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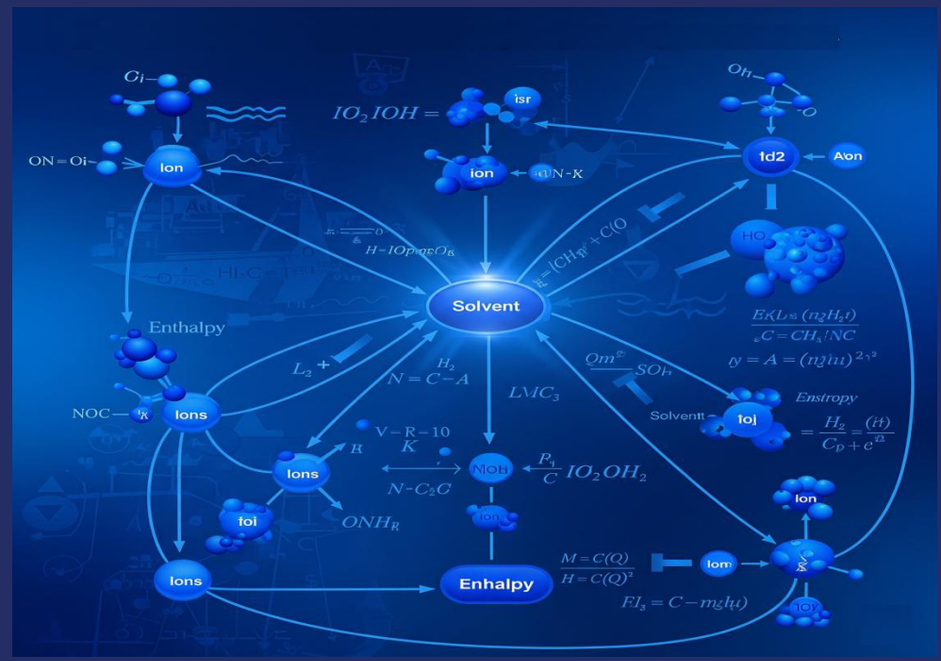
A Thermodynamic Approaches for Electrolyte Models



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Preface

Aqueous solutions of multicomponent electrolytes solutions are analogues to natural brines encountered in water pollution control, oceanography and petroleum drilling. A thorough knowledge of the thermodynamic properties of these solutions is useful in understanding the behavior of these solutions. Therefore, in present work the activity coefficient (γ) of NaCl in several aqueous quaternary electrolyte mixtures were determined using the Na ion selective electrode by EMF method at temperatures viz., 25°C, 35°C and 45°C over an ionic strength range of 0.1 to 3.0m. This experimental activity coefficient data were analyzed using the Pitzer equations. With a view to ascertain the validity of Pitzer equations for mixed electrolyte solutions.

The introduction which starts with a brief description on concepts of activity, activity coefficient and osmotic coefