CHAPTER-V

SUMMARY
In the present study, the information regarding solute-solute and solute-solvent interactions and structure making /breaking capacity of nickel sulphate, copper sulphate and zinc sulphate solutions (0.01m-0.12m) in water, 0.1m aqueous sodium chloride and 5,10 and 15 wt. % of dextrose in 0.1m aqueous sodium chloride at temperatures 303.15, 308.15, 313.15 and 318.15K have been obtained from the following studies:

A) Apparent molar volume studies

B) Viscosity and conductance studies

C) Ultrasonic studies.

(A) Apparent molar volume studies:

The apparent molar volumes of nickel sulphate, copper sulphate and zinc sulphate solutions (0.01m-0.12m) in water, 0.1m aqueous sodium chloride and 5,10 and 15 wt. % of dextrose in 0.1m aqueous sodium chloride solutions have been determined by using the following relation:

\[
\phi^\circ = \frac{M_2}{d_0} + \frac{1000(d_0 - d)}{Cd_0}
\]  

Where \(d\) and \(d_0\) are densities of the solution and solvent respectively, \(M_2\) is the molecular weight of solute and \(C\) is the molar concentration.

The variation of \(\phi^\circ\) with concentration for the electrolyte has been found to be linear in accordance with the Masson’s equation:

\[
\phi_v = \phi^\circ_v + S_v^* C^{1/2}
\] 

Where \(\phi^\circ_v\) is the limiting apparent molar volume and is equal to partial molar volume \(\bar{V}^\circ_v\) i.e. \(\phi^\circ_v = \bar{V}^\circ_v\) and \(S_v^*\) is the experimental slope. The limiting apparent molar volumes \(\phi^\circ_v\) and \(S_v^*\) has been obtained by least square method applied to the
linear plots of $\phi$ Vs $C^{1/2}$ and these values have been interpreted in terms of solute-solvent and solute-solute interactions respectively. The values of $\phi^0_v$ for nickel sulphate, copper sulphate and zinc sulphate solutions (0.01m-0.12m) in water, 0.1m aqueous sodium chloride and 5,10 and 15 wt. % of dextrose in 0.1m aqueous sodium chloride solutions were found to be large at different temperatures (303.15, 308.15, 313.15 and 318.15K) indicate the presence of strong solute-solvent interactions. The small values of $S_v^*$ for solutions of nickel sulphate, copper sulphate and zinc sulphate in water, 0.1m aqueous sodium chloride and 5, 10, 15 wt. % of dextrose in 0.1m aqueous sodium chloride indicate the weak solute-solute interactions.

The limiting apparent molar volume expansibility $\phi^0_h = \left[ \frac{\partial \phi^0_v}{\partial T} \right]_p$ shows decrease in magnitude with the increase in temperature, indicating that nickel sulphate, copper sulphate and zinc sulphate do not show any "caging effect" in water, 0.1m aqueous sodium chloride and 5,10 and 15 wt. % of dextrose in 0.1m aqueous sodium chloride solutions.

The structure maker/breaker nature of nickel sulphate, copper sulphate and zinc sulphate have been inferred from the sign of $\left[ \frac{\partial^2 \phi^0_v}{\partial T^2} \right]_p$, the criteria suggested by Hepler. The negative sign of $\left[ \frac{\partial^2 \phi^0_v}{\partial T^2} \right]_p$ has been found for nickel sulphate, copper sulphate and zinc sulphate in water, 0.1m aqueous sodium chloride and 5,10 and 15 wt. % of dextrose in 0.1m aqueous sodium chloride solutions suggests that these metal sulphate act as structure breaker in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. % of dextrose in 0.1m aqueous sodium chloride. at different temperatures (303.15-318.15K).

The limiting excees molar volume of nickel sulphate, copper sulphate and zinc sulphate for different compositions of dextrose in 0.1m aqueous sodium chloride has been estimated from equation:

$$\Delta \phi^0_v = \phi^0_v(\alpha) - \phi^0_v(\beta)$$  \hspace{1cm} (3)
Where $\phi^0_{(A)}$ is limiting apparent molar volume of nickel sulphate, copper sulphate and zinc sulphate for different compositions of dextrose in 0.1m aqueous sodium chloride and $\phi^0_{(B)}$ is limiting apparent molar volume of nickel sulphate, copper sulphate and zinc sulphate in 0.1m aqueous sodium chloride.

The positive values of $\Delta\phi^0$ suggest solvation of ions of nickel sulphate, copper sulphate and zinc sulphate. The increase in value of $\Delta\phi^0$ with increase in concentration of dextrose suggests increase in solute-solvent interactions for nickel sulphate, copper sulphate and zinc sulphate with increase in composition of dextrose in 0.1m aqueous sodium chloride.

**(B) Viscosity and conductance studies:**

**(I) Viscosity studies:**

The concentration dependence of viscosity for nickel sulphate, copper sulphate and zinc sulphate solutions (0.01m-0.12m) in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. % of dextrose in 0.1m aqueous sodium chloride solutions, at different temperatures (303.15, 308.15, 313.15 and 318.15K) has been analysed with Jones -Dole equation:

$$\eta_r = \eta / \eta_0 = 1 + AC^2 + BC$$  \(\text{(4)}\)

Where $\eta$ and $\eta_0$ are viscosities of the solutions and solvent respectively. $A$ and $B$ parameters have been obtained by using the least square method. The values of parameter $A$ represents solute-solute interactions and it decreases with increase in temperature for nickel sulphate, copper sulphate and zinc sulphate in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. percent of dextrose in 0.1m aqueous sodium chloride. This shows that solute-solute interactions are weakened with rise of temperature. The $B$-coefficient represents the solute-solvent interactions and the values of $B$-coefficient for nickel sulphate, copper sulphate and zinc sulphate in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. percent of dextrose in 0.1m aqueous sodium chloride are positive and increase with increase in temperature. This shows that there is increase in solute-solvent interactions with rise in temperature. The
positive temperature coefficient of B (i.e. dB/dT) for nickel sulphate, copper sulphate and zinc sulphate in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. percentage of dextrose in 0.1m aqueous sodium chloride show that these metal sulphates behave as structure breaker at different temperatures (303.15-318.15K).

The viscosity data has also been analysed on the basis of transition state theory of relative viscosities of electrolytic solutions. The values of $\Delta \mu_1^{o*}$ and $\Delta \mu_2^{o*}$ were calculated by using the following relations:

$$\Delta \mu_1^{o*} = \Delta G_1^{o*} = 2.303RT \log (\eta_0 V_1^{o}/Nh)$$  \hspace{1cm}  (5)$$

$$\Delta \mu_2^{o*} = \Delta G_2^{o*} = \Delta \mu_1^{o*} + RT/ V_1^{o} [1000B - (\bar{V}_1^{o} - \bar{V}_2^{o})]$$  \hspace{1cm}  (6)$$

Where $\Delta \mu_1^{o*}$ and $\Delta \mu_2^{o*}$ are the free energy of activation per mole of pure solvent and solute respectively. The values of $\Delta \mu_2^{o*}$ greater than $\Delta \mu_1^{o*}$ for nickel sulphate, copper sulphate and zinc sulphate in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. percent of dextrose in 0.1m aqueous sodium chloride solutions show that these metal sulphates behave as structure-breaker at different temperatures (303.15-318.15K).

The values of $\Delta \mu_2^{o*}$ at various temperatures can also be used to calculate the activation entropy for metal sulphates as:

$$d(\Delta \mu_2^{o*})/dT = -\Delta S_2^{o*}$$  \hspace{1cm}  (7)$$

Further, the activation enthalpy $\Delta H_2^{o*}$ was also calculated with the help of following equation:

$$\Delta H_2^{o*} = \Delta \mu_2^{o*} + T\Delta S_2^{o*}$$  \hspace{1cm}  (8)$$

$\Delta H_2^{o*}$ and $T\Delta S_2^{o*}$ are negative for nickel sulphate, copper sulphate and zinc sulphate in different wt. percent of dextrose in 0.1m aqueous sodium chloride which show that
transition state is associated with weakening of bond among solute and solvent molecules and increase in order may be due to the solvation of ions.

(II) Conductance studies:

The concentration dependence of molar conductance $\Lambda_m$ for nickel sulphate, copper sulphate and zinc sulphate solutions (0.01m-0.12m) in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. percent of dextrose in 0.1m aqueous sodium chloride solutions at temperatures (303.15, 308.15, 313.15 and 318.15K) has been analysed with Onsager’s equation.

$$\Lambda_m = \Lambda_m^0 - KC^{1/2}$$ (9)

The limiting molar conductance $\Lambda_m^0$ has been obtained from the intercept of Onsager’s plot of $\Lambda_m$ Vs $C^{1/2}$ for nickel sulphate, copper sulphate and zinc sulphate solutions (0.01m-0.12m) in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. percent of dextrose in 0.1m aqueous sodium chloride solutions at different temperatures (303.15-318.15K). The magnitude of $\Lambda_m^0$ increases with increase in temperature which may be due to increase in the mobility of ions at infinite dilution with rise in temperature. The conductance data of nickel sulphate, copper sulphate and zinc sulphate solutions (0.01m-0.12m) in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. percent of dextrose in 0.1m aqueous sodium chloride solutions has also been analysed on the basis of Walden product $\Lambda_m^0 \eta_0$.

The Walden product decreases with increase in temperature for nickel sulphate, copper sulphate and zinc sulphate solutions (0.01m-0.12m) in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. percent of dextrose in 0.1m aqueous sodium chloride solutions which may be due to increase in solvation of ions with rise in temperature. The temperature coefficient of Walden product for nickel sulphate, copper sulphate and zinc sulphate solutions (0.01m-0.12m) in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. percent of dextrose in 0.1m aqueous sodium chloride solutions at different temperature is found to be negative, thereby indicating that nickel sulphate, copper sulphate and zinc sulphate act as structure-breaker.
(C) Ultrasonic studies:

The ultrasonic velocities for nickel sulphate, copper sulphate and zinc sulphate solutions (0.01m-0.12m) in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. % of dextrose in 0.1m aqueous sodium chloride over temperature range 303.15 – 318.15K have been determined. The values of ultrasonic velocities for nickel sulphate, copper sulphate and zinc sulphate solutions (0.01m-0.12m) in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. % of dextrose in 0.1m aqueous sodium chloride suggest that ultrasonic velocity increase with increase in concentration of nickel sulphate, copper sulphate and zinc sulphate solutions (0.01m-0.12m) in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. % of dextrose in 0.1m aqueous sodium chloride at different temperatures (303.15-318.15K).

Molar sound velocities for all these systems were estimated by using following relation

\[ R = C^{1/3} V_m \]  \hspace{1cm} (10)

Where \( V_m \) is molar volume of solution which has been taken as \( M/\rho \). \( M \) is the molecular weight of mixtures and \( \rho \) is the density of the solution.

The molar sound velocities estimated were found to be in good agreement with Rao'o Law.

Specific acoustic impedenced is related to the ultrasonic velocity and density by relation.

\[ Z = U \rho \]  \hspace{1cm} (11)

Where \( U \) and \( \rho \) are the ultrasonic velocity and densities of solutions respectively.

The values of specific acoustic impedance for nickel sulphate, copper sulphate and zinc sulphate solutions (0.01m-0.12m) in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. % of dextrose in 0.1m aqueous sodium chloride increase with increase in concentration of nickel sulphate, copper sulphate and zinc sulphate in
water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. % of dextrose in 0.1m aqueous sodium chloride which indicates the increase in solute-solvent interactions.

The adiabatic compressibilities for nickel sulphate, copper sulphate and zinc sulphate solutions (0.01m-0.12m) in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. % of dextrose in 0.1m aqueous sodium chloride at different temperatures (303.15-318.15) were estimated by using the relation:

$$\beta = \frac{1}{U^2 \rho}$$  \hspace{1cm} (12)

It was observed that adiabatic compressibility decreases with increase in concentration of nickel sulphate, copper sulphate and zinc sulphate in water, 0.1m aqueous sodium chloride and different wt. % of dextrose in 0.1m aqueous sodium chloride as well as with increase in wt. % of dextrose in 0.1m aqueous sodium chloride.

The intermolecular free length for nickel sulphate, copper sulphate and zinc sulphate solutions (0.01m-0.12m) in water, 0.1m aqueous sodium chloride and 5, 10 and 15 wt. % of dextrose in 0.1m aqueous sodium chloride at different temperatures (303.15-318.15) were estimated by using the relation:

$$L_t = \frac{K}{U_{exp} \rho_{1/2 \exp}} = K \sqrt{\beta}$$  \hspace{1cm} (13)

The values show that intermolecular free length decrease with increase in concentration of nickel sulphate, copper sulphate and zinc sulphate in water, 0.1m aqueous sodium chloride and different wt. % of dextrose in 0.1m aqueous sodium chloride and increase with rise in temperature. It indicates the interaction between the solute and solvent molecules, due to which structural arrangement is considerably changed.

The relative association (R.A.) is estimated from the following expression:

$$R.A. = \frac{\rho \cdot U_0}{\rho_0 \cdot U}$$  \hspace{1cm} (14)
Where $\rho$ and $U$ are the density and ultrasonic velocities of solutions and $\rho_0$ and $U_0$ are the density and ultrasonic velocity of solvent.

The values of relative association increase with increase in concentration for nickel sulphate, copper sulphate and zinc sulphate in water, 0.1m aqueous sodium chloride and different wt. % of dextrose in 0.1m aqueous sodium chloride.

The solvation number or association number is estimated from the relation:

$$S_n = \frac{n_1}{n_2} \left( 1 - \frac{\beta}{\beta_0} \right)$$  

Where $n_1$ and $n_2$ are the number of moles of solute and solvent and $\beta$ and $\beta_0$ are the compressibilities of solutions and solvent respectively.

The Wada’s constant is estimated by using the following relation:

$$W = M \beta^{-1/7} / \rho$$  

Where $M$, $\beta$, and $\rho$ are the average molecular mass, adiabatic compressibilities and densities of the solutions respectively.

The relaxation time for systems studied has been estimated by using relation:

$$\tau = \frac{4\eta}{3\rho U^2} = \frac{4}{3} \eta \beta$$  

For better interpretation of relaxation time the activated states for systems studied was estimated by using the relation:

$$\frac{1}{\tau} = \frac{KT}{h} \exp \left( -\frac{\Delta G^*}{KT} \right)$$  

The values of the Gibb’s free energy of activation for the relaxation process were found to be constant with increase in concentration of nickel sulphate, copper sulphate and zinc sulphate in water, 0.1m aqueous sodium chloride and different wt. % of dextrose in 0.1m aqueous sodium chloride and the Gibb’s free energy of activation values increase with increase in temperature for nickel sulphate, copper
sulphate and zinc sulphate in water, 0.1m aqueous sodium chloride and different wt.
% of dextrose in 0.1m aqueous sodium chloride.

From molar volume, viscosity, conductance and ultrasonic studies it has been found that nickel sulphate, copper sulphate and zinc sulphate behave as structure-breaker in water, 0.1m aqueous sodium chloride and 5, 10 and 15%(w/w) of dextrose in 0.1m aqueous sodium chloride at different temperatures (303.15-318.15K).