

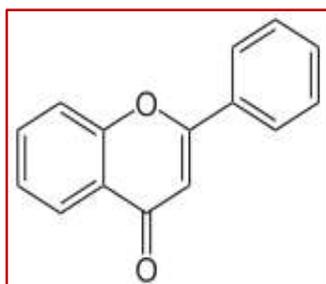
CHAPTER II

GENERAL INTRODUCTION

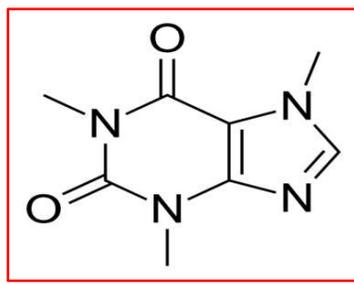
(REVIEW OF THE EARLIER WORKS)

2.1. Solution Chemistry

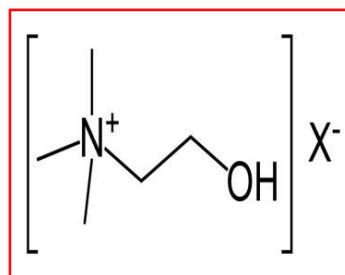
Solution chemistry is an important branch of physical chemistry. It deals with the physicochemical properties when any component is dissolved into another. The homogeneous mixing of two or more components gives rise to a solution which does not behave ideally. The deviation from ideality of a solution may be defined by many physicochemical and thermodynamic parameters. These parameters help to study of intermolecular interactions and arrangements in solute/solvent system. The interactions acting in solution are between solute-solute, solvent-solvent and solute-solvent species in case of non-electrolyte solute. Another important property is the ion- solvation which is also dependent on interactions between solute and solvent species. The primary object of this research work is to examine the molecular interactions of various biologically active molecules in diverse solvent systems and gather the details information about the nature and extend of various interactions. Bioactive plant foods are of intense interest among the scientists at present due to their well accepted beneficial characteristics especially against cancers, diabetes, cardiovascular diseases etc. Bioactive compound are basically extra nutritional constituents which is present in very small amount in foods and has effect on living cells. The advantageous properties of bioactive compounds are termed on the basis of pharmacological activities of these compounds. The diet rich in bioactive compounds are vegetables, variety of fruits, legumes, oils, whole grains and nuts.



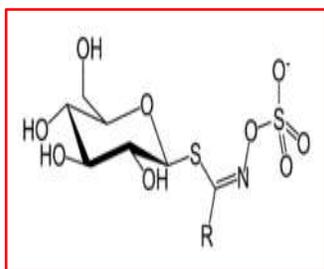
Flavone



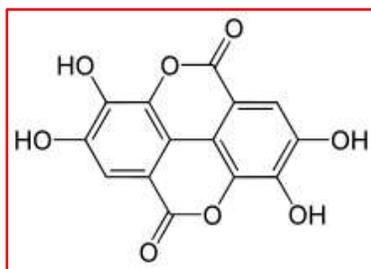
Caffeine



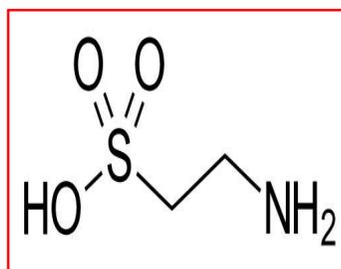
Choline



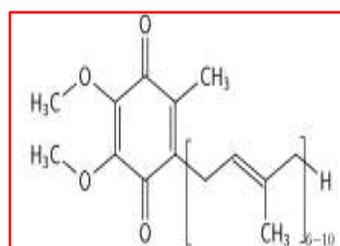
Glucosinolate



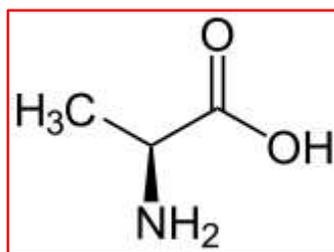
Ellagic acid



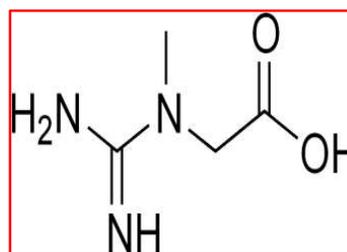
Taurine



Coenzyme Q₁₀



Glycine



Creatine

Some bulk properties of solution like viscosities, densities, excess molar enthalpies, refractive indices, isentropic compressibility etc. provide us for understanding the molecular/ionic arrangement of the solution and also help to evaluate some thermodynamic parameters of solute-solvent system. The intermolecular interactions at microscopic and macroscopic level can be studied from physicochemical properties of mixed components system. Viscosity study provides us valuable detail information about the interactions between solute and solvent or ion and solvent prevailing in the solution. The investigation of viscous synergy and antagonism is important for the multicomponent industrial products to retain the desired quality. Extend of molecular interactions can be interpreted by some physicochemical and thermodynamical parameters derived from viscosity measurement. High-energy batteries, double-layer capacitors or super capacitors, and electroplating are some field where non-aqueous electrolyte solutions was used successfully and opened the eyes of scientists to carry out more and more researches. The transport and acoustic properties of electrolytes provides significant information about molecular interactions in aqueous and non-aqueous solutions [1-3].

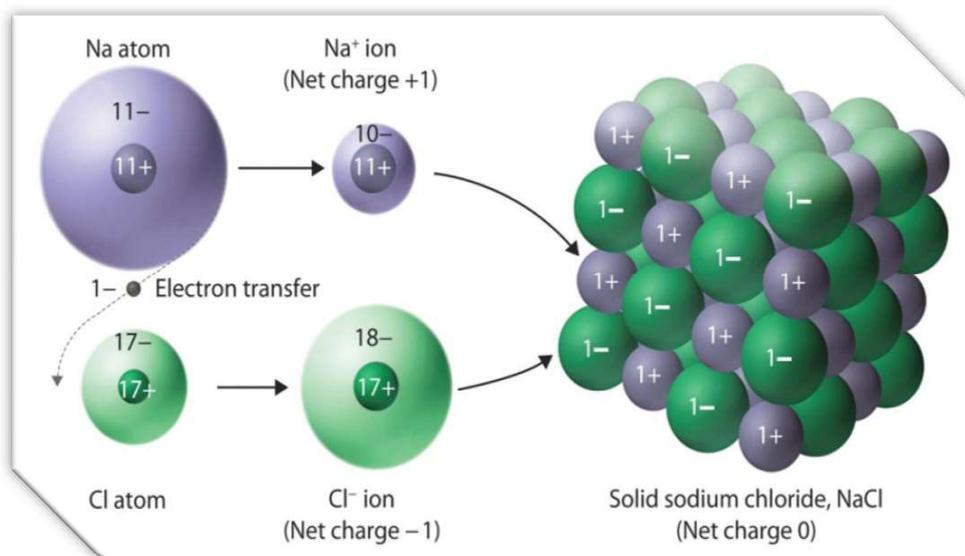
2.2. Various forces of Attraction

The force acting between acting between nearby molecules is called intermolecular force. The atoms in a molecule are held together by chemical bonding and the molecules are

held together by intermolecular forces. Properties of a substance are dependent on the intermolecular forces playing within it.

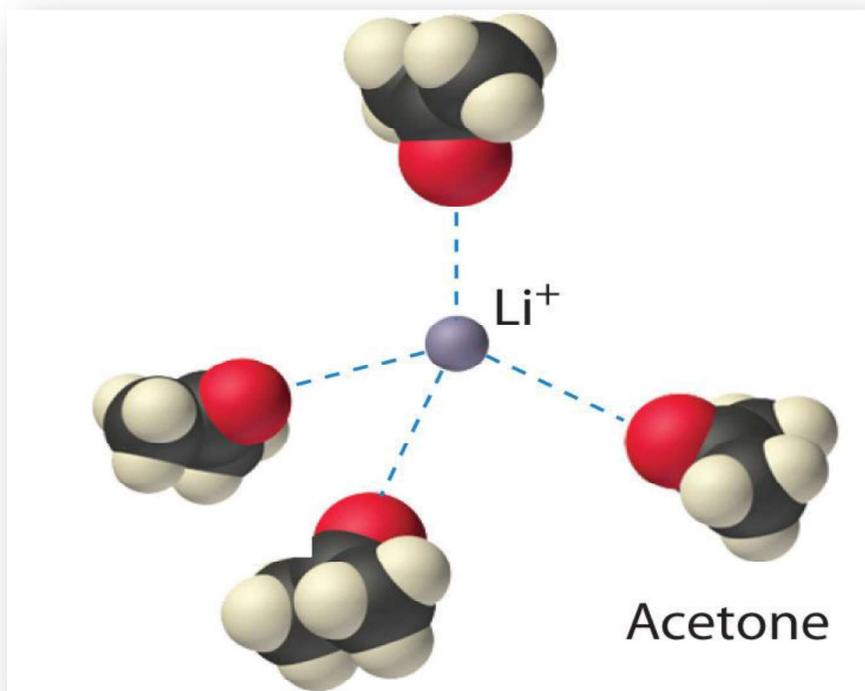
Intermolecular forces can be divided into several categories discussed as follows:

- a. Strong ionic attraction:** The strong ionic attraction is generated from the electrostatic force of attraction between two or more oppositely charged ions in an ionic compounds. The ion which gains one or more electrons is called anion and which loses one or more electrons is called cation. The anion is a negatively charged species whereas a cation is a positively charged species.



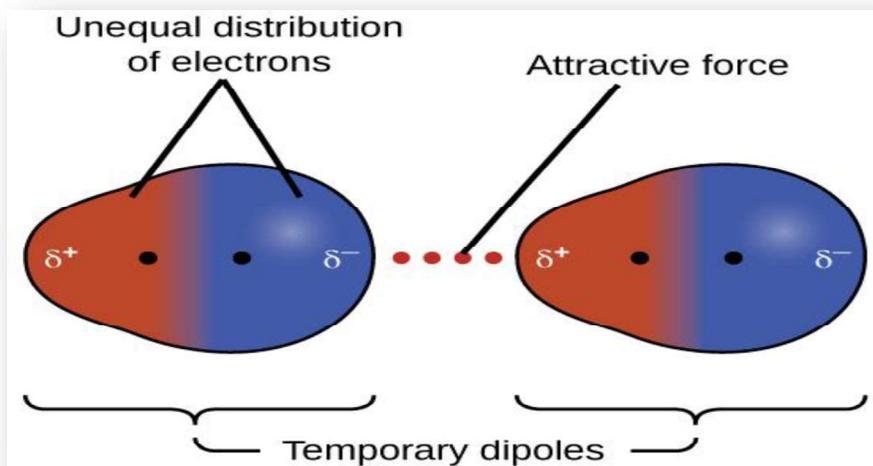
b. Intermediate dipole-dipole forces:

The intermolecular electrostatic force between the positive end of a polar molecule and the negative end of another polar molecule is called dipole-dipole Force. Dipole-dipole forces are active in case of polar molecules having partial negative and partial positive. The electrostatic force between an ion and a polar molecule is termed ion-dipole force and force between ion and a non-polar molecule is termed ion-induced dipole. Dipole-dipole force is weaker than ionic and covalent bond.



