CHAPTER-I

INTRODUCTION

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Gases and liquids possess a property known as Viscosity, which may be defined as the resistance that one part of fluid offers to the flow of another part of the fluid. Viscosity is produced by the shearing effect of moving one layer of the fluid 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.

To define viscosity let us visualize a fluid as being stratified into layers or planes of molecules. When a liquid flows in contact with the wall of the tube which is stationary the liquid in the centre has the highest velocity; intermediate layers move with a gradation of velocities. The flowing liquid may therefore be regarded as composed of a number of concentric tubes sliding past one another like the tubes of a telescope. Each layer exerts a drag on the next, and work must be done to maintain the flow. 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. $F \propto A \cdot dv/dx$

OR $F = \eta \cdot A \cdot dv/dx$

Where 'η' 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 'η' 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 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

$$1\,N = 1\,kg\cdot m\cdot s^{-2}$$

$$1\,Pa\,s = 1\,kg\cdot m^{-1}\cdot s^{-1}$$

A fluid has viscosity of 1 Pas if a force of 1N is required to move a plane of 1m^{2} at a velocity of 1 ms^{-1} with respect to a plane surface a meter away and parallel with it. In C.G.S. units viscosity is expressed in 'poise' that is 1 g.cm^{-1}.s^{-2} in the honour of French scientist Poiseuille who derived the formula and gave the method for measurment of viscosity of liquids.

0.1 Pas = 1 Poise.

Low values of viscosity are expressed in centi-poise (1/100 poise) and millipoise (1/1000 poise). The usual symbol for viscosity is the Greek letter 'ETA' (η).

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 times 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 frictional coefficient times the velocity. The frictional coefficient f 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 'η' the coefficient of viscosity. If the density of the sphere is ρ and the density of the medium is ρ_0 , the force causing motion is

$$4/3\,\pi r^3(\rho-\rho_0)g$$

where 'g' is the acceleration of gravity.

b) POISEUILLE METHOD

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

$$\eta = \pi p \cdot r^4 \cdot t / 8 L \cdot V$$

where 'V' is the volume of the liquid of viscosity 'η' 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 volumes of two liquids through the same capillary using an instrument called viscometer. Then according to the poiseuille equation the ratio of the viscosity coefficients of the two liquids is given by -

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

Since the pressures p1 and p2 are proportional to the densities of the two liquids ρ_1 and ρ_2 then we may write also 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 ρ_1 and ρ_2 and η_2 are known, determination of t1 and t2 permits the calculation of η_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.

The variation of viscosity with temperature may be represented quite well by

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

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 molecules to move around each other.

1.2 VISCOSITY OF ELECTROLYTIC SOLUTIONS :

Poiseuille[5], the great pioneer 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 solutions of barium chloride and found that it increased the viscosity of water. Arrhenius[7] made some viscosity measurements on solutions. He found that the change in the viscosity caused by the addition of a salt was roughly proportional to the concentration at low concentrations but increased more rapidly than the concentration at moderate concentrations. ($\approx$1 normal). He proposed new formula for the relationship between viscosity and concentration namely

$$\eta = A^{c}$$

where 'η' 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 within a few tenths of 1 percent between 1/8 and 1/2 normal and within about 1% up to 1 normal.

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

The next outstanding investigator on this subject 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 concentration. He made measurements with more dilute solutions, than his predecessor, 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. Grüenisen 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 deviations would not be readily apparent on the scale, but the deviation are clearly systematic and greater than the experimental error. For a salt which increases the viscosity of water, the curve starts at $\eta=1.0000$ when $c=o$ 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 molal) and then the 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 η -- C curve with the origin, but it is approximately the same as the slope of the η -- 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. Grüneisen 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 Grüneisen'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 concentration, including solutions even more dilute (c=0.007 M) than those studied by Grüneisen. 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 molecules, which tends to diminish the viscosity;
2) an increase in the viscosity due to the presence of the ions of the salt and the 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 the viscosity of Barium chloride solution have been carried out by Sprung[6], Arrhenius[7], Wagner[9] and many other workers[12,15].

1.2 a JONES-DOLE-EQUATION :-

The relation of Jones-Dole equation[76] is

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

Where A and B are the inter-ionic forces in the viscosity and solute-solvent interaction coefficient[16] and C is the concentration of the solute electrolyte in Ml^{-1}. This equation is only applicable to dilute solutions ($C \leqslant 0.1$ M)[59].

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 of 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 D. Patnaik[18] found that satisfactory explaination has been advanced on therotical grounds for 'A' by Falkanhegen and Vernon[19], but no such explaination has yet been offered for the constant 'B'. They studied the relative viscosity of solutions of KCl in varying compositions of dioxan-water mixtures to explain the nature of 'B'. Cox and Wolfenden[20] have attributed specific 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 value of 'B'also increased, thus furnishing the proof that the magnitude of 'B' is dependent 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, $BaBr_2$, $Ba(ClO_4)_2$, $Mg(ClO_4)_2$ have been studied by P.B. Das[22,23] in aquesous solutions and in dioxane-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 B.K. Parida and P.B. Das[24], P.K. Das[25], P.B. Das and co-workers[26-38] studied the viscosity of nitrate, bromate, chloride, bromide, & iodide. They recorded the 'B' coefficient for different solutions and discussed the influence of the anion in such solutions. The 'B' coefficient for the anions decrease in order IO_3^- > Br^- > BrO_3^- > NO_3^-. This order changes with increasing solvent concentration. 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 as a function of 'B' coefficients. They noted that the dependence of viscosity on the ionic strength of electrolyte solutions at high concentrations, is corelated with the 'B' coefficients 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 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 connections. This conviction is held because the relatively simple alcohol-water mixtures may serve as models helpful to the better understanding of more complex system, and because these mixtures are so frequently used as solvents in studies of chemical equillibria 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 determined the viscosity 'η' of MNO_3 (M = Na,K,NH_4) solutions in aqueous EtOH and PrOH. They observed that addition of all salts decreases η of mixed solvents. For 4% $NaNO_3$, KNO_3 and NH_4NO_3. In H_2O - EtOH the decrease in η is 1.9, 5.4 and 7.8% respectively. 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 discussed the selection of convenient equation for the description of the 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, η_r, is generally used in most of the empirical relations.

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

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

where ϕ denotes the volume fraction and is equal to $C\bar{V}$, $\bar{V}$ being the molar volume of electrolyte in solution.

Unlike the viscosity behaviour of dilute solutions, representation of viscosity at concentrations > 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 of limited range by Moulik[54], based on the Eyring[55] theory of absolute rate for viscous flow of liquids.

1.2.C THOMAS EQUATION :-

Thomas gives equation as

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

where ϕ has usual meaning.

Breslau and Miller[56] used the Thomas equation and calculated the molar volumes of a number of aqueous electrolyte solutions. The eqution of Thomas has been rearranged 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 electrolytes and may not be valid for many non-electrolytes[57].

1.2 d VAND EQUATION :-

The theor~~i~~etical equation of Einstein has been modified by Vand[51] to represent viscocity of aqueous solutions of both electrolytes and non-electrolytes at higher concentrations.

The equation may be given as -

$$\ln(\eta_r) = \frac{2\cdot 5\,\phi}{1 - Q\phi}$$

where ϕ 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 have been rearranged in the linear form as -

$$\frac{1}{c} = \left(\frac{0\cdot 921}{\bar{V}}\right)\cdot\frac{1}{\log \eta_r} + Q\bar{V}$$

and the plot of $\frac{1}{\log \eta_r}$ Vs $\frac{1}{c}$ is the straight line with $Q\bar{V}$ as the intercept and $\frac{0\cdot 921}{\bar{V}}$ 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 and Thomas 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 these equations over a wide range of concentration for a number of salts is 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. They evaluated the parameters of the equations, which can be used to calculate viscosity of aqueous solutions in the concentration range in which above equation is valid.

Mahapatra, Naik, Mishra and Behera[58] measured viscocities 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' coefficients from a knowledge of molar volume of the electrolye in solution 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] represented the variation of relative viscosity η_r of concentrated aqueous solutions of 1:1 type electrolytes with electrolyte concentration by a general equation by extending the limiting equation of Einstein. They obtained an emprirical equation relating B and $\bar{V}$ of electrolyte in aqueous solutions by least square analysis, which resembles more closely to $B \sim 2.5\ \bar{V}$. 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 $B_{\pm}$ 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 techniques for obtaining different parameters of the 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.

1.3 TRANSPORT PROPERTIES

Latimer[60] studied the entropy of aqueous ions and the nature of the entropy of hydration and made the following conclusions.

1. Onsager suggested that the entropy of an ion could be computed theoretically as the temperature coefficient of the work required for charging.
2. Latimer answered that the entropy deficiency expected on this basis would amount to about one-third of the observed effect.
3. Onsager emphasized the importance of this disagreement. Any satisfactory theory of ionic entropies must take into account the anomalous dielectric properties of the

solvent in the neighbourhood of an ion.

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 reported that, "permanent gases, when dissolved in normal liquids loosen the forces on neighbouring solvent molecules producing a solvent reaction which increases the partial molal entropy of the solute. Entropies of vaporization from aqueous solutions diverge strikingly from the normal behaviour established for nonaqueous solutions. The nature of the deviations found for non-polar solutes in water together with the large effect of temperature upon them leads to the idea that the water forms frozen patches of microscopic icebergs around such solute molecules the extent of the iceberg increasing with the size of the solute molecule. Such icebergs are apparently formed also about the nonpolar parts of the molecules of polar substances such as alcohols and amines dissolved in water, in agreement with Butler's observation that the increasing insolubilility of large non-polar molecules is an entropy effect. The entropies of hydration of ions are discussed from the same point of view, and the conclusion is reached that ions, to extent which depends on their size and charges, may cause a breaking down of water structure as well as a freezing or saturation of the water nearest them. The influence of temperature on certain salting-out coefficients is interpreted in terms of entropy changes. It appears that the salting-out phenomenon is at least partly a structural effect. It is suggested that structural influences modify the distribution of ions in an electrolyte solution and reasons are given for postulating the existence of a super-lattice structrure in solutions of $LaCl_3$ and of $EuCl_3$. An example is given of a possible additional influence of structural factors up on reacting tendencies in aqueous solutions".

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 strong electrolyte. Using this relation they calculated viscosity B- coefficients for the fluoride and periodate ions at 25°C which are 0.0965 and -0.0647 respectively. They also calculated energies and entropies of activation for viscous flow at 25°C for a number of ionic species. They observed that large ions such as Ba^{+2}, IO_3^{-} and SO_4^{-2}, exhibit a minimal 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-α- aminobutyric acid, 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 enthanol-water solvent, largely a result of parturbation by highly polar zwitterion 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.

B. Das, Singh and P.K. Das[17] studied viscosity of solutions of Potassium chloride, Sodium chloride, Potassium bromide and Sodium bromide in dioxane - water mixtures at 30° and 40° and the activation energies and entropies of viscous flow.

P.B. Das, N.C. Das and P.P. Misra[27] studied solute-solvent interaction of $NaNO_3$ solutions in dioxane-water mixtures at 30, 35, 40 and 45 °C. They computed the energy of activation, ΔE^{*}, free energy of activation ΔF^{*} and entropy of activation ΔS^{*}. From these values they conclude that ΔE^{*}, ΔF^{*} and ΔS^{*} of the 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°, Calcium chloride at 35°, 40° and 45° and Barium chloride at 30°, 40° and 45 and claculated free energy (ΔF^{*}), energy of activation for viscous flow (ΔE^{*}) and the entropy of activation (ΔS^{*}) 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 dioxane-water mixtures from viscosity, apparent-molar volume and conductance data at 35^{o}C. Das determined the viscosities, apparaent molar volumes and electrical conductivities of K and Na salts in aqueous dioxane (o-30 wt. %) at 35^{o}. He calculated dissociation constants and free energies of the solutions in 10-30 wt. % dioxane. He reported that the ion-solvent interaction follows the order $BrO_3^- > Br^- > Cl^- > IO_3^- > NO_3^- > SO_4^{2-}$, and due to the bulkiness the dioxane breaks down the 3-dimensional water structure of the solvent and the additivity law does not hold.

Renz, M; stelmle, F.[65] studied thermodynamic properties of the binary system, methanol-lituium bromide.

D.K. Dash and P.B. Dash[37] studied thermodynamics of $Sr(NO_3)_2$ and $Cd(NO_3)_2$ in mixed solvents from viscosity data.

Taniewska-Oninska, stefania; Piekarska, Alina[66] studied thermodynamic functions of activation of viscous flow in sodium iodide-water-amide systems. They calculated the thermodynamic parameters of activation of viscous flow, ΔH^* and ΔS^* at 298.15^{o}K and ΔG^* at 278.15, 318.15^{o}K for the systems NaI-water-formamide and NaI-water-D.M.F.

1.4 SCOPE OF THE PRESENT WORK

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

1. Potassium Bromide and Sodium Bromide in Dioxane-water mixtures at 35^{o}C.
2. Potassium Nitrate, Sodium Nitrate, Sodium Bromate and Potassium Iodate in Dioxane - water mixtures at 35^{o}C.
3. Magnesium Nitrate in Dioxane - water mixture at 35^{o}C.
4. $MgCl_2$, $MgBr_2$, $Mg(ClO_4)_2$, $BaCl_2$, $BaBr_2$, $Ba(Cl_4)_2$, $SrCl_2$,

$CaCl_2$, Na_2SO_4 and K_2SO_4 in Dioxane-water mixtures at 35°C.

5. Potassium Chloride and Sodium Chloride in Dioxane water mixture at 40°C.
6. Magnesium Bromide, Sodium Sulphate and Calcium Chloride in Dioxane water mixtures at 35°C.
7. Sodium Chloride in Dioxane - water mixtures at 35°C.
8. Potassium Chloride in Dioxane - water mixtures at 35°C.
9. Sodium nitrate solutions in Dioxane - water mixtures at 30, 35, 40 and 45°C.
10. KNO_3 solutions in Dioxane - water mixtures at different temperatures.
11. $CaCl_2$ and $SrCl_2$ in water at different temperatures.
12. Chlorides, Bromides, Nitrates, Bromates Iod ates and Sulphates of Potassium and Sodium in Dioxane - water mixtures at 35°C.
13. KCl, KBr, KNO_3, $KBrO_3$, KIO_3, K_2SO_4 in Dioxane - water mixture at different temperatures.
14. Bromates, Iodates and Sulphates of Potassium and Sodium in Dioxane - water mixtures at different temperatures.
15. NaCl, KCl, $NaBr_2$, KBr, $NaNO_3$, KNO_3 in Dioxane - water mixtures at different temperatures.
16. Sodium Formate in water and in Aqueous formic Acid at different temperatures.
17. Potassium Halides in water-Pyridine and Water -γ- Picoline mixtures.
18. Glycine in Alcohol - water mixtures at 308.15°K.

19. $Sr(NO_3)_2$ and $Cd(NO_3)_2$ in Dioxane, Glycol Methanol - water mixtures at different temperatures.

20. $AlNH_4(SO_4)_2 \cdot 12H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$ in water - methanol mixtures at different temperatures.

21. $AlNH_4(SO_4)_2 \cdot 12H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$ in water-Tert Butyl alcohol mixtures at different temperatures.

It is clear, therefore, that the viscosity measurements on Barium nitrate and Calcium nitrate solutions in water and in methanol-water mixtures have not yet been done so far. Hence, it is proposed to study the viscosity of these salts in aqueous solutions and in methanol - water mixtures at different temperatures.

We report here viscosity and density data for Barium nitrate and Calcium nitrate tetrahydrate in methanol - water (MeOH - H_2O) solutions (0%, 10%, 20%, 30% MeOH, w/w) at 298 ^{o}K, 303 ^{o}K, 308 ^{o}K, 313 ^{o}K. The experimental results have been analysed using various standard viscosity-concentration equations.