# CHAPTER - I

## INTRODUCTION

# INTRODUCTION

Liquids and gases exhibit a characteristic property of flowing under an applied force, which could be even the force of their own weight. When a liquid flows through a tube, the liquid layer in contact with the wall of a tube is stationary whereas that in the centre has the maximum velocity, the intermediate layers have the gradiation of velocities. Similarly, in a liquid flowing over a glass plate the layer in contact with the plate remains stationary, the velocity of different layers increases continuously with the distance from the fixed surface, being the highest in the free surface of the liquid. On account of relative motion each layer experiences a frictional force and behaves as if it is being dragged in backward direction, and work is to be done to maintain the flow. This internal friction or resistance which resists the relative motion of its parts, i.e. the flow of the liquid, is known as viscosity.

Viscosity is produced by the shearing effect of moving one layer of the liquid past another, and is quite distinct from intermolecular attraction. It may be thought of as caused by internal friction of the molecules themselves and it is present in ideal gases as well as in real gases and liquids.

Newton deduced that the internal friction or viscosity would produce retarding force proportional to the velocity gradient (dv/dx) normal to the direction of flow and to the area of contact, (A) between the moving sheets of liquid.

i.e. $F \propto A \quad dv/dx$

or $F = \eta \; A. \, dv/dx$

where '$\eta$' is the constant. This law holds for all homogeneous liquids, but not for suspensions or colloidal solutions, which are therefore, called non-Newtonian fluids[1]. The proportionality constant '$\eta$' is the coefficient of viscosity. The coefficient of viscosity or in brief, the viscosity, is defined as the force that must be exerted between two parallel layers of unit area and unit distance apart, in order to maintain a unit velocity of streaming of one layer past the other.

The reciprocal of the coefficient of viscosity, usually represented by $\phi$, is called as the fluidity. It is the measure of ease with which a liquid can flow.

$$\text{Fluidity } \phi = \frac{1}{\eta}$$

In c.g.s. system $\eta$ has the dimensions of gram $cm^{-1}$ $sec^{-1}$ and is expressed in units of dyne sec $cm^{-2}$. When a force of one dyne can maintain a velocity difference of 1 cm/sec between two layers of a liquid 1 cm apart and having an area of contact of 1 square cm, the viscosity of the liquid is said to be 1 poise. The name 'poise' is given in the honour of french scientist Poiseuille, who derived the formula and gave method for measurement of viscosity of liquids.

Since in practice a poise has been found to be rather too large for many liquids, smaller units of centipoise ( $\frac{1}{100}$ poise ) and millipoise ( $\frac{1}{1000}$ poise ) are generally used. In case of gases, viscosity is expressed in still smaller unit, micropoise ($10^{-6}$ poise).

The SI unit of viscosity is the pascal second$^2$. The pascal (abbreviated 'Pa') is the name of the SI unit of pressure that is one Newton per square meter. Since

$$1\ N = 1\ Kg.\ m\ S^{-2}$$

$$1\ Pas = 1\ Kg.\ m^{-1}\ S^{-1}$$

The fluid has viscosity of 1 PAS if a force of 1 N is required to move a plane of 1 cm$^2$ at a velocity of 1 m S$^{-1}$ with respect to a plane surface a meter away and parallel with it.

$$0.1\ Pas = 1\ poise$$

The usual symbol for viscosity is the Greek letter 'ETA' ($\eta$).

The variation of viscosity with temperature may be represented as,

$$\eta = A.\ e^{E/RT}$$

Where 'E' is the activation energy for viscosity.

The viscosity of liquid increases as the pressure is increased because the number of holes is reduced and it is therefore, more difficult for molecule to move round each other.

## 1.1 METHODS OF VISCOSITY MEASUREMENTS :

The coefficient of viscosity of a liquid may be measured by a number of methods.

### a) STOKES METHOD :

The force causing a particle to settle in a fluid is equal to its effective mass multiplied by the acceleration due to gravity.

The effective mass is the mass of the particle minus the mass of the fluid it displaces. The force retarding motion is the frictiional coefficient multiplied by the velocity. The frictional coefficient is the force required to maintain a particle at unit velocity.

Stokes showed that for spheres and nonturbulent flow[3],

$$F = 6\pi\eta r$$

Where 'r' is the radius of the sphere and '$\eta$' the coefficient of viscosity. If density of the sphere, is $\rho$ and the density of the medium is '$\rho_o$', the force 'F' causing motion is

$$\frac{4}{3}\pi r^3 (\rho - \rho_o) g$$

Where 'g' is the acceleration of gravity.

### b) POISEUILLE METHOD :

The Poiseuille equation for the coefficient of viscosity of a fluid is[4]

$$\eta = \pi P r^4 t / 8 L.V.$$

Where 'V' is the volume of the liquid of viscosity '$\eta$' which flows in time 't' through a capillary tube of radius 'r' and length 'L' under the pressure of 'P' dynes per square centimeter.

### c) OSTWALD METHOD :

This method is generally used for the measurement of viscosity. In Ostwald method, one compares the viscosity of liquid with that of another liquid of known viscosity. This is done by comparing the time of flow of equal volume of two liquids through the same capillary using an instrument called viscometer. Then according to the Poiseulle equation, the ratio of the viscosity coefficients of the two liquids is given by -

$$\frac{\eta_1}{\eta_2} = \frac{\pi P_1 r^4 t_1}{8 L V} \times \frac{8 L V}{\pi P_2 r^4 t_2} = \frac{P_1 t_1}{P_2 t_2}$$

Since the pressures $P_1$ and $P_2$ are proportional to the densities of the two liquids $\rho_1$ and $\rho_2$ then we may write as

$$\frac{\eta_1}{\eta_2} = \frac{P_1 t_1}{P_2 t_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$$

Consequently, once $\rho_1$ and $\rho_2$ and $\eta_2$ are known, determination of $t_1$ and $t_2$ permits the calculation of $\eta_1$ the viscosity coefficient of the liquid under consideration.

Water is usually taken as the reference standard for viscosities, because viscosity of water at different temperature is given in literature.

## 1.2 LITERATURE SURVEY :

Poisceuille[5], the great poineer in research on viscosity, found that some salts increase the viscosity of water whereas others decrease the viscosity. Sprung[6] appears to have been the first to measure viscosity of solutions of barium chloride and found that it increased the viscosity of water. Arrhenius[7] made viscosity measurements on solutions of some salts and found that the change in viscosity caused by the addition of a salt was roughly proportional to the concentration at low concentrations but increased more rapidly at moderate concentrations, ($\sim$ 1 normal). He proposed new formula for the relationship between viscosity and concentration namely

$$\eta_r = A^c$$

Where '$\eta_r$' is the relative viscosity compared to that of water at the same temperature and 'A' is the constant for any given salt and temperature.

This equation has been tested by Reyher[8], by Wagner[9] and by others; and found to hold good within a few tenths of 1 per cent between 1/8 and 1/2 normal and within about 1% upto 1 normal.

Sutherland[10] suggested that the depolymerization of triple water molecules by the dissolved salts causes diminution in viscosity.

The next outstanding investigator was Gruneisen[11], who made a careful and critical study of the experimental technique with the Ostwald form of viscometer and then made measurements which were probably more precise than any previously made, on aqueous solutions of sixteen salts and sucrose over a wide range of concentrations. He made measurements with more dilute solutions than his predecessors and thereby discovered that viscosity-concentration curves instead of becoming more nearly straight line at the dilute end, exhibit a negative curvature. This behaviour is not in accord with Arrhenius equation which must, therefore, be regarded as invalid, even as a limiting law for low concentrations.

Gruenisen found that both the salts which increase the viscosity and those which decrease viscosity show a negative curvature of the viscosity - concentration curves at low concentrations. The viscosity - concentration curves for salts which increase the viscosity are so nearly straight lines that the deviatioins would not be readily apparent on the scale, but the deviation are clearly systematic and greater than the experimental error.

For a salt which increase the viscosity of water, the curve starts at $\eta = 1.00$ when $C = 0$ with a positive but diminishing slope, giving a negative curvature, then straightens out, passes through a point of inflection at moderate concentrations (about 0.3 molar) and then curvature becomes slightly positive.

These changes in the curve are more apparent, if following suggestions of Gruneisen, we plot $(\eta - 1)/C$ against C. $(\eta - 1)/C$ is strictly the slope of the chord connecting a point on the $\eta$-C curve with the origin, but it is approximately the same as the slope of the $\eta$-C curve at the same point. If the relationship between the viscosity and concentration were a linear one, $(\eta - 1)/C$ would be a constant and its plot would be a straight line parallel with 'C' axis. Gruneisen pointed out that the smaller the electrical mobility of an ion the greater is its influence in increasing the viscosity of solutions.

Schneider[12] has made measurements similar to Gruneisen's with many other salts and obtained similar results.

Among the many investigators of the viscosity of solutions the next who deserves mention in this brief review is Applebey[13], who made careful measurements on solution of $LiNO_3$, a salt which increases the viscosity of water. He extended the work over a wide range of concentrations, including solutions even more dilute (C = 0.007 M) than those studied by Gruneisen. His results show that the negative curvature becomes more pronounced at very low concentrations and that the curvature in this region is much greater. He also showed that the negative curvature becomes greater as the temperature is lowered. Applebey made the suggestion that when a salt is dissolved in water, there are two different effects on the viscosity.

1) a depolymerization of triple water molecules, $(H_2O)_3$ to form single molecule, which tends to diminish the viscosity.

2) an increase in the viscosity due to the presence of the ions and un-ionized molecules of the salt.

It is assumed that the friction depends primarily on the size of the ions of the molecule.

The work of Merton[14] on cesium nitrate appears to be the most accurate and extensive study of a salt which diminishes the viscosity of water.

Measurements of viscosity of Barium chloride solutions have been carried out by Sprung[6], Arrhenius[7], Wagner[9] and many other workers[12,15].

### 1.2.a. JONES DOLE EQUATION :

The Jones-Dole equation[15] is given as

$$\eta r = 1 + A\sqrt{C} + BC .$$

Where 'A' and 'B' are inter-ionic forces in the viscosity and solute-solvent interactioin coefficient[16] and C is the concentration of the solute electrolyte in $Ml^{-1}$. This equation is only applicable for dilute solutions ($C \leq 0.1$ M) and it has been seen in many cases that the Jones-Dole equation is the most appropriate equation for calculating the viscosity of dilute aqueous solutions of electrolytes.[59] The equation has been used for concentrated solutions ($C \geq 0.1$ M) in the form

$$\eta_r = 1 + BC \, .$$

B seems to swamp out the effect of A resulting into the above equation

D.Patnaik and P.K.Das[17] examined the viscosity of solution of potassium chloride in mixed solvents of different compositions, with a view to determine the nature 'A' and 'B', the constants of the Jones-Dole equation. They suggested that the value of 'B' depends on the nature and composition of solvent.

R.C.Acharya, P.K.Das and Patnaik[18] found that satisfactory explanation has been advanced on theoretical grounds for 'A' by Falkenhagen and Vernon[19], but no such explanation has yet been offered for the constant 'B'. Cox and Wolfenden[20] have attributed additive character to 'B' depending on the constituent ions.

Asmus[21] suggests that 'B' depends on the lyotropic number and the entropy of hydration of the ionic species present in the medium. R.C.Acharya, P.K.Das and Patnaik[18] reported that with the increase of the dioxane content in the solvent the values of 'B' also increased thus furnishing the proof that the magnitude of 'B' depends on the composition of the solvent. They also suggest that the sphere of solvation of the ions is responsible for the value of 'B'.

The viscosity of $MgBr_2$, $Na_2SO_4$, KCl, $K_2SO_4$, $BaBr_2$, $Ba(ClO_4)_2$ $Mg(ClO_4)$ have been studied by P.B.Das[22,23], in aqueous solutions and in dioxan-water mixtures. They suggest for the above mixtures modified form of Jones-Dole equation[17].

$$\eta_r = 1 + A\sqrt{C} + BC^x$$

Where 'x' is the empirical constant which varies from electrolyte to electrolyte near about unity. Similarly, many workers such as B.K. Parida and P.B.Das[24], P.K.Das[25], P.B.Das and coworkers[26-38] studied the viscosity of nitrate, bromate, iodite of alkali metal and alkaline earth metals. They have determined the 'B' coefficients for different solutions and have discussed the influence of the anion in such solutions. The 'B' coefficient for anions decrease in order $IO_3^{--}$ > $BrO_3^{--}$ > $NO_3^{-}$. This order changes with increasing solvent concentration. It was found that the viscosity data for all such salts obeyed the modified Jones-Dole equation.

Moulik S.P. and Rakshit A.K.[39] studied the viscosity of aqueous electrolyte solutions. They noted that the dependence of viscosity on the ionic strength of electrolyte solutions at high concentrations and is correlated with the 'B' coefficient of the electrolyte.

Doan, Thi-Hoa, Sangster, and James[40] measured the viscosities and densities of concentrated aqueous solutions of nitrates of K, Na, Cd, Cu(II), Ba, Pb, Sr, Mg, Ni, Zn and Fe(III). The viscosity data for all such salts obeyed the modified Jones-Dole equation.

Franks and Ives[41] carried out exhaustive review and confined attention to monohydric alcohol-water mixtures which are of greatest interest from the structural view point. They studied viscosity over the wide range of concentrations and concluded that hydrogen bonding which plays a principal role in the ion-solvent interactions cannot alone account for additivities in properties that are observed. They surveyed the properties of the system, with special reference to their structural implications, and with the conviction that the problems concerned must be very significant in many concentrations. This convention is held because the relatively simple alcohol-water mixtures may serve as models helpful to better understanding of more complex system, and because these mixtures are so frequently used as solvents in studies of chemical equilibria and reaction rates which can hardly devoid of "solvent participation".

Ivanova Shangina[42] studied viscosity of water-alcohol solutions of potassium, sodium and ammonium nitrates. They observed that addition of all salts decreases '$\eta$' of mixed solvents. They also interpreted that $NH_4^+$ has the greater effect on breaking the solvent structure.

Kodejs, Slama, Novak[42-46] followed the viscosity of the highly concentrated aqueous solutions of $Ca(NO_3)_2$ - $CaCl_2$ mixtures with the ionic ratio $NO_3^-/Cl^-$ equal to 1.5 and 2.33 respectively in a metastable super saturation and the concentration of the solution varying from

5 to 23 mole %. They have also discussed the selection of convenient equation for the description of temperature and concentration dependence of the viscosity of the solution.

## 1.2(b) EINSTEIN EQUATION :

The viscosity behaviour of dilute aqueous solutions of electrolyte has been studied in detail and numerous empirical relations have been reported[47-49] to explain the relations of viscosity with concentration. The relative viscosity '$\eta_r$' is generally used in most of the empirical relations.

For dilute solutions ($C \leq 0.1$ M) the theoretical relation of Einstein[50] gives

$$\eta_r = 1 + 2.5\Phi$$

Where $\phi$ denotes the volume fraction and is equal to $c\bar{V}$, $\bar{V}$ being the molar volume of electrolyte in solution.

The representation of viscosity at concentration $\geq 0.1$ M by one general equation becomes difficult. Vand[51], Thomas[52] and Moulik[53] have extended the limiting equation of Einstein to higher concentrations and have advanced some useful relations which have been tested for their general validity in higher concentration. Based on the Eyring[55] theory of absolute rate for viscous flow of liquids, Moulik[54] applied the equation for limited range of concentration.

## 1.2(c) THOMAS EQUATION :

Thomas gives equation as[52]

$$\eta_r = 1 + 2.5\phi + 10.05\phi^2$$

where $\phi$ has usual meaning.

Breslan and Miller[56] used the Thomas equation and calculated the molar volumes of number of aqueous electrolyte solutions. The equation of Thomas has been re-arranged in the linear form and used as

$$\frac{\eta_r - 1}{C} = 2.5\,\bar{V} + (10.05\,\bar{V}^2)\,C$$

The plot of $(\eta_r - 1)/C$ Vs $C$ must be linear one, and on this basis, the linearity of the results has been tested. Thomas equation is not valid for few electrolytes and may not be valid for many non-electrolytes[57].

## 1.2(d) VAND EQUATION :

The theoretical equation of Einstein has been modified by Vand[51] to represent viscosity of aqueous solutions of both electrolytes and non-electrolytes at higher concentrations. The equation may be given as -

$$\ln(\eta_r) = \frac{2.5\phi}{1 - Q\phi}$$

Where $\phi$ is volume fraction and is equal to $C\bar{V}$, $\bar{V}$ being the molar volume of electrolyte in solution and $Q$ is the interaction coefficient. The equation of Vand can be re-arranged in the linear form as

$$\frac{1}{C} = \left(\frac{0.921}{V}\right)\frac{1}{\log\eta_r} + Q\,\bar{V}$$

The plot of $\frac{1}{\log\eta_r}$ Vs $\frac{1}{C}$ should be a straight line with $Q\bar{V}$ as the intercept and $\frac{0.921}{V}$ as the slope. From the intercept and slope, Q and $\bar{V}$ can be calculated.

S.P.Moulik[53] used this equation for different electrolytes and observed that the Vand equation holds a far better way, and the calculated values of $\bar{V}$ and Q are nearly equal with the theoretical one.

### 1.2(e) MOULIK EQUATION :

Moulik[53] made a comparative testing of viscosity equations of Vand[51] and Thomas[52] in detail for electrolytes and non-electrolyte solutions. He observed that Thomas equation in its full form, is not applicable for majority cases. The equation of Vand is a better relation.

For higher concentration of electrolyte, he put forward the equation.

$$\eta_r^2 = M + K' C^2$$

Where M and K' are the constants. The comparative study of this equation over a wide range of concentrations for a number of salts has been reported[53]. The calculated molar volume ($\bar{V}$) and the 'B' coefficients bear the simple relation[57]

$$B = 2.5 \ \bar{V}$$

a single viscosity equation may not be sufficient to cover the viscosity data of most aqueous systems containing high fractions of dissolved solutes. The parameters of the equation have been evaluated and have been used to calculate viscosity of aqueous solutions in the concentration range in which above equation is valid.

## 1.2(f) BRESLAU AND MILLER EQUATION :

Vishnu and Misra have calculated B coefficients using Breslau and Miller's equation,[56] for sodium and potassium halides

$$\bar{V}_e = \frac{-2.5\ C + [(2.5\ C)^2 - 40.20\ C^2\ (1-\eta_{re})]^{1/2}}{20.10\ C^2}$$

and the average $\bar{V}_e$ values thus obtained were fitted into the equation

$$B = 2.90\ \bar{V}_e - 0.018$$

for 1 : 1 electrolytes.

Mahapatra, Naik, Mishra and Behera[58] measured viscosities of sodium chloride, bromide and iodide in aqueous sucrose solutions of varying concentrations. They employed both graphical and computational methods for obtaining parameters of different viscosity equations for concentrated solutions. They obtained the viscosity 'B' coefficient from a knowledge of molar volume of the electrolyte in solutions and concentration of sucrose solution. They calculated hydration number of ions from the ionic 'B' ± coefficients and discussed their role in light of "structure making" and "structure breaking" of water.

Sahu and Behera[57] have extended the limiting equation of Einstein and represented the variation of relative viscosity $\eta_r$ of concentrated aqueous solutions of 1:1 type electrolytes with electrolyte concentration by a general equation. They obtained an empirical equation relating B and $\bar{V}$ of electrolyte in aqueous solutions by least square analysis, which resembles more closely to $B \simeq 2.5\ V$. Assuming the applicability of this equation to ions in solution they calculated the hydration numbers of ions and their dependence on ionic radii, ionic molar volumes and ionic B ± coefficients and discussed in the light of 'structure-making' and 'structure-breaking' properties of ions in solution.

Mohanty and Das[59] determined viscosities of concentrated solutions of potassium chloride and sodium chloride in aqueous urea solutions of varying concentration. They employed graphical technique for obtaining different parameters of viscosity equations and suggested an empirical relation for 'B' values, molar volume and concentration of urea. They found that water structure is broken down in presence of urea.

Vishnu and Vinod Kumar Singh[104] measured the viscosity of systems comprising sodium and potassium halides and aqueous D-glucose solution at different temperatures. The molar volume (V), ionic B-coefficient (B±) and hydration number ($N_B$) of various ions have been calculated on the basis of these data. It has been found that different ions show structure breaking behaviour in the order $I^- > Br^- > Cl^- > K^+ > Na^+$.

Howard Macdonald, Gerrard Marangoni and Palepu[111] have done viscometric investigation on several alkali halides in aqueous D-mannitol at different temperatures. Free volumes, ionic viscosity coefficients and hydration numbers have been calculated and discussed in terms of 'structure making' or 'breaking properties' of electrolyte in aqueous D-mannitol solutions.

## 1.3 THE TRANSPORT PROPERTIES (Activation Parameters)

The interpretation of viscous flow according to the theory of absolute reaction rates has been presented by Eyring and co-workers.[55] Nightingale and Benck[62] and Feakins[60] have shown that the theory of reaction rate can be successfully applied to electrolyte solutions. Nightingale calculated the activation energy $\Delta E^*$, (which does not differ appreciable from activatiion enthalpy), free energy of activation, $\Delta F^*$ and the entropy of activation $\Delta S^*$ for water and a number of electrolytic solutions.

The energy of activation for viscous flow $\Delta E^*$ is given by

$$\Delta E^* = R \frac{d \ln \eta}{d(1/T)}$$

The plot of $\ln \eta$ vs $1/T$ is linear and $\Delta E^*$ can be calculated as

$$\Delta E^* = \text{slope} \times R$$

In a similar manner the free energy of activation for viscous flow is given by[55]

$$\Delta F^* = RT \ln \frac{\eta V}{hN}$$

where $h$ is the planck constant and $N$ is the Avogadro number. $V$ may be regarded as the volume of one mole of solution particles and is given by

$$V = \frac{1000}{n_1 + \nu n_2} \quad cm^3$$

where $\nu$ is the number of species into which a solute molecule dissociates and $n_2$ is the number of moles of solute per litre of solution. The number of moles of solvent, $n_1$, per litre of solution is given by

$$n_1 = \frac{1000 - n_2M_2}{M_1}$$

where $M_1$ and $M_2$ are the molecular weights of the solvent and solute, respectively. Assuming that the activation enthalpy does not differ appreciably from the activation energy, the entropy of activation $\Delta S^*$ may also be calculated as

$$\Delta S^* = (\Delta E^* - \Delta F^*) / T .$$

Proceeding along similar lines, energy of activation ($\Delta E^*$) the free energy of activation ($\Delta F^*$) and entropy of activation ($\Delta S^*$) can be calculated.

Frank and Evans[61] studied entropy in binary liquid mixtures, partial molal entropy in dilute solutions; structure and thermodynamics in aqueous solutions of electrolytes.

They showed that gases, when dissolved in normal liquids loosen the forces on neighbouring solvent molecules producing a solvent reaction which increase the partial molal entropy of the solute.

Nightingale and Benck[62] measured the viscosities of aqueous sodium fluoride and sodium periodate solutions in the concentration range 0.0005 to 1 molar. They interpreted viscosity data in terms of the Jones-Dole equation for the strong electrolyte, using this relation, they have calculated viscosity B-coetticients for the fluoride and periodate ions at 25°C and also the energies and entropies of activation for viscous flow at 25°C for a number of ionic species. It has been observed by them that large ions such as $Ba^{+2}$, $IO_3^-$ and

$SO_4^{-2}$ exhibit a minimum hydration for their respective charge types to decrease the activation energy for viscous flow in the solution from that for the pure solvent even though the ion itself increases the bulk viscosity of the solution. They discussed the influence of such ions up on the water structure.

Spink and Auker[63] discussed entropies of transfer of amino acids from water to aqueous solutions. They measured heats of solution of the amino acids, glycine, DL-alanin, DL- -aminobutyric acids, and L-valine, in water and in aqueous ethanol solutions. They combined the results with published free energy data to obtain the entropies of transfer of the amino acids from water to the alcohol-water mixture They conclude that the transfer entropies suggest that the amino acids cause a breakdown of structure in the mixed ethanol-water solvent, largely a result of parturbation by highly polar Zwitter ion portion of the molecule, and the effect of the side chains is to produce order in proportion to the size of the side chain, and the ordering effect is greater in water than in the mixed solvent systems.

P.B.Das, N.C.Das, and P.P.Misra[27] studied solute solvent interaction of $NaNO_3$ solution in dioxan-water mixture at different temperatures. They calculated the energy of activation, $\Delta E^*$, free energy of activation $\Delta F^*$ and entropy of activation $\Delta S^*$. They conclude that $\Delta E^*$, $\Delta F^*$ and $\Delta S^*$ of viscous flow is less than that of the solvent indicating the solute-solvent interaction.

B.K.Das, Singh and P.K.Das[28] studied viscosity of solutions of sodium bromate and potassium iodate at 30°, 35° and 40°C calcium chloride at 35°, 40° and 45°C and Barium chloride at 30°, 40° and 45°C and calculated free energy ( Δ F*) energy of activation for viscous flow ( ΔE*) and the entropy of activation ( Δ S*) with respect to the solvent.

Nayak, Misra, and P.B.Das[29] studied viscosities and apparent molar volumes of $CaCl_2$ and $SrCl_2$ in water at different temperatures. They calculated the energy and entropy of activation of the viscous flow.

P.B.Das[64] studied thermodynamics of salts in dioxan-water mixture from viscosity, apparent molar volume and conductance data at 35°C. He determined viscosities, apparent molar volumes and electrical conductivities of potassium and sodium salts in aqueous dioxan (0-30 Wt%) at 35°C. He reported that the ion solvent interaction follows the order $BrO_3^- > Br^- > Cl^- > IO_3^- > NO_3^- > SO_4^-$ and due to bulkiness the dioxan breaks down the three dimensional water structure of the solvent and additivity law does not hold good.

Renz M. Stelmel F.[65] studied thermodynamic properties of binary system methanol-lithium bromide.

Taniewska-Oninska, Stefania, Piekarska, Alina[66] studied thermodynamic functions of activation of viscous flow in sodium iodide-water amide system. They calculated the thermodynamic parameters of activation of viscous flow, Δ H* and Δ S* at 298.15°K and Δ G* at 278.15, 318.15°K for the systems NaI-water-formamide and NaI-water D.M.F.

## 1.4 THE THEORY OF ELECTROLYTIC CONDUCTANCE :

The equivalent conductance of an electrolyte depends upon the number of ions, on the charge carried by each ionic species and on their speed. For a given solute, the charge on the ions is constant and the variation of equivalent conductance with concentration means that there is either a change in the number of ions present or in their velocities or in both.

In early development of the theory of electrolytic dissociation Arrhenius made the tacit assumption that the ionic speeds were independent of the concentration of the solution, the change of equivalent conductance would then be due to change in the number of ions produced from the one equivalent of electrolyte as a result of the change of concentration. In other words, the change in the equivalent conductance should then be attributed to the change in the degree of dissociation.

All electrolytes are probably completely dissociated into ions at infinite dilution and so, if the speeds of the ions do not vary with the concentration of the solution. It is seen that the ratio of the equivalent conductance $\Lambda$ at any concentration to that $\Lambda_o$ at infinite dilution i.e. $\Lambda/\Lambda_o$ which is also termed as 'conductance ratio' should be equal to the degree of dissociation of the electrolyte. There are good reasons for believing that the speeds of the ions do vary as the concentration of the solution of electrolyte is changed, and so the departure of the conductance ratio ( $\Lambda/\Lambda_o$) from unity with increasing concentration can not be due to merely a decrease in the degree of dissociation. For strong electrolytes, in which the ionic concentration is high, the mutual interaction of oppositely charged ions results in a considerable decrease in velocities of the ions as the concentration of solution is increased, hence, the fraction $\Lambda/\Lambda_o$ under these conditions bears no relation to the degree of dissociation In solution of weak electrolytes, the number of ions in unit volume is relatively small, and so also is the inter-ionic attraction and hence the ionic speeds do not change greatly with concentrations, the conductance ratio gives a reasonably good value of the degree of dissociation.

In case of strong electrolyte, the possibility that the attraction forces between ions might have some influence on electrolytic conductance was considered by Noyes (1904), Sutherland (1906), Bjerrum (1909) and Milner (1912) and others, but the modern quantitative treatment of this concept is due to mainly the work of Debye and Huckel and its extension chiefly by Onsager and by Falken-Hagen.[67] The essential postulate of the Debye Huckel theory is that every ion may be considered as being surrounded by ionic atmosphere of opposite sign. They calculated the thickness of ionic atmosphere which was seen to be of the order of $10^{-8}$ cm. It decreases with increasing concentration and increasing valence of the ions present in the electrolyte, and increases with increasing dielectric constant of the solvent and with increasing temperature. When the ion is made to move under the influence of an external force, e.g., by the application of an electrical field, the symmetry of the ionic atmosphere is disturbed. The asymmetry of the ionic atmosphere will result in a retardation of the speed of ion moving under the influence of an applied field. This influence on the speed of an ion is called the 'relaxation effect' or asymmetry effect. Another factor which tends to retard the motion of an ion is the tendency of the applied potential to move the ionic atmosphere with its associated solvent molecules, in a direction opposite to that in which the central ion, with its solvent molecules is moving. An additional retarding influence, equivalent to an increase in the viscous resistance of the solvent, is thus exerted on the moving ion. This is known as the electrophoretic effect.

Considering these factors, Dehye Huckel and Onsager derived the equation for equivalent conductivity of a strong electrolyte as

$$\Lambda = \Lambda_o - \left[ \frac{82.4}{(D1)^{\frac{1}{2}} n} + \frac{8.20 \times 10^5}{(DT)^{\frac{1}{2}}} \Lambda_o \right] \sqrt{C}$$

Where $\Lambda$ = Eq. conductivity at conc. c moles/lit

D = Dielectric constant

$\Lambda_o$ = Eq. conductivity at infinite dilution.

This equation is based on the assumption that the dissociation of the electrolyte is complete. The first term in the brackets gives the effect due to the electrophoretic force and the second term represents the influence of the relaxation or asymmetry. For uniuni valent electrolyte, assuming complete dissociation Onsager equation may be written as

$$\Lambda = \Lambda_0 - (A + B\Lambda_0)\sqrt{C}$$

Where A & B are constants dependent on the nature of the solvent and the temperature.

$$A = \frac{82.4}{(DT)^{\frac{1}{2}}n}$$

and

$$B = \frac{8.20 \times 10^5}{(DT)^{\frac{1}{2}}}$$

For testing the validity of equation, it is not sufficient to show that the equivalent conductance is a linear function of square root of concentration but the important point is that the slope of the line must be numerically equal to $(A+B\Lambda_0)$. The conductivity data obtained for uni-univalent and uni-bi (or bi-uni-) valent electrolytes indicated that the Onsager equation represents in a satisfactory manner the behaviour of 1:1 type electrolytes but with bi-bivalent solutes, very marked discrepancies are observed. The plot of equivalent conductance against the square root of concentration is not a straight line but concave to the $\sqrt{C}$ axis. Further, the slopes at appreciable concentrations are much greater than those calculated theoretically. It is probable that these results are to be explained by incomplete dissociation at the experimental concentrations, the shapes of the curves do in fact, indicate that in sufficiently dilute solutions the slopes would probably be very close to the theoretical Onsager value.

NON-AQUEOUS SOLUTIONS :

A number of cases of satisfactory agreement with theoretical requirements have been reported for non-aqueous solutions. In the particular case of the chlorides and thiocyanates of the alkali metals.[68-69.] Other electrolytes such as nitrates, tetralkyl ammonium salts and salts of higher valence types however, exhibit appreciable deviations. These discrepancies become more marked the lower the dielectric constant of medium and especially if it is non-hydroxylic in character. At lower dielectric constants, even greater discrepancies have been recorded in many cases. Substances which are strong electrolytes and hence almost completely dissociated in water, behave as weak, in solvents of low dielectric constants and find departures from the theoretical Onsager behaviour.

## EXTENDED FORMS OF ONSAGER EQUATION :

The main deviation from the Onsager equation has been observed, in case of number of salts in aqueous solutions which give conductances that are too large at relatively high concentrations. It is probably due to the approximations made in the deviation of Onsager equation which can only be expected to hold good for point charges in dilute solution. An emperical correction, involving C and log C, has been applied by Shedlovsky[70,71] to give the equation in the form

$$\Lambda_o = \frac{\Lambda + A\sqrt{C}}{1 - B\sqrt{C}} - C_c - D_c \log C + EC^2.$$

Where C, D and E are empirical constants. In some cases, D & E are very small and equation becomes

$$\Lambda_o = \frac{\Lambda + A\sqrt{C}}{1 - B\sqrt{C}} - C_c$$

This Shedlovsky equation adequately represents the behaviour of a number of electrolytes in relatively concentrated solutions. For many electrolytes the plot of equivalent conductance against the square-root of concentration is slightly concave to concentration axis, and experimental slopes are numerically greater than those expected theoretically. The conductance is less than required by theory. The explanation offered for the discrepant behaviour is that dissociation of electrolyte is incomplete, the number of ions available for carrying the current is thus less than would be expected from the stoichiometric concentration.

The modified equation includes a factor $\frac{1}{\alpha}$ where $\alpha$ is degree of dissociation and the concentration term should really be $\alpha C$. So for uni-univalent electrolyte the correct equation would be

$$\Lambda = \alpha[\,(\Lambda_0 - (A+B\Lambda_0)\sqrt{C\alpha}\,]$$

This equation can be written as $\Lambda = \alpha\Lambda'$

where $\Lambda' = \Lambda_0 - (A+B\Lambda_0)\sqrt{C\alpha}$

It is the equivalent conductance of 1 equiv. of free ions at the concentration $(\alpha C)$ equiv. Per Liter.

The extended form of Onsager equation explains following facts.

(1) The plot of $\Lambda$ against $\sqrt{C}$ will be straight line for strong electrolyte, degree of dissociatioin $\alpha$ is numerically equal to $\Lambda/\Lambda'$ instead of $\Lambda/\Lambda_0$ as proposed by Arrhenius.

(2) For weak electrolyte $\alpha$ is small, and $\alpha C$ will also be small the difference between $\Lambda'$ and $\Lambda_0$ is thus not large and degree of dissociation will be approximately equal to conductance ratio.

## INFLUENCE OF TEMPERATURE ON CONDUCTANCE :

Increase of temperature invariably results in an increase of ion conductance, the variation with temperature may be expressed with fair accuracy by means of the equation,

$$\lambda^o_t = \lambda^o_{25} [ 1 + \alpha (t-25) + \beta (t-25)^2 ]$$

Where $\lambda^0_t$ is the ion conductance at infinite dilution at the temperature t, and $\lambda^0_{25}$ is the value at 25°. The factors $\alpha$ and $\beta$ are constants for a given ion in the particular solvent for a narrow temperature range e.g., about 10° on either side of 25°, the constant may be neglected. The temperature coefficient $\alpha$ is very close to 0.02 at 25°C for most of the electrolytes.

## INFLUENCE OF SOLVENT ON CONDUCTIVITY (Walden Product) :

Walden (1906), in the course of his investigation of the conductance of tetraethylammonium iodide in various solvents, noted that the product of the equivalent conductance at infinite dilution and the viscosity of the solvent was approximately constant and independent of the nature of latter[72-73]. This conclusion known as walden rule and expressed as,

$$\Lambda_o \eta_o \simeq \text{constant}$$

for a given electrolyte in a given solvent.

The walden rule is approximately independent of temperature. Walden rule is based on stokes law of viscosity. If stokes law were obeyed, the value of $\Lambda_o \eta_o$ would be constant only if the effective radius of the ion were same in the different medium. Since there are reasons for believing that most ions are solvated in solution, the dimensions of the moving unit will vary to some extent and exact constancy of conductance-viscosity product is not to be expected. Secondly, the ions should be large in comparison with the molecules of the medium. In case of tetraethyammonium ions and picrate ions due to large size of ions $\Lambda_0 \eta_0$ values are much more constant. While in case of other smaller ions deviations are seen. The 'larger size' ions are probably solvated to a small extent only and have the same size in all solvents.

## LITERATURE SURVEY :

In recent years a number of results have appeared regarding conductance in non aqueous medium. These studies led to few generalizations of definite values viz. degree of dissociation of salts, triple ion formation, solvent structure maker or breaker phenomena etc. Besides providing a test for conductivity relationships predicted by modern theory of ionic solutions, Such measurements are used for determination of transference numbers. They give values for individual ionic mobilities.

Theodore Shedlovsky[70] has studied the electrolytic conductivity of some uniuni valent electrolyte in water at 25°C.
He measured the conductance of lithium chloride in water at 25°C. The measurement confirms the Onsager equation. The measurements on solutions of nitrates, however, show deviations from this equation which may be due to partial association.

Sears, Lester and Dawson[74] measured conductance of nineteen salts in dilute ( $< 10^{-2}$M) DMSO solution. The equivalent conductance values were found to fit excellently to Onsager equation, indicating that all the salts studied are completely dissociated in DMSO at concentrations below $10^{-2}$M. Ionic mobility values were calculated from limiting conductance. The value for mobility of solvated hydrogen ion in DMSO were obtained from a polarographic diffusion coefficient[75]. The large variation in cation mobility compared to anion mobility indicates that anions are only slightly solvated in DMSO, if at all. The conductance of Lithium chloride goes through a maximum values at approximately 1 M concentration which may result either from ion-pairing or from the large increase in viscosity of DMSO solutions containing high concentrations of salts.

P.K.Das[76] measured viscosity and conductance of sodium chloride in dioxan water mixtures. The viscosity data was analysed by modified Jones Dole equation and additive character of 'B' has been examined for NaCl and KCl. Conductance results indicated no ion association of the electrolyte in the solvents studied.

J.S.Dunnett and R.P.H. Gasser[77] measured the activity coefficient, conductivities, viscosities and n.m.r. spectra of solutions of lithium chloride in dimethyl suphoxide. The anomalies in the activity coefficients and conductivity were attributed to ion-pair formation. R.L.Blokhra and V.P.Sehgal[78] studied conductance of cesium iodide, potassium thiocyanate and tetraethyl ammonium bromide in ethylene glycol. They compared the walden product values in case of cesium chloride and cesium iodide and inferred that iodide ion is more solvated as compared to chloride ion in ethylene glycol at 30°C. This is in accordance with the fact that larger anions are more solvated.

R.L.Blokhra and M.L.Parmar[79] studied the conductance of cesium iodide, ammonium chloride, ammonium bromide and potassium sulphocyanide in dimethyl suphoxide, Dimethyl sulphoxide is a highly associated solvent and it is found that cations are mostly solvated in it whilst anions remain relatively unsolvated by DMSO.[80] The negative temperature coefficient of Walden product[81] for ammonium bromide indicates that ammonium bromide acts as structure breaker and this was in accordance with the observations made from viscosity measurements.[82] The ion-solvent interaction increases with decrease in temperature.

R.L.Blokhra and Y.P.Sehgal[83] studied the conductance of tetraethyl ammonium halides in ethylene glycol. The data were also analysed using the Fuoss-Onsager-Skinner equation.[84] They calculated limiting equivalent conductance $\Lambda_0$, the contact distance 'a' (A°) of the ions in solution along with walden products at different temperatures.The negative temperature coefficient showed strong ion solvent interaction in ethylene glycol. Tetraethyl ammonium chloride acts as a structure breaker. Increase in ion-size parameter also supports this structure breaking tendency, which was attributed to weakening of the hydrogen bonds in ethylene glycol and hence breaking of the structure of the solvent.

P.B.Das[85] examined the viscosity, conductivity of Chlorides, Bromides, Nitrates, Bromates, Iodates and Sulphates of potassium and sodium in dioxan water mixture at 35°C at different mass fractions of dioxan (10,20 and 30%). The ions appear to interact and ion-solvent interaction or structure breaking effect of anions changes with the change in dioxan content. Lesser the value of $\lambda\eta$, greater is the electrostatic ion solvent interaction. It appears that during migration, the ions are covered with a sheath of solvent molecules which results in larger size of thermodynamic unit and hence a decrease in $\lambda\eta$. Since dioxane is a better proton accepter it cannot be accommodated in the structure of water due to its bulky size and cause a break down in the three dimensional water structure and additivity law does not hold good.

R.C.Sharma and H.C.Gaur[86] studied conductivity of highly concentrated aqueous electrolyte solutions $NH_4NO_3 + H_2O + LiNO_3$ system at the temperatures ranging between 295 to 345°K. The conductivity-composition isotherms were non-linear. Peleg[87] showed that in concentrated $NH_4NO_3 + H_2O$ solution, $NH_4^+$ ions were present as hydrated species and as suggested by Keenan.[88] Hence, anion-water interactions are weaker relative to cation-water interactions. Introduction of $Li^+$ ions having higher charge density would strongly compete for preferential hydration and more and more water of hydration will be taken up by $Li^+$ ions resdulting in increase in coulombic interaction and hindering the ionic migration. This results in decrease in conductivity.