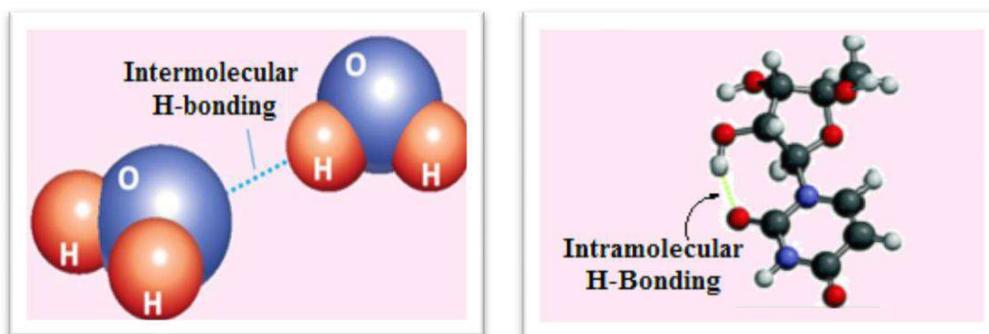
c. Weak London dispersion forces or van der Waal's force:

The force arising from instantaneous dipole moments of all matters is termed London dispersion force. Polarization of a molecule may be caused either by a polar species or by the electron clouds in non-polar molecules. Higher is the atomic number higher is the London dispersion force. Unsymmetrical distribution of electron around the atom generates temporary dipole which binds the atoms together.

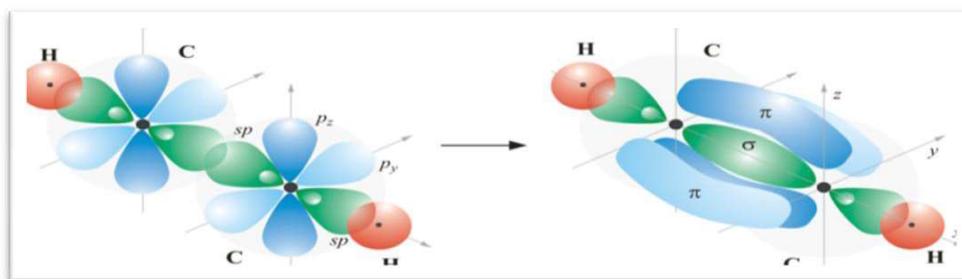


d. Hydrogen bond:

A partially electrostatic force arising when hydrogen atom is bonded with more electronegative atom like nitrogen, oxygen, or fluorine is called hydrogen bond. When hydrogen bond take place within different parts of a molecule, it is called intra-molecular hydrogen bond and hydrogen bond take place between two molecules, it is called intermolecular hydrogen bond. The energy of hydrogen bond is greater a van der Waals interaction, but smaller than covalent or ionic bonds.

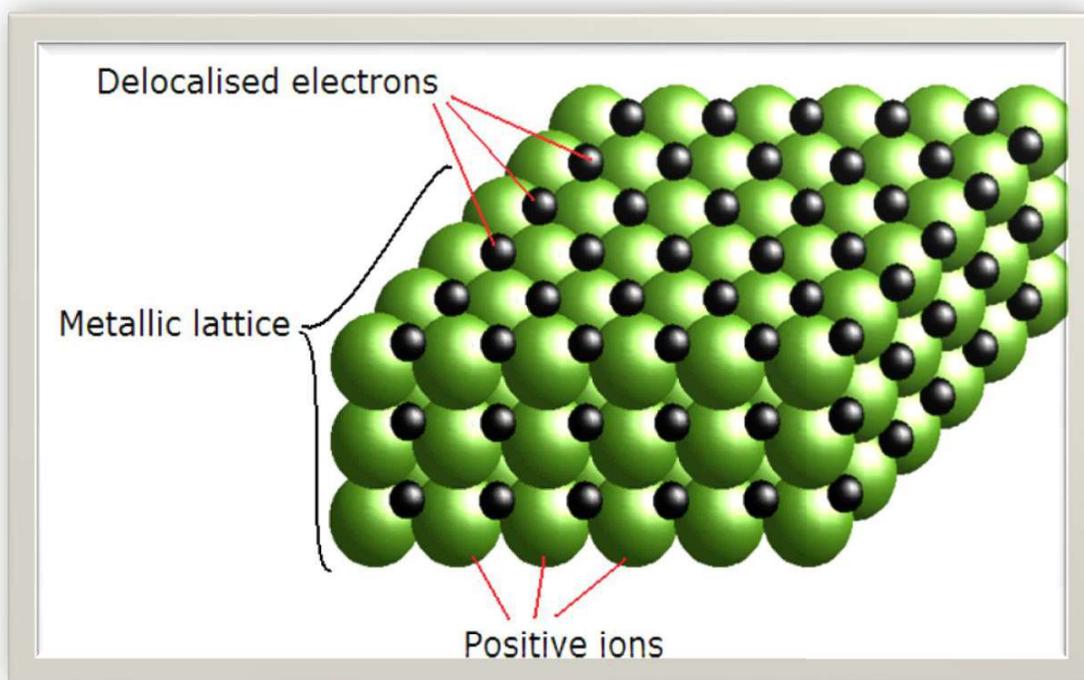


e. Covalent bonding: The molecular bond which is formed by sharing of electron pairs between the atoms is called covalent bond and the electron pair involved in the formation of covalent bond is called bonding pair or shared pair. There are mainly two types of covalent bond namely sigma bond (σ) and pi (π) bond. A sigma bond (σ) is formed by to head-on overlapping of orbitals of two atoms and a pi (π) bond is formed by lateral or side-wise overlapping of two p or d orbitals. The σ -bonds are stronger than the π bonds. Another kind of covalent bond is the three-center two-electron bond where two electrons are shared by three atoms.



f. **Metallic bonding**

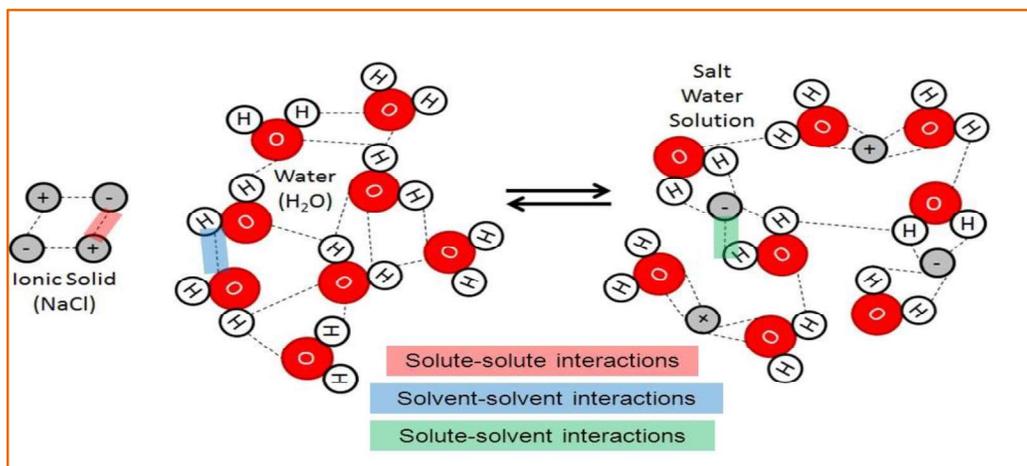
The bonds which bind the metallic atoms together are called metallic bonds. It is the freely moving valence electrons that hold the metal atoms together. The attractive force between the positively charged metallic ion and the moving are responsible to form the metallic bonds. Unlike the others chemical bonds, the valence electrons in metallic bonds move through the entire metallic lattice. These valence electrons are called sea of electrons. Metallic bonds are responsible for accounting some unique physical properties of metals like ductility, opacity, malleability, thermal and electrical conductivity and luster.



2.2.1. **Interactions in Solution Phase**

Three types of interactions are operating in the non-electrolyte solution:

- a. Solvent – solvent interactions: Energy necessary for breaking weak bonds between solvent molecules.
- b. Solute – solute interactions: Energy required to break bonds between the solute molecules.
- c. Solute – solvent interactions: Energy necessary for breaking between the solute and solvent molecules.

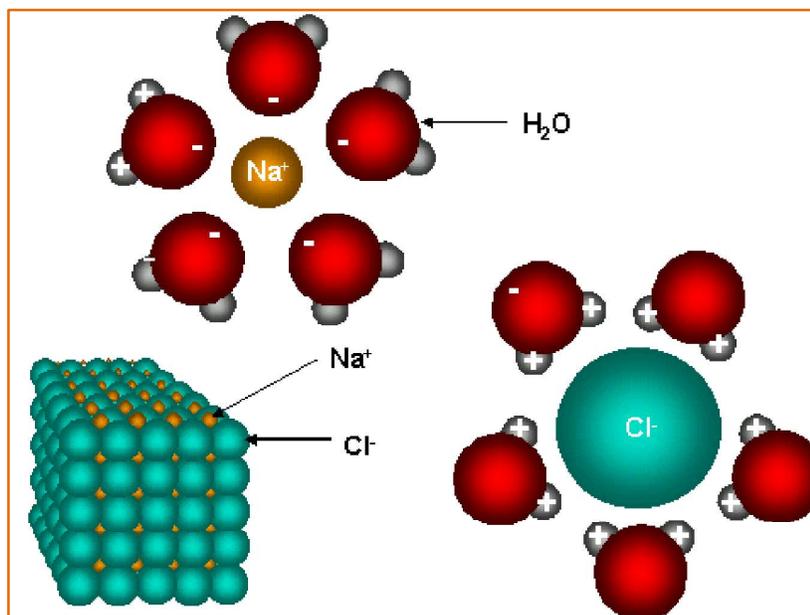


2.2.2. Investigation on different Kind Of Interactions

The forces which operate in the solution may be attractive or repulsive depends on closer approach of like or unlike charges. The polar solvents orient themselves in such a manner so that an attractive interaction generates within the bulk of solution. When a salt is added in water, the water molecules surround the crystal surfaces and isolate the constituent ions. This phenomenon of separation of the constituting ions of a salt by the solvent molecules is termed solvation.

2.2.3. Ion-Solvent Interaction

The implication of the chemistry of electrolytes solution in mixed solvents is now well accepted. The various types of interaction of electrolytes and non-electrolytes in diverse solvent or mixed solvents are yet to be understood properly. But, studies on solution properties provide some valuable information to understand the variation in ionic structure, ionic mobility and thermodynamic properties of different electrolytes and non-electrolytes in their aqueous or non- aqueous solutions. Attention in the behavior of electrolytes or solutes in non-aqueous and mixed solvents to investigate solute-solute and solute-solvent interactions under various conditions is increasing severely. The use of non-aqueous electrolyte solutions in the field of High-energy batteries, double-layer capacitors or super capacitor and electroplating with remarkable successes has opened the eyes of scientists to carry out more and more researches.



Determination of physicochemical and thermodynamic parameters provides significant information about molecular interactions in aqueous and non-aqueous solutions. The thermodynamic parameters like enthalpy, entropy, changes in free energy etc. can be estimated qualitatively which enable us to study the ion-solvent interactions of a solution system [4, 5]. Similarly, the information about the ion-solvent interactions can also be obtained from physicochemical properties like density, viscosity, refractive index, conductance, ultrasonic speed refractive index etc. of the electrolyte solution using solvation approaches [6, 7].

2.2.4. Ion-Ion Interaction

An ion in electrolyte solution not only sees the surrounding solvent compounds but also the counter ions. There is a mutual interaction between the constituting opposite ions of an electrolyte in solution which is defined as ion-ion interactions which influence the properties of solution. The magnitude of ion-ion interactions is dependent not only on the characteristics of both the electrolyte and solvent under investigation but also on the concentration of the solution and temperature. . The ion-ion interactions decrease with dilution whereas ion-solvent interactions increase with dilution.

2.2.5. Solvent-Solvent Interaction (Theory of Mixed Solvents)

Since non-aqueous mixed solvents are at present used progressively in chromatography, in the interpretation of reaction mechanism, solvent extraction, in preparing high capacity batteries, etc. many molecular theories have been established. The theories are

formulated on the basis of radial distribution function and applied successfully in case of pure and mixed solvents system successfully [27, 28]. The scientists fore-footed in this field were L. Jones and Devonshire who developed thermodynamic functions applicable for a single fluid system only. They observed that the excess molar volume (V^E) was negative in case of mixtures of same sized molecules but large positive in case of mixtures of different sized molecules. Later on Treszczanowicz et al. proposed that V^E is contributed by several opposing factors which depend on physical, chemical and structural aspects. The Physical aspect has positive contribution to V^E whereas the chemical aspect is associated with decrease in volume and has negative contribution to V^E [8, 9]. The third one i.e. structural aspect is associated with interstitial accommodation and also change in the free volume always has negative contribution. It was assumed that if V^E is negative then the viscosity deviation ($\Delta\eta$) is positive or vise-versa. But this hypothesis is not always true [10, 11]. Rastogi et al. later proposed that the excess property may be considered a combination of two parts namely, interaction and non-interaction parts [12]. Later on Pitzer, L. Huggins proposed a new approach which is based on perturbation theory [13, 14]. According to them, the properties of a mixture may be achieved from the concept of intermolecular force and thermodynamic property of each constituent in pure form. Recently Flory proposed a new approach based on cell theory to predict the excess properties in case of binary mixtures. The theory is formulated from the concept of equation of state and property of pure constituents and also some others related parameters. This theory may be applied to the multi-components system of different sizes [15-25]. Recently another model known as Extended Real Associated Solution model (ERAS) was proposed by Heintz and co-workers which is formulated on the basis of statistical mechanical derivation applicable for solvents mixture having hydrogen bond. It considered all the aspect of association and non-associative intermolecular forces operating in solvents mixture. Similarly there is another model known as ERAS model are also used by many researchers for describing the excess properties of alcohol-amine solvents mixture [26-30]. In recent time some revision of Real Associated Solution model (ERAS) has been done by Gepert et al. which is termed as Symmetrical Extended Real Association (S-ERAS) model [31]. This model can be applied to evaluate some thermodynamic properties such as excess molar enthalpies and also excess molar volumes of binary mixtures satisfactorily.

2.3. Density

The physicochemical investigation of solute-solvent system is very essential from the theoretical and practical purposes because this kind of studies can provide valuable information about the nature as well as extend of molecular interactions prevailing in electrolytic or non- electrolytic solution of single or mixed solvents. The determination of thermodynamic parameters from volumetric properties is well- accepted approaches to interpret the solute-solvent and solute-solute interactions acting in the solution phase. Interpretation of macroscopic properties like enthalpy, entropy, Gibbs free energy etc. in the light of molecular interaction are usually difficult. The volumetric approaches are very helpful in these cases. We can interpret many properties like co-sphere overlapping, electrostriction, micellization, hydrophobic and solute-solvent or solute- solute interactions by an important parameter apparent molar volume (ϕ_V) [32-35].

2.3.1. Apparent and partial Molar Volumes

Molar volume can be measured from the density of a compound easily. But it is problematic to determine the contribution of volume of a solvent in presence of any electrolyte because influence of electric field of constituting ions compresses the volume of solvent by breaking up the solvent structure. The compression of volume of the solvent by the influence of electric field of ions is called electrostriction. The apparent molar volumes, (ϕ_V), of any solute in solution phase can be determined using the equation as follows [36]:

$$\phi_V = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \quad (1)$$

Where M is the molar mass of studied solute, c is concentration of the solution in molarity; ρ and ρ_0 are the densities of the solution and the solvent respectively. The partial molar volume ϕ_{2V} can be calculated from the relation [37-40]:

$$\phi_{2V} = \phi_V + \frac{(1000 - c\phi_V)}{2000 + c^{3/2} \left(\frac{\partial \phi_V}{\partial \sqrt{c}} \right)} c^{1/2} \left(\frac{\partial \phi_V}{\partial \sqrt{c}} \right) \quad (2)$$

The apparent molar volumes, (ϕ_V) of any solute at infinite dilution is termed as limiting apparent molar volumes, (ϕ_V^0) can be obtained by plotting the graph of apparent molar volumes (ϕ_V) against square root of molar concentration.

$$\phi_V = \phi_V^0 + S_V^* \sqrt{c} \quad (3)$$

Where, S_V^* is the experimental slope. The, (ϕ_V^0) provides the idea about solute-solvent interaction and S_V^* provide the idea about solute-solute interaction [41-46].

ϕ_V^0 of any electrolyte varies with temperature as follows:

$$\phi_V^0 = a_0 + a_1T + a_2T^2 \quad (4)$$

Where, T is temperature (K) and a_0, a_1, a_2 are the coefficients.

The limiting apparent molar expansibilities, (ϕ_E^0) may be defined as the variation of (ϕ_V^0) with temperature at constant pressure. The (ϕ_E^0) can be derived from the following relation:

$$\phi_E^0 = \left(\delta \phi_V^0 / \delta T \right)_P = a_1 + 2a_2T \quad (5)$$

S_V^* alone cannot interpret the structure-making and breaking tendency of a solute. According to Helper, the sign of the parameter, $(\delta \phi_E^0 / \delta T)_P$ is very important to interpret the structure-making and breaking property of any solute. $(\delta \phi_E^0 / \delta T)_P$ can be expressed from the above equation as follows [47]:

$$\left(\delta \phi_E^0 / \delta T \right)_P = \left(\delta^2 \phi_V^0 / \delta T^2 \right)_P = 2a_2 \quad (6)$$

The sign of $(\delta \phi_E^0 / \delta T)_P$ is positive for an electrolyte which acts as a structure maker and the sign of $(\delta \phi_E^0 / \delta T)_P$ is negative for an electrolyte which acts as a structure breaker. According to Redlich and Meyer, (ϕ_V) can be expressed as follows:

$$\phi_V = \phi_V^0 + S_V \sqrt{c} + b_V c \quad (7)$$

$$\text{Where, } S_V = Kw^{3/2} \quad (8)$$

S_V is theoretical slope which depends on molar concentration and valences of the electrolyte.

$$w = 0.5 \sum_i^j Y_i Z_i^2 \quad (9)$$

$$\text{and } K = N^2 e^2 \left(\frac{8\pi}{1000 \epsilon^3 RT} \right)^{1/2} \left[\left(\frac{\partial \ln \epsilon}{\partial p} \right)_T - \frac{\beta}{3} \right] \quad (10)$$

Where, K is the compressibility and the other terms have their usual meaning.

The Redlich-Meyer's equation may be applied in case of 1:1 and 2:1 electrolytes only [48-50]. For polyvalent electrolytes the well-known Owen-Brinkley equation may be applied which used the ion-size parameter.

$$\phi_V = \phi_V^0 + S_V \tau(\kappa a) \sqrt{c} + 0.5 w_V \theta(\kappa a) c + 0.5 K_V c \quad (11)$$

The symbols have their usual meaning. But, this equation is not applicable in case of non-aqueous solutions.

Now a days, the Pitzer equation is used for multivalent single salt $M \gamma_M M \gamma_X$ which is as follows [50]:

$$\phi_V = \phi_V^0 + V |Z_M Z_X| A_V |2b \ln \left(I + bI^{\frac{1}{2}} \right) + 2\gamma_M \gamma_X RT \left[m B_{MX}^2 + m^2 (\gamma_M \gamma_X)^{\frac{1}{2}} C_{MX}^V \right] \quad (12)$$

Where, all the terms have their usual meaning.

2.3.2. Excess Molar Volumes

The excess molar volumes, V^E of a solution may be derived from the following relation [51, 52].

$$V^E = \sum_{i=1}^n x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \quad (13)$$

Where, M_i is the molar masses, ρ_i is the density of the i^{th} component and ρ is the density of the solution. V^E is contributed by three opposing effects. Physical contribution originated from nonspecific interactions has +ve contribution to V^E . The chemical contribution originated from specific intermolecular interactions decrease the volume and has -ve contribution. The 3rd one is the structural contributions originated from deviation of free volume from interstitial accommodation has negative contribution. . The structure breaker solute has positive contribution on excess volume while structure maker solute has positive contribution on excess volume

2.4. Viscosity

Viscosity of a fluid is a measure of resistance to flow. It measures the resistance to gradual deformation caused by tensile stress or shear stress. Viscosity and volume provide much valuable information such as structures and molecular interactions of solution phase. It

also provides information regarding ion-solvent or ion- ion interactions of any electrolytic solution [53, 54]. Viscosity together with partial molar volume may also be used to examine the structures of the electrolytic solutions.

2.4.1. The Reaction rate Theory for Viscous Flow

In case of viscous flows there needs activation energy to overcome the potential barrier. According to Eyring viscosity is related to activation energy as follows [55]:

$$\eta = \frac{\lambda_i h F_n}{\kappa \lambda^2 \lambda_2 \lambda_3 F_a^*} \exp \frac{\Delta E_{act}}{kT} \quad (14)$$

Where, λ =distance between the equilibrium positions (toward motion),

λ_1 = perpendicular distance between two neighbouring layers in relative motion,

λ_2 = distance between neighbouring molecules (toward motion),

λ_3 = distance between molecules in the plane(toward motion)

κ = transmission coefficient,

F_n = partition function, F_a^* = partition function of the activated molecule,

ΔE_{act} = energy of activation for the flow process,

h = Planck's constant,

k = Boltzmann constant.

Ewell and Eyring proposed that ΔE_{act} is a function of ΔE_{vap} in case of viscous flow.

Considering this idea they suggested the following relations [56]:

$$\eta = \frac{N_A h (2\pi mkT)^{\frac{1}{2}}}{Vh} \frac{bRTV^{\frac{1}{3}}}{N_A^{\frac{1}{3}} \Delta E_{vap}} \exp \frac{\Delta E_{vap}}{nRT} \quad (15)$$

Where, n and b are constants and T is temperature in K.

