R} \]  \hspace{1cm} (S.17)

where the subscripts 'e' and 's' represent the phenomena of electro-osmosis and streaming potential respectively. The maximum conversion efficiencies for electro-osmotic flow and streaming potential have been found to be equal and independent of the applied input forces. The optimum value of the energy conversion efficiency has been observed to occur when the output force equals half its steady state value. Conditions of maximum conversions efficiency have also been deduced.

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