B.K.Blokhra and V.P.Sehgal[89] studied conductance of cesium halides, Rubidium nitrate and Rubidium iodide in Diethyleneglycol and aqueous Diethylene glycol at 25°C. Experimental data analysed for limiting equivalent conductance at infinite dilution. Walden products mobilities and solvation numbers of the single ions in these solutions had been estimated. The limiting equivalent conductance and walden products for both the cation ($CS^+$ and $Rb^+$) and all the anions ($Cl^-$,$Br^-$, $I^-$ and $NO_3^-$) had greater magnitudes in aqueous diethylene glycol than in diethylene glycol. This may be attributed to the greater structure breaking ions viz. $Cl^-$, $Br^-$, $I^-$, $Rb^+$ and $Cs^+$ will break more structure in aqueous DEG than in DEG and produced in increase in walden product for these ions in aqueous DEG over that in DEG the conclusion agree with those deduced from greater B-values obtained from viscosity data[90] in case of AQ DEG.

V.K.Syal and Prakashchand Ranowt.[91] studied conductance of amines in 0-chlorophenol and its mixture solvent with nitrobenzene. (1:1 by volume). The possibility of formation of extensive ion pair was indicated and supported by results from plots of $\lambda_c\sqrt{c}$ versus C and log $\lambda_c$ against log C. The equivalent conductance values for all the amines in mixture solvent decreases with the increase of concentration of solute and then becomes constant showing the absence of formation of triple ions. The values of equivalent conductance for various amines are higher in mixture solvent than in pure O-chlorophenol due to the increase of dielectric constant of the mixture solvent with the addition of nitrobenzene to o-chlorophenol which has a higher value of dielectic constant than o-chlorophenol. Because of higher value of dielectric constant of the medium, higher is the dissociation of solute and hence higher is the conductance of the solution.

V.K.Syal and Gurdev Kaur[92] studied conductance of various solutes in monobromoacetic acid and its mixture solvent with nitrobenzene (1:1 by volume) at 50°C, Triple ion formation was indicated by the plots $\lambda\sqrt{c}$ against c. It is found that there is an extensive ion-pair formation in solution which is further supported by results from plots of log $\lambda_c$ against log c.

V.K.Syal and Prakash Ranowt[93] studied limiting ionic conductances of some tetra alkylammonium ions in dimethyl suphoxide + dioxane mixtures at 25°C. The experimental data was analyzed using Shedlovsky's equation. Limiting ionic conductances have also been calculated. The limiting ion conductance increases with decrease in dielectric constant of medium, reaches maximum at a dielectric constant value of 29.5 and decreases with the further decrease in dielectric constant. Walden product of the electrolyte as well as ion decreases with decrease in dielectric constant of medium.

Z.Kodejs, J.Novak and Slama[94] studied the viscosity and conductivity of solutions of lithium nitrate in dimethyl sulfoxide in the temperature range 10-60°C for composition x = 9 - 28 mole % $LiNO_3$. As the salt concentration is increased, viscosity of the system $LiNO_3$-DMSO increases and molar conductivity decreases far more markedly than in aqueous solution since the solvent structure is destroyed by the solute, the increase in relative viscosity reflects a more increased ordering in the system $LiNO_3$ - DMSO compared to the aqueous system, the ratio of viscosities of DMSO and water is about two hence the increase in relative viscosity indicates that $Li^+$ - DMSO interaction is stronger than analogous interaction in the aqueous system. The structure formed in DMSO is much stronger.

## 1.5 SCOPE OF THE PRESENT WORK :

From the survey of the above work, it has been noticed that following systems have been studied so far.

The viscosity measurements in different solvents have been done in following systems :

1) Potassium bromide and Sodium bromide,
Potassium chloride and Sodium chloride,
Magnesium bromide and Magnesium chloride,
Barium chloride and Barium bromide,
Sodium sulphate and Potassium sulphate
in dioxan water mixtures at different temperature.

2) Sodium formate in water and in aqueous formic acid.

3) Potassium halides in water-pyridine and water -$\gamma$-picoline mixture.

4) Glycine in alcohol-water.

5) $Sr(NO_3)$ and $Cd(NO_3)_2$ in dioxan, Glycol, methanol water mixtures

6) Al $NH_4(SO_4)_2.12\ H_2O$ and K $Al(SO_4)_2.12\ H_2O$ in water-methanol mixtures.

7) Al $NH_4(SO_4)_2.\ 12\ H_2O$ and K Al $(SO_4)_2.\ 12\ H_2O$ in water-terbutyl alcohol mixtures at different temperaturs.

Similarly conductance measurements have been done in following systems.

1) Conductance of lithium chloride, sodium chloride, bromides, nitrates ~~and~~ of potassium and sodium in diaxon water mixture.

2) Conductance of lithium chloride, ammonium chloride, ammonium bromide, potassium sulpho cyanide etc. in dimethyl sulphoxide.

3) Conductance of cesium iodide and potassium thiocyanate and tetra ethyl ammonium bromide in ethylene glycol.

4) Conductance of ammonium chloride, ammonium chloride in dimethyl sulphoxide.

5) Conductance of cesium halide in Rubidium nitrate and Rubidium iodide in Diethylene glycol and aqueous diethylene-glycol.

6) Conductance of highly concentrated aqueous electrolyte solutions $NH_4NO_3 + H_2O + LiNO_3$ at different temperature.

7) Conductance of various solutes in monobromo acetic acid and its mixtures solvents with nitrobenzene.

8) Conductance of lithium nitrate in dimethyl sulphoxide.

It is clear, therefore, that the viscosity and conductivity measurements on lithium chloride in water and urea-water mixture have not yet been done so far.

Hence, it is proposed to study the viscosity and conductivity of this salt in aqueous solution and in urea-water mixture at different temperatures. It is also proposed to make an attempt to confirm the results obtained from viscosity measurement by conductivity measurement such as structure maker or structure breaker phenomena. These results, further, can be confirmed by calculating thermodynamic properties.

We report here, viscosity, density, conductivity data for lithium chloride in urea-water solutions (0%, 5%, 10%, 15% and 20% urea w/w) at 293°K, 298°K, 303°K and 308°K. The experimental results have been analysed using various standard viscosity concentration equations.