According to Eyring and coworkers liquid state has solid like properties for a very short time then attains instantly gaseous property and jump into the adjacent vacant sites. Considering this idea of significant structures they proposed the following equation:

$$\eta = \frac{V_s}{V} \eta_s + \frac{V - V_s}{V} \eta_g \quad (16)$$

Where, V_s = molar volume at the melting point,

V = molar volume at studied temperature,

η_s and η_g are the viscosities for solid-like and gas-like state.

From the above idea Carlson, Eyring and Ree [57] proposed the following relation:

$$\eta = \frac{N_A h}{Z_K} \frac{V}{V_S} \frac{6}{2^{\frac{1}{2}}} \frac{1}{V - V_S} \frac{1}{1 - e^{-\frac{\theta}{T}}} \exp \frac{aE_S V_S}{(V - V_S)RT} \quad (17)$$

Where, N_A = Avogadro's number,

Z = Number of nearest neighbours,

θ = Einstein characteristic temperature,

E_S = Energy of sublimation and

a' = Proportionality constant.

On the other hand, the term η_g is obtained from the kinetic theory of gases by the relation:

2.4.2. Viscosity of Electrolytic Solutions

That the structure making ions increase the inter-surface friction of any solution. We also know that the ions which increase the extend of hydrogen bonding in the solution will also promote viscosity. Grüneisen in 1905 measured the viscosities of different electrolytic solutions in varying concentrations [58]. He obtained non-linearity and negative curvature of viscosity in low as well as high concentrations. The Jones and Dole proposed a relation of relative viscosities with molar concentrations of any electrolytic solution as following [59].

$$\frac{\eta}{\eta_o} = \eta_r = 1 + A\sqrt{c} + Bc \quad (18)$$

This equation may be written as:

$$\frac{\eta_r - 1}{\sqrt{c}} = A + B\sqrt{c} \quad (19)$$

Where, A and B are coefficients signifying ion-ion and ion-solvent interactions. The equation may be applied for both the aqueous and non-aqueous solvent systems. The significance of A and B coefficients was obtained from Debye-Hückel theory [60]. The A –coefficient signifying ion-ion interactions can be derived from the following Falkenhagen Vernon equation [61-63] :

$$A_{Theo} = \frac{0.2577 A_o}{\eta_o (\epsilon T)^{0.5} \lambda_+^o \lambda_-^o} \left[1 - 0.6863 \left(\frac{\lambda_+^o \lambda_-^o}{A_o} \right)^2 \right] \quad (20)$$

Where, all the symbols have their usual meaning.

The Jones and Dole equation may not be used for higher concentration in case of aqueous and non-aqueous electrolytic solutions [64]. For higher concentration (more than 0.01 M) the above equation was reduced to the following equation by Kaminsky [65-69].

$$\frac{\eta}{\eta_o} = \eta_r = 1 + A\sqrt{c} + Bc + Dc^2 \quad (21)$$

The D coefficient of the above cannot be estimated and the physical importance of it was not understood. Thus most of the researchers are using the Jones and Dole equation. The plot of $(\eta/\eta_o - 1)/\sqrt{c}$ against \sqrt{c} gives a straight line with the slope B and a intercept A [70-71]. But it is observed that in many cases there is a deviation from the linearity and also gives negative A values. Therefore A coefficient is determined from Falkenhagen-Vernon equation. The value of A should be zero for non-electrolyte solution. The B – coefficient is called ion-solvent interaction parameter value of which may be either positive or negative.

The factors which effect B - coefficient are discussed below [72, 73].

1. The ionic solvation and effect of ion in creating order in solvent increase η or B – value.
2. The loss of three dimensional structures in case of solvents decreases η values.
3. Higher molal volume and lower dielectric constant gives higher B value.
4. B-values are lower in case of sterically hindered solvent

2.4.3. Division of B-Coefficient into Ionic Values

Many researchers evaluated viscosity B-values of aqueous or non-aqueous electrolytic solution from Jones-Dole equation [74-104]. It is very necessary to determine the B values of the component ions of any electrolyte to find the any impression about ion-solvent interactions in the solution. B-values of the constituent ions of any electrolyte can be determined by the following ways.

- (1) According to Cox and Wolfenden, B-values of the of the constituent ions are proportional to the ionic volumes and the ionic volumes of the constituent ions are proportional to the third power of the ionic mobilities electrolyte are proportional to the third power of the ionic mobility [105, 106].

(2) The method proposed by Desnoyers and Perron is based on the fact that B-value of ions which is neither structure breaker not a structure maker may be determined with high accuracy from the partial molar volume value by the following Einstein's equation [107].

$$B = 0.0025 \overline{V}_o \quad (22)$$

(3) Sacco et al. proposed another important technique which is known as "reference electrolytic" method for the division of B-values. According to them B-value of the constituent ions of tetraphenyl phosphonium tetraphenyl borate in water may be evaluated as follows:

$$B_{BPh_4^-} = B_{PPh_4^+} = B_{BPh_4PPh_4} / 2 \quad (23)$$

B value of tetraphenyl phosphonium tetraphenyl hmay beas been obtained by the following relation:

$$B_{BPh_4PPh_4} = B_{NaBPh_4} + B_{PPh_4Br} - B_{NaBr} \quad (24)$$

The B-values determined from the above equation are in good agreement with those calculated by other process.

(4) The division of B-coefficients in dimethyl sulphoxide was calculated by Yao and Beunion by the following equation.

$$B_{[(i-pe)_3Bu_4N^+]} = B_{Ph_4B^-} = \frac{1}{2} B_{[(i-pe)_3BuNPh_4B]} \quad (25)$$

(5) Another valuable process was given by Krumgalz based on fact that tetraalkylammonium cations which has large alkyl group are not solvated in organic solvents and hence the ionic B-values in organic solvents has proportionality relation to their ionic dimensions [108, 109]:

$$B_{R_4NX} = a + br^3 R_4N^+ \quad (26)$$

Where, a = B_{X⁻} and b is a constant which depend on temperature and nature of solvent.

The B-ion values can also be evaluated from the following equations:

$$B_{R_4N^+} - B_{R'_4N^+} = B_{R_4NX} - B_{R'_4NX} \quad (27)$$

$$\frac{B_{R_4N^+}}{B_{R'_4N^+}} = \frac{r^3_{R_4N^+}}{r^3_{R'_4N^+}} \quad (28)$$

According to Krungalz, Bu_4N^+ and Ph_4B^- ions not solvated in non-aqueous solvents and their ionic radii will remain constant. They suggested the equations [110-111]:

$$\frac{B_{\text{Ph}_4\text{B}^-}}{B_{\text{Bu}_4\text{N}^+}} = \frac{r_{\text{Ph}_4\text{B}^-}^3}{r_{\text{Bu}_4\text{N}^+}^3} = \left(\frac{5.35}{5.00}\right)^3 \quad (29)$$

$$B_{\text{Bu}_4\text{NBBPh}_4} = B_{\text{Bu}_4\text{N}^+} B_{\text{Ph}_4\text{B}^-} \quad (30)$$

The B-ion values determined by this method were very similar to those agree well those obtained by Sacco et al. in diverse organic solvents according to the following.

$$B_{[(i-Am)_3\text{Bu}_4\text{N}^+]} = B_{\text{Ph}_4\text{B}^-} = \frac{1}{2} B_{[\text{Bu}_4\text{NPh}_4\text{B}]} \quad (31)$$

In recent times, tetrabutylammonium tetra-butylborate (Bu_4NBBu_4) was considered as reference electrolyte by Lawrence and Sacco because both the cation and have symmetrical shape and almost equal van der Waals volume. Thus, according to them

$$\frac{B_{\text{Bu}_4\text{N}^+}}{B_{\text{Bu}_4\text{B}^-}} = \frac{V_{W(\text{Bu}_4\text{N}^+)}}{V_{W(\text{Bu}_4\text{B}^-)}} \quad (32)$$

$$B_{\text{Bu}_4\text{N}^+} = \frac{B_{\text{Bu}_4\text{NBBPh}_4}}{\left[1 + \frac{V_{W(\text{Bu}_4\text{B}^-)}}{V_{W(\text{Bu}_4\text{N}^+)}}\right]} \quad (33)$$

All these methods discussed above are proposed on basis of some approximations and may not applicable universally and needed a revision.

2.4.4. Thermodynamics of Viscous Flow

According to Eyring's [112], viscous flow may be considered as rate process and viscosity (η) can be written as

$$\eta = A e^{\frac{E_{\text{vis}}}{RT}} = \left(\frac{hN_A}{V}\right) e^{\frac{\Delta G^*}{RT}} = \left(\frac{hN_A}{V}\right) e^{\left(\frac{\Delta H^*}{RT} - \frac{\Delta S}{R}\right)} \quad (34)$$

Where, E_{vis} is the experimental entropy of activation which is determined from a plot of $\ln \eta$ vs $1/T$ and ΔG^* , ΔH^* and have their own meaning.

Nightingale and Benck proposed another equation on the basis of the Jones-Dole equation [113].

Thus, we have:

$$R \left[\frac{d \ln \eta}{d \left(\frac{1}{T} \right)} \right] = r \left[\frac{d \ln \eta_o}{d \left(\frac{1}{T} \right)} \right] + \frac{R}{1+Bc} \frac{d(1+Bc)}{d \left(\frac{1}{T} \right)} \quad (35)$$

$$\Delta E_{\eta(\text{Soln})}^{\neq} = \Delta E_{\eta(\text{Solv})}^{\neq} + \Delta E_V^{\neq} \quad (36)$$

ΔE_V^{\neq} is the change of activation energies for viscous flow of solvents in absence and presence of electrolyte. Feakins et al. proposed another equation of the relative viscosity which is formulated based on the transition state theory [114].

$$B = \frac{(\phi_{v,2}^0 - \phi_{v,1}^0)}{1000} + \phi_{v,2}^0 \frac{(\Delta \mu_2^{0\neq} - \Delta \mu_1^{0\neq})}{1000RT} \quad (37)$$

Where, $\phi_{v,1}^0$ and $\phi_{v,2}^0$ represent the partial molar volumes of the solvent and solute respectively and $\Delta \mu_2^{0\neq}$ represents the free energy of activation per mole of solute for viscous flow. $\Delta \mu_1^{0\neq}$ represents the free energy of activation per mole of the solvent for viscous flow per mole which may be written as follows:

$$\Delta \mu_1^{0\neq} = \Delta G_1^{0\neq} = RT \ln(\eta_0 \phi_{v,1}^0 / h N_A) \quad (38)$$

We can evaluate the entropy and enthalpy of activation of viscous flow at different temperatures from the following equations:

$$\frac{d(\Delta \mu_2^{0\neq})}{dT} = -\Delta S_2^{0\neq} \quad (39)$$

$$\Delta H_2^{0\neq} = \Delta \mu_2^{0\neq} + T \Delta S_2^{0\neq} \quad (40)$$

2.4.5. Effects of Shape and Size

Stokes and Mills studied extensively about the effect shape and size on viscosity B-constant of electrolytic or non- electrolytic solution. According to them, the component the in a solution may be viewed as rigid spheres suspended in continuum.

Stokes and Mills have dealt in the aspect of shape and size extensively. The ions in solution can be regarded to be rigid spheres suspended in continuum. Applying the hydrodynamic theory proposed by Einstein, we get the following equation:

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi \quad (41)$$

Where, ϕ is the total volume occupied by the particles. Considering the fact that hydrated ions has large effective size, we get the following equation.

$$2.5\phi = A\sqrt{c} + Bc \quad (42)$$

The term $A\sqrt{c}$ can be neglected in comparison with Bc and putting $\phi = c\phi_{v,1}^0$ where $\phi_{v,1}^0$ represents partial molar volume of the ion, we get:

$$2.5\phi_{v,1}^0 = B \quad (43)$$

So B -coefficient varies linearly with partial molar volume of the ion. with a slope of 2.5. Thus, the effective radii in a continuum can be determined as follows:

$$B_{\pm} = 2.5\phi_{\pm}^0 = \frac{2.5 \times 4 (\pi R_{\pm}^3 N)}{3 \times 1000} \quad (44)$$

It is observed that R_{\pm} value of the ion is higher than its crystallographic radii which may be regarded due to its solvation appreciably. The number of solvent molecules

The number of solvent molecules around the ion in the primary solvation shell, n_b can be evaluated by the following equation:

$$B_{\pm} = \frac{2.5}{1000(\phi_i + n_b\phi_s)} \quad (45)$$

Where, ϕ_i represents the molar volume of the cation of electrolyte and ϕ_s represents the molar volume of the solvent.

2.4.6. Viscosity of Non-Electrolytic Solutions

The following equations are given by Vand [115], Thomas [116] and Moulik for the viscosity of the concentrated solutions of nonelectrolytes [117-119].

Vand equation:
$$\ln \eta_r = \frac{\alpha}{1-Q} = \frac{2.5V_h c}{1-QV_h c} \quad (46)$$

Thomas equation: $\eta_r = 1 + 2.5V_h + 10.05cV_h^2c$ (47)

Moulik equation: $\eta^2 = I + Mc^2$ (48)

where η_r represents the relative viscosity, a is constant which depends on axial ratios of the solute, Q represents the interaction constant, V_h represents the molar volume of the solute surround by solvent molecules, c represents the concentration of the solutes in molar; I and M represent constants. The following viscosity equation was given by Eyring and coworkers for mixed solvents system:

$$\eta_m = \frac{6N_A h}{\sqrt{2}r_m(V_m - V_{Sm})} \left[\sum_i^n \left\{ 1 - \exp\left(\frac{-\theta_i}{T}\right) \right\}^{-x_i} \right] \exp\left[\frac{a_m E_{Sm} V_{Sm}}{RT(V_m - V_{Sm})}\right] + \frac{V_m - V_{Sm}}{V_m} \left[\sum_i^n \frac{2}{3d_i^2} \left(\frac{m_i kT}{\pi^3}\right)^{\frac{1}{2}} x_i \right] \quad (49)$$

Where, n is 2 and 3 for binary and ternary solvents system respectively. The parameters, r_m , E_{Sm} , V_m , V_{Sm} and a_m were estimated from the following equations :

$$r_m = \sum_i^n x_i^2 r_i + \sum_{i \neq j} 2x_i x_j x_{ij} \quad (50)$$

$$E_{Sm} = \sum_i^n x_i^2 E_{Si} + \sum_{i \neq j} 2x_i x_j E_{Sij} \quad (51)$$

$$V_m = \sum_i^n x_i V_i \quad V_{Sm} = \sum_i^n x_i V_{Si} \quad a_m = \sum_i^n x_i a_i \quad (52)$$

$$r_{ij} = (r_i r_j)^{\frac{1}{2}} \quad \text{and} \quad E_{Sij} = (E_{Si} E_{Sj})^{\frac{1}{2}} \quad (53)$$

$$\theta = \frac{h}{\kappa 2\pi} \left(\frac{b}{m}\right)^{\frac{1}{2}} \quad (54)$$

$$b = 2Z\varepsilon \left[22.106 \left(\frac{N_A \sigma^2}{V_s}\right)^4 - 10.559 \left(\frac{N_A \sigma^3}{V_s}\right)^2 \right] \frac{1}{\sqrt{2}\sigma^2} \left(\frac{N_A \sigma^3}{V_s}\right)^{\frac{2}{3}} \quad (55)$$

Here, σ and ε represent Lennard-Jones potential parameters and the other symbols have their usual implication.

The viscosity of ternary mixture may be estimated with the help of binary contribution accurately using the following relations [120-126].

$$\begin{aligned}\eta_m = & \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] \\ & + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] \\ & + x_3 x_1 [A_{31} + B_{31}(x_3 - x_1) + C_{31}(x_3 - x_1)^2]\end{aligned}\quad (56a)$$

The correlation of ternary can be modified to the following method:

$$\begin{aligned}\eta_m = & \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] \\ & + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] \\ & + x_3 x_1 [A_{31} + B_{31}(x_3 - x_1) + C_{31}(x_3 - x_1)^2] \\ & + A_{123}(x_1 x_2 x_3)\end{aligned}\quad (56b)$$

But better result may be achieved when the following relation is used:

$$\begin{aligned}\eta_m = & \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] \\ & + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] \\ & + x_3 x_1 [A_{31} + B_{31}(x_3 - x_1) + C_{31}(x_3 - x_1)^2] \\ & + x_1 x_2 x_3 [A_{123} + B_{123} x_1^2 (x_2 - x_3)^2 + C_{123} x_1^3 (x_2 - x_3)^3]\end{aligned}\quad (56c)$$

Where, A_{12} , B_{12} , C_{12} , A_{23} , B_{23} , C_{23} , A_{31} , B_{31} and C_{31} , represent constants for binary solvents mixtures; A_{123} , B_{123} and C_{123} represent constants for the ternary solvents system and the other symbols have their usual implication.

2.4.7. Gibbs Excess Energy of Activation for Viscous Flow

The Gibbs excess energy of activation of viscous flow ΔG^* can be estimated by the following relation [127]:

$$\Delta G^E = RT \left[\ln \eta V - \sum_{i=1}^j (x_i \ln \eta_i V_i) \right] \quad (57)$$

Where, η is the viscosity and V is molar volume of the solution; η_i the viscosity and V_i is the molar volume of i^{th} component respectively.

2.5. Ultrasonic Speed

The ultrasonic speeds and isentropic compressibility measurements of electrolytic and non- electrolytic solutions give us very valuable information about molecular interactions

playing in the solutions. We can determine a lot of parameters such as molar isentropic compressibility, isentropic compressibility, apparent molal compressibility, etc. from the ultrasonic speeds and density values of any solutions. Isentropic compressibility plays a remarkable role for binary and ternary liquid mixtures where partial molar volume data alone can't provide any well accepted interpretation about the interactions.

2.5.1. Apparent Molal Isentropic Compressibility

The isentropic compressibility (β) of any solvent/solution can be elucidated from the following Laplace's equation [128]:

$$\beta = \frac{1}{u^2 \rho} \quad (58)$$

Where, ρ represents the density and u represents the ultrasonic speed in the solvent/solution. The isentropic compressibility (β) evaluated from the above equation is adiabatic one, because heat is produced during the rapid compressions.

The apparent molal isentropic compressibility (ϕ_K) of any electrolytic and non- electrolytic solutions may be determined using the following equation:

$$\phi_K = M\beta / \rho + 1000(\beta\rho_0 - \beta_0\rho) / m\rho\rho_0 \quad (59)$$

M denotes the molar mass of the solute, β_0 denotes the isentropic compressibility of the solvent mixture and m denotes the molality of the solution.

The plot of ϕ_K against the square root concentration in molal gives a straight line with the intercept ϕ_K^0 which is known as limiting apparent isentropic compressibility.

$$\phi_K = \phi_K^0 + S_K^* \sqrt{m} \quad (60)$$

The limiting apparent molal isentropic compressibility (ϕ_K^0) signifies solute-solvent interaction and the experimental slope S_K^* signifies solute-solute interactions prevailing in electrolytic and non- electrolytic solutions respectively [129, 130]. Solvation of an electrolyte by electrostriction always leads to reduction in compressibility of the solution. If the solute molecules fit poorly in the bulk of solvent than there will be increase in ϕ_K^0 value due to the appearance of compressible environment. Similarly formation of poor hydrogen bond also leads to increase in ϕ_K^0 value [131-134].

2.6. Conductance

Conductance study along with viscosity measurements, gives very much valuable information regarding ion-ion and ion-solvent interaction of electrolytic aqueous or non-aqueous solution. In this regard well-known Kohlrausch's equation based on Debye-Hückel theory molar conductance of symmetrical electrolytic solution is worth mentioned [268].

$$\Lambda = \Lambda_0 - S\sqrt{c} \quad (61)$$

where,

$$S = \alpha\Lambda_0 + \beta \quad (62)$$

$$\alpha = \frac{(z^2)k}{3(2 + \sqrt{2})\epsilon_r kT \sqrt{c}} = \frac{82.406 \times 10^4 z^3}{(\epsilon_r T)^2} \quad (63a)$$

$$\beta = \frac{z^2 e F k}{3\pi\eta\sqrt{c}} = \frac{82.487 z^3}{\eta\sqrt{\epsilon_r T}} \quad (63b)$$

The Λ_0 values at infinite dilution obtained from Fuoss-Onsager theory differed significantly from that obtained from Pitt's theory. Later on Fuoss and Hsia modified Fuoss-Onsager equation as follows [136-141].

$$\Lambda = \frac{\Lambda_0 - \alpha\Lambda_0\sqrt{c}}{(1 + \kappa\alpha)} \left(\frac{1 + \kappa\alpha}{\sqrt{2}} \right) - \frac{\beta\sqrt{c}}{(1 + \kappa\alpha)} + G(\kappa\alpha) \quad (64)$$

Where, $G(\kappa\alpha)$ is a function of the variable. The simplified form:

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec \ln c + J_1 c + J_2 \sqrt[3]{c} \quad (65)$$

However, it has been found that these equations have certain limitations, in some cases it fails to fit experimental data. Some of these results have been discussed elaborately by Fernandez-Prini [142, 143]. Further correction of the equation was made by Fuoss and Accascini. They took into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation becomes:

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec \ln c + J_1 c + J_2 \sqrt[3]{c} - F\Lambda c \quad (66)$$

where,
$$F_c = \frac{4\pi R^3 N_A}{3} \quad (67)$$

In most cases, however, J_2 is made zero but this leads to a systematic deviation of the experimental data from the theoretical equations. It has been observed that Pitt's equation gives better fit to the experimental data in aqueous solutions [144].

2.6.1. Ionic Association

The dissociation or association of an electrolyte may be evaluated from the plots of Λ vs. \sqrt{c} following the Onsager equation. Completely dissociation of electrolyte takes place when Λ_{exp} is greater than Λ_{theo} and association of occurs when Λ_{exp} is less than Λ_{theo} . The association constant, KA may be determined from conductance study by the following ways [145]:

$$M^{z+} + A^{z-} = MA \quad (68)$$

$$K_A = \frac{(1-\alpha)}{\alpha^2 c \gamma_{\pm}^2} \quad (69)$$

$$\alpha = 1 - \alpha^2 K_A c \gamma_{\pm}^2 \quad (70)$$

The association constant for strongly associated electrolytes may be determined from Fuoss-Kraus equation 40 or Shedlovsky's equation as follows [146, 147]:

$$\frac{T(z)}{\Lambda} = \frac{1}{\Lambda_0} + \frac{K_A}{\Lambda_0^2} \cdot \frac{c \gamma_{\pm}^2 \Lambda}{T(z)} \quad (71)$$

For Fuoss-Kraus method, $T(Z) = F(Z)$ and for Shedlovsky's method $1/T(Z) = S(Z)$.

$$F(z) = 1 - z(1 - z(1 - \dots)^{\frac{1}{2}})^{\frac{1}{2}} \quad (72a)$$

and

$$\frac{1}{T(z)} = S(z) = 1 + z + \frac{z^2}{2} + \frac{z^3}{8} + \dots \quad (73b)$$

$1/\Lambda_0$ for its intercept and K_A/Λ_0^2

The plot of $T(z)/\Lambda$ against $c \gamma_{\pm}^2 \Lambda/T(z)$ gives a straight line with a slope of K_A/Λ_0^2 and an intercept $1/\Lambda_0$. It is seen that there significant uncertainty when the KA Very large.

The Fuoss-Hsia equation for associated electrolytes is given below:

$$A = A_o - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{\frac{3}{2}} - K_A A \gamma_{\pm}^2(\alpha c) \quad (74)$$

The modification of above equation for symmetrical electrolytes in dilute solutions was done by Justic which is shown below [148]:

$$A = \alpha(A_o - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1 R(\alpha c) - J_2 R(\alpha c)^{\frac{3}{2}} \quad (75)$$

$$\frac{(1-\alpha)}{\alpha^2 c \gamma_{\pm}^2} = K_A \quad (76)$$

$$\ln \gamma_{\pm} = \frac{-k\sqrt{q}}{(1+kR\sqrt{\alpha c})} \quad (77)$$

The related parameter may be determined from a least square treatment after putting q value in the above equation:

$$R = q = \frac{e^2}{2\epsilon kT}$$

The distance of closest approach, a_0 of two ions for the formation of ion-pair may be evaluated from the value of an association constant by two methods [149].

$$K_A = \frac{4\pi N_A \alpha^3}{3000} \exp\left(\frac{e^2}{\alpha \epsilon kT}\right) \quad (78)$$

It is observed that in some cases, the extend of K_A values are very small to calculation the a_0 . In such cases the following more general equation may be used to find the distance parameter [150].

$$K_A = \frac{4\pi N_A \alpha}{1000} \int_{r=a}^{r=q} r^2 \exp\left(\frac{z^2 e^2}{r \epsilon kT}\right) dr \quad (79)$$

In this equations the short-range interactions was not considered and the solvated ion was approximated following the hard sphere model [151].

2.6.2. Ion Size Parameter and Ionic Association

Omitting the J_2 term, the equation (93) can be rewritten as follows:

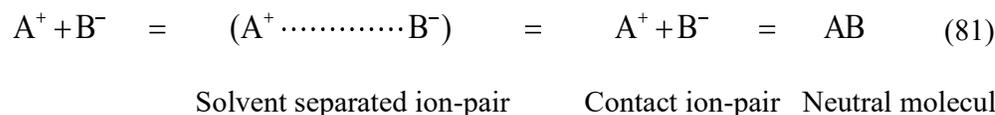
$$A_1 = A + S\sqrt{c} - Ec \ln c = A_o + J_1 c + J_2 \sqrt[3]{c} = A_o + J_1 c \quad (80)$$

Thus, from the plot of Λ_0 vs. c , we can determine Λ_0 and J_1 and also 'a' values of the above equation.

It is observed that 'a' values calculated by this method were smaller in some extent than the crystallographic radii which may be supposed due to the fact that the ion-solvent interactions was not considered in continuum theory [152-154]. Latter Fuoss and co-workers proposed a new equation of conductance equation. They divided the ion of electrolytic solutions into three categories. a) Any ion is surrounded oppositely charged ions in the first shell of nearest neighbors. b) When ions are overlapping Gurney's co-spheres, then $r_{ij} = a + ns$, where, n is 1, 2, 3 etc. and 's' is the average diameter per solvent molecule

(iii) Ions find no other unpaired ion in a surrounding sphere of unpaired ions.

The following equilibrium exist in the solution due to thermal motions and interionic



If, γ represents the fraction of solute present as unpaired ($r > R$) ions, α represents the fraction of paired ions ($r \leq R$), then the concentration of unpaired ion will be $c(1-\alpha)(1-\gamma)$ and that of contact pair will be $\alpha c(1-\gamma)$.

The equilibrium constants K_R may be written as:

$$K_R = \frac{(1-\alpha)(1-\gamma)}{c\gamma^2 f^2} \quad (82)$$

$$K_S = \frac{\alpha}{1-\alpha} = \exp\left(\frac{-E_S}{kT}\right) = e^{-\epsilon} \quad (83)$$

K_S is the constant which describe ion-solvent and ion-ion interactions and E_S represents the difference of energy from states ($r = R$) to state ($r = a$);

We may write

$$(1-\alpha) = \frac{1}{1+K_S} \quad (84)$$

The conductometric pairing constant may be written as:

$$K_A = \frac{(1-\alpha)}{c\gamma^2 f^2} = \frac{K_R}{1-\alpha} = K_R(1+K_S) \quad (85)$$

Here, both contact pairs and ion pairs separated by solvent behave like dipoles to an external field X their interaction with unpaired ions were neglected in determining the long-range effects. The various patterns can be written in the following form:

$$\Lambda = p \left[\Lambda_o \left(\frac{1 + \Delta X}{X} \right) + \Delta \Lambda_e \right] = p \left[\Lambda_o (1 + R_x) + E_L \right] \quad (86)$$

This is an equation which depends on three parameters, $\Lambda = \Lambda(c, \Lambda_o, R, E_s)$, $\Delta X / X$ and $\Delta \Lambda_e$ considering the interionic electrostatic forces.

The parameter K_R (or E_s) is a measure of all short range effects:

$$p = 1 - \alpha(1 - \gamma) \quad (87)$$

The α is very close to unity for the solvents of low dielectric constant, $(-E_s/kT) \gg 1$. In such cases the equation becomes:

$$\Lambda = \gamma \left[\Lambda_o \left(\frac{1 + \Delta X}{X} \right) \right] + \Delta \Lambda_e \quad (88)$$

The equilibrium constant for the reaction, $A^+ + B^- + AB$, is then

$$K_A = \frac{(1 - \gamma)}{c\gamma^2 f^2} \approx K_R K_S \quad (89)$$

Since, $K_S \gg 1$. The variables are represented by the following equations:

$$\gamma = 1 - \frac{K_R c \gamma^2 f^2}{(1 - \alpha)} \quad (90)$$

$$K_R = \left(\frac{4\pi N_A R^3}{3000} \right) \exp\left(\frac{\beta}{R}\right) \quad (91)$$

$$-\ln f = \frac{\beta \kappa}{2(1 + \kappa R)}, \quad \beta = \frac{e^2}{\epsilon \kappa T} \quad (92)$$

$$\kappa^2 = 8\pi\beta\gamma\eta = \frac{\pi\beta N_A \gamma c}{125} \quad (93)$$

$$-\epsilon = \ln \left[\frac{\alpha}{1 - \alpha} \right] \quad (94)$$

In this ways the limitations of the previous equations have been resolved and the present equation can be universally used for all concentrations [149].

2.6.3. Limiting Equivalent Conductance

Experimental observations and theoretical equations are applied to determine the limiting equivalent conductance of any electrolyte. The motion of an ion is restricted by the neighboring solvent molecules at infinite dilutions since the ions are at infinite distance. According to Kohlrausch's law of independent migration of ions,

$$\Lambda_0 = \lambda_o^+ + \lambda_o^- \quad (95a)$$

Limiting equivalent conductance of the ionic components will be,

$$\lambda_o^+ = t_+ \Lambda_0 \quad \text{and} \quad \lambda_o^- = t_- \Lambda_0 \quad (95b)$$

But, transference number except few solvents cannot be determined accurately

Several efforts were made for developing indirect methods to get the limiting ionic equivalent conductance of any ion in such a solvent for which accurate transference numbers are not known.

The method has been summarized by Krumgalz [155] proposed some important opinions for determination of limiting ionic equivalent conductance of any ion as follows:

(i) Walden equation [156]

$$(\lambda_o^\pm)_{\text{water}}^{25} \cdot \eta_{\text{o,water}} = (\lambda_o^\pm)_{\text{acetone}}^{25} \cdot \eta_{\text{o,acetone}} \quad (96)$$

$$(ii) (\lambda_{\text{o,pic}} \cdot \eta_{\text{o}}) = 0.267, \quad \lambda_{\text{o,Et}_4\text{N}^+} \cdot \eta_{\text{o}} = 0.269^{[156, 157]} \quad (97)$$

based on $\Lambda_{\text{o,Et}_4\text{N}_{\text{pic}}} = 0.563$

According to Walden the products should be independent of temperature and solvent. But it is observed that the $\Lambda_{\text{o,Et}_4\text{N}_{\text{pic}}}$ values differ significantly from more precise experiments.

$$\lambda_o^{25}(\text{Bu}_4\text{N}^+) = \lambda_o^{25}(\text{Ph}_4\text{B}^-) \quad (98)$$

$$(iii) \lambda_o^{25}(\text{Bu}_4\text{N}^+) = \lambda_o^{25}(\text{Ph}_4\text{B}^-) \quad (99)$$

The equation may be successively applied in case of some solvents but fails in case of methanol, nitro methane and acetonitrile [158].

$$(iv) \lambda_o^{25}(\text{Bu}_4\text{N}^+) = \lambda_o^{25}(\text{Bu}_4\text{B}^-)^{[159]} \quad (100)$$

This method was applicable in case of most of the solvents.

(v) The equation proposed by Gill is as follows [160]:

$$\lambda_o^{25}(R_4N^+) = \frac{zF^2}{6\pi N_A \eta_o [r_i - (0.0103\varepsilon_o + r_y)]} \quad (101)$$

where Z and r_i are the charge and radius of ion, respectively; η_o and ε_o are viscosity and dielectric constant of the medium respectively; r_y = adjustable parameter.

But, huge inconsistencies were detected between the experimental and calculated values [300(a)]. Afterwards, Krumgalz proposed a different approach to eliminate the above inconsistencies [161].

$$(vi) \lambda_o^{25} [(i-Am)_3 BuN^+] = \lambda_o^{25} (Ph_4B^-)^{[305]} \quad (102)$$

It is observed from measurements transference number that the $\lambda_o^{25} [(i-Am)_3 BuN^+]$ and

$\lambda_o^{25} (Ph_4B^-)$ values vary each other by 1% [161].

$$(vii) \lambda_o^{25} (Ph_4B^-) = 1.01 \lambda_o^{25} [(i-Am)_4 B^-]^{306} \quad (103)$$

The values obtained from this equation are correct for most organic solvents.

Krumgalz proposed a technique for calculating the limiting ion conductance in organic solvents considering the fact that large tetraalkyl (aryl) onium ions are not solvated in organic solvents due to the presence of weak electrostatic interactions between solvent molecules and the large ions.

The radius of the moving particle from Stokes equation can be evaluated as follows:

$$r_s = \frac{|z|F^2}{A\pi\eta_o\lambda_o^\pm} \quad (104)$$

Where, A is a coefficient which varies from 6 to 4. The ionic radius of the non-solvated tetraalkyl (aryl) onium ions is constant.

$$\lambda_o^\pm \eta_o = \text{constant} \quad (105)$$

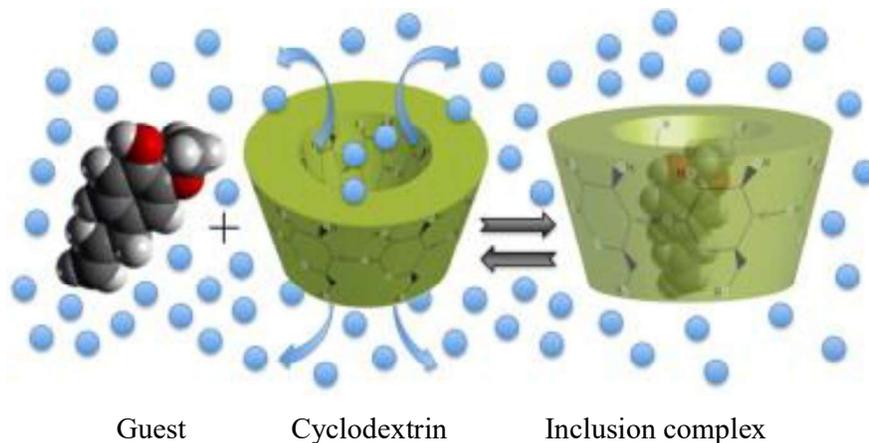
The product is constant and not dependent on the nature of the organic solvents like $i\text{-Am}_4\text{B}^-$, Ph_4As^+ , Ph_4B^- ions and for tetraalkylammonium cation and the equation may be utilized for determination of λ_o^\pm values for most of the organic.

2.6.4. Conductance-Some Recent Trends

Recently Blum, Turq and coworkers have proposed a conductivity theory considering mean spherical approximation (MSA) assuming the continuity and hydrodynamic equations used in the more classical treatment [162, 163]. This theory is applicable in wider range of concentrations than the classical equations. However, the experimental performance of the new equation is yet available in the literature. Chandra and Bagchi [164, 165] proposed a new approach for ionic conductance and viscosity calculation which is formulated on the basis of mode coupling theory. This equation may be applied both low and high concentration range. This theory seems to be satisfactory for conductance study up to 1 (M) solution.

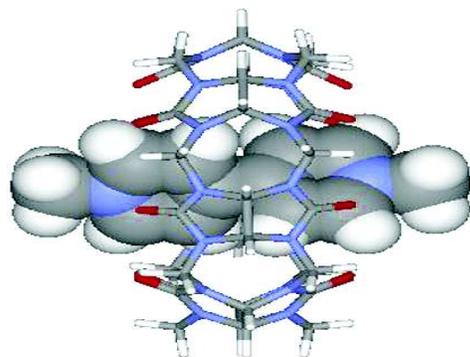
2.7. Inclusion Complexes

A complex in which a compound or part of a compound enters into the cavity or tunnel or canal of another compound partially or entirely is termed as inclusion complex. The compound which becomes encapsulated into the cavity or tunnel or canal of another compound is called guest molecule and the compound into which the other compound becomes encapsulated is called host molecule. No any covalent bond formation between the guest and the host molecules in inclusion complex take place rather there is non-bonding interaction. The host molecules may be considered as vacant capsules with certain cavity diameter and the cavity is occupied by another molecule then the so called inclusion complex is formed [166-174].

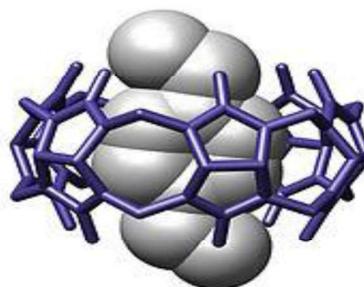


Pictorial representation of inclusion complex formation

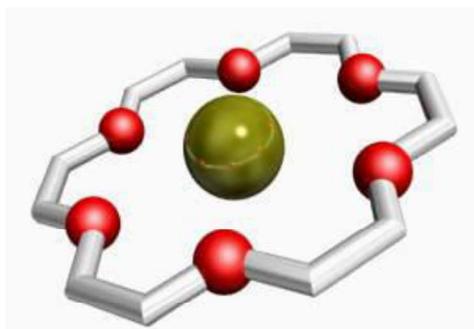
The examples of host molecules for inclusion complexes are cyclodextrin, cucurbiturils, crowns, calixarenes, porphyrins, etc. and examples of guest molecules are vitamins, ionic liquids, amino acid and its derivatives, surfactant, various drug molecules, etc.[175-180]



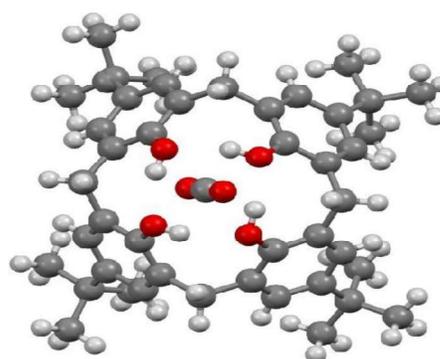
(i)



(ii)



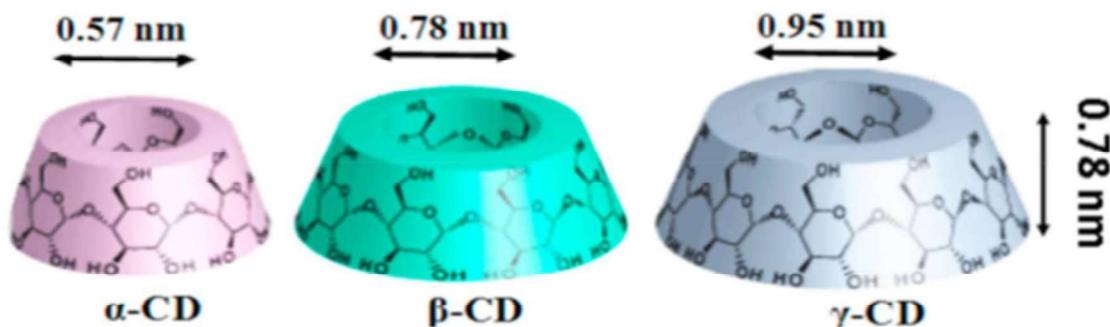
(iii)



(iv)

Pictorial diagram of (i) Inclusion complex cyclodextrin (ii) Cucurbituril[6], (iii) 18-Crown-6 and (iv) P-tert-butylcalix-4-arene.

Inclusion complexes play a significant role in the formulation progress of drugs molecules. Some methods used to improve the solubility of drugs molecules are Solid dispersion, micronization, solvent deposition etc. All the approaches are used for improving dissolution rate, miscibility and bioavailability of sparingly soluble drugs. But each method has some boundaries and advantages.

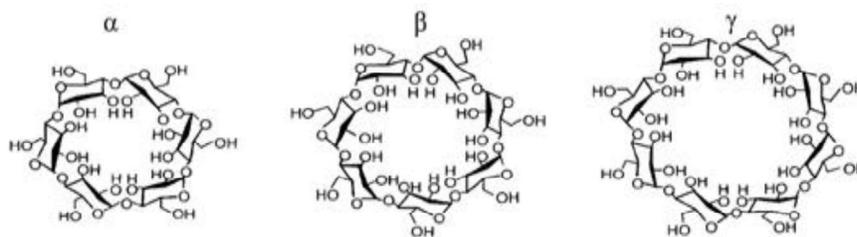


3D structures of three different cyclodextrins

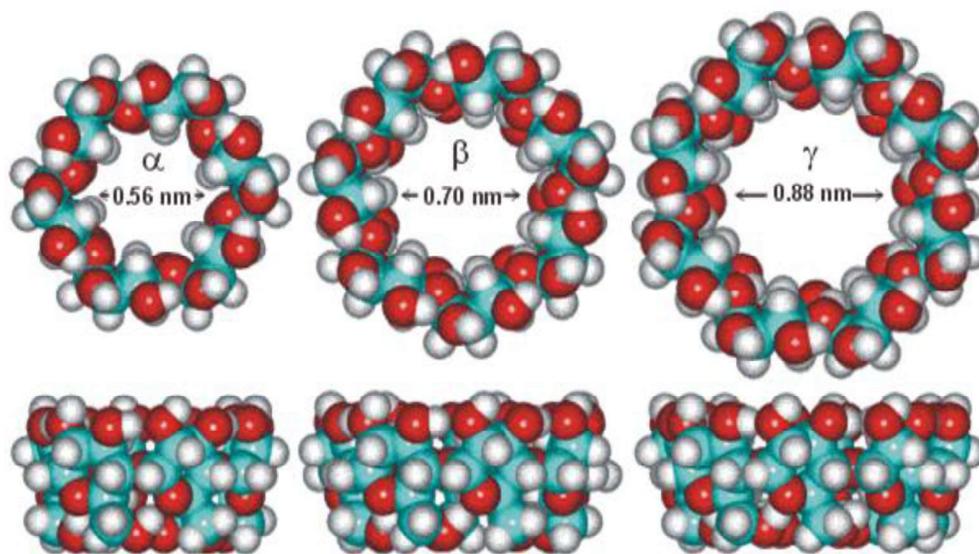
Inclusion complexation with cyclodextrin is the most efficient method to improve the solubility of weakly soluble drugs. Cyclodextrin by the formation of Inclusion complexation are capable to modify the physicochemical properties of drugs such as solubility, particle size, thermal behavior and thus providing a highly water miscible amorphous forms. The CDs are not only capable of enhancing the dissolution rate but also bio-availability of the sparingly soluble drugs. The permeation of drugs through various biological membranes can also be improved by formation of drug-cyclodextrin inclusion compounds [181].

2.7.1. Structure and Properties of Cyclodextrins

The cyclodextrins (CDs) are cyclic oligosaccharides having n glucopyranose units. There are three kinds of cyclodextrins namely α -cyclodextrin (α -CD), β -cyclodextrin (β -CD) and γ -cyclodextrin (γ -CD) which have 6, 7 and 8 numbers of glucopyranose units respectively and the glucopyranose units are joined together by α -(1-4) linkages [182-186]. The inner cavities of all the three cyclodextrins are hydrophobic in nature and exterior parts are hydrophilic in nature. This unique feature make cyclodextrins appropriate for complexation with different kind of molecules such as vitamins, amino acids, hormones, ionic liquids, dyes polymers, etc. The hydrophobic parts of the guest molecules become encapsulated into the hydrophobic cavity of cyclodextrins and thus forming an inclusion complex [187-191].



STRUCTURE OF CYCLODEXTRINS



Structures of α -Cyclodextrin, β -Cyclodextrin and γ -Cyclodextrin

Some physical properties of α -Cyclodextrin, β -Cyclodextrin and γ -Cyclodextrin are mentioned below:

Properties of Cyclodextrins

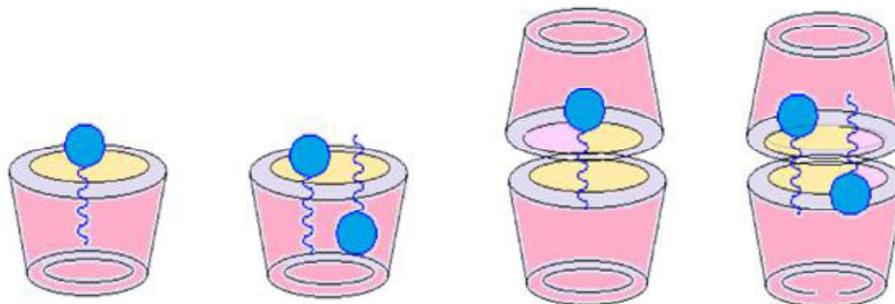
Property	α -Cyclodextrin	β -Cyclodextrin	γ -Cyclodextrin
Number of glucopyranose units	6	7	8
Molecular weight (g/mol)	972.84	1134.98	1541.33
Solubility at 25°C (% w/v)	14.5	1.85	23.2
Outer diameter (Å)	14.6	15.4	17.5
Cavity diameter (Å)	4.7–5.3	6.0–6.5	7.5–8.3
Height of torus (Å)	7.9	7.9	7.9
Cavity volume (Å ³)	174	262	427

2.7.2. Formation of Inclusion Complex

When any guest molecule fits into the cavity of the host molecule both in dimensionally and characteristically, the inclusion complex is formed[192]. During the process of encapsulation the water molecules are released from the cavity of CDs and the hydrophobic part of the guest molecule enters into the cavity of CD due to the presence of hydrophobic-hydrophobic interaction between the hydrophobic inner cavity of CDs and the hydrophobic part of the guest molecule. The host-guest inclusion complex may be prepared by different methods such as co-precipitation, slurry method, dry mixing etc [193]. The hydrophilic part of the guest remains outside the cavity. The presence of hydrophilic-hydrophilic interaction between the hydrophilic part of guest molecule and the peripheral primary or secondary $-OH$ of the CDs also makes the inclusion process thermodynamically feasible.

2.7.3. Stoichiometry

The stoichiometry of host-guest inclusion complex depends on the size of the guest molecule and the available space of the cavity of the host molecule. Various kind of stoichiometries of host-guest inclusion complex are possible such as 1:1, 1:2, 2:1, 2:2 etc.



Different stoichiometric ratios in host-guest inclusion complexes.

The stoichiometry of inclusion complex may be evaluated using various techniques such as UV-Vis spectroscopic study, conductance and surfacetension studies etc. The number of break-points in surface tension vs. [CD] graph or conductance vs. [CD] graph provide the clues about the stoichiometry of inclusion complex. If there is only one break-point in these graph then the stoichiometry is 1:1. The presence of more break-points indicate 1:2, 2:1, 2:2

stoichiometry [194-201]. We can also get idea about the stoichiometry from the Job's plot of UV-VIS spectroscopy.

2.7.4. Association Constant

The affinity of formation of inclusion complex can be ascertain from association constant values of host-guest system. Asociation constant may be determined using various techniques such as UV-Vis, NMR, fluorecence spectroscopy, conductance and surfacetension studies etc.

The association constant gives idea about how effectively the guest molecule is incorporated inside the host molecule. Asociation constant (also termed as binding constant, formation constant and equilibrium constant) is determined using various chemical approaches such as UV-Vis, NMR, fluorecence spectroscopy and gas and liquid chromatography. [202] . The well-known Benesi-Hildebrand method may be applied for calculation of association constant of the inclusion complexes from UV-Vis spectroscopy.

$$\frac{1}{\Delta A} = \frac{1}{\Delta \varepsilon [H] K_a} X \frac{1}{[H]} + \frac{1}{\Delta \varepsilon [G]} \quad (106)$$

2.7.5. Detection of Inclusion Complex

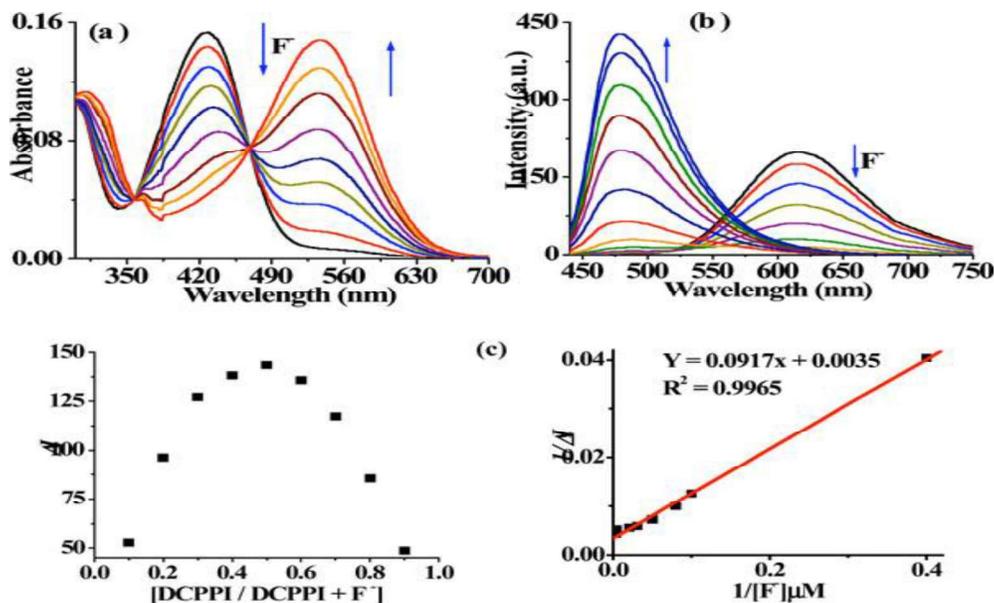
The formation of inclusion complex can be probed by many and spectroscopical techniques such as NMR, FT-IR, UV-Vis spectroscopies as well as physicochemical techniques such as surface tension, conductance, refractive index, density and viscosity studies.

¹H NMR and 2D NMR spectroscopies are the sophisticate techniques to probe the formation of host-guest inclusion complexes. The considerable chemical shifts of H3 and H5 protons of cyclodextrins and the protons of hydrophobic part of the guest molecule may be regarded as the formation of inclusion complexes [203-208].

FT-IR spectroscopy may also be employed to confirm the formation of inclusion complexes. The significant shift of various groups of ICs from the host and guest molecules may be regarded due to the encapsulation of the Guest into the cavity of host molecules [209-213].

Another widely used technique for characterization of inclusion complex formation is UV-VIS spectroscopy. The stoichiometry of the IC may be determined by from Job's plot

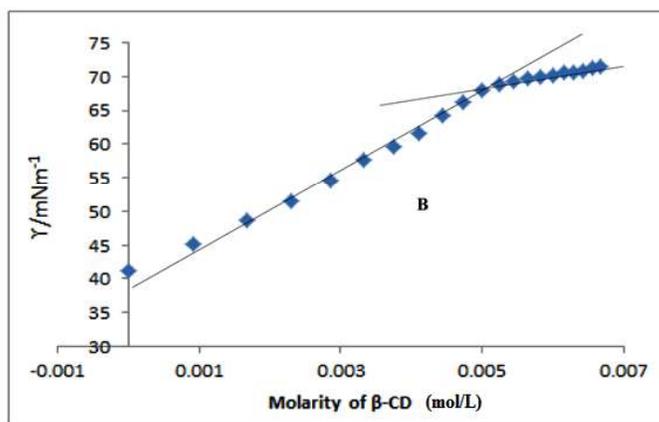
and however, the association constant of the formation of IC can be calculated by Benesi-Hildebrand equation [214-219].



UV-VIS spectra of guest molecule with varying concentration of host molecule β -CD and Job's plots

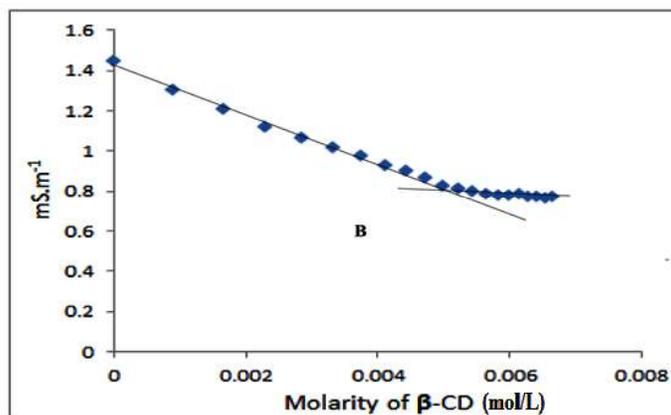
The surface tension study is another reliable technique for characterization of inclusion complex. The surface tension of the guest molecules are measured with the successive addition of CD solution. The presence of break-point in the graph of surface tension vs. [CD] indicates the formation of ICs. If there is only one break-point the the inclusion complex is of 1:1 stoichiometry. The presence of more break-points signify 1:2, 2:1, 2:2 stoichiometries which may be determined from the concentrations of host and guest at the break-points. We can also calculate the association constant of the formation of IC from the surface tension study also [220-222].

Variation of surface tension of ionic liquid (0.01m solution) corresponding to the added concentration of (A) α -cyclodextrin (0.01m solution) and (B) β -cyclodextrin (0.01m solution).



Variation of surface tension of ionic liquid corresponding to the added concentration of β-cyclodextrin.

Similarly the conductance study may be applied to ascertain the formation of inclusion complexes. The conductivity of the guest molecule changes with the successive addition of CD solution which important clues about the formation of inclusion complexes [223, 224].



Variation of conductance of ionic liquid corresponding to the added concentration of aqueous β-cyclodextrin

The change of entropy and enthalpy can be calculated from the association constant using Van't Hoff equation (II.c) [1]

$$2.303 \log K_a = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (107)$$

From this equation we can calculate some thermodynamic parameters such as The Gibbs free energy change (ΔG), enthalpy change (ΔH°) and entropy change (ΔS°) etc. The negative values of ΔG indicate the feasibility of the inclusion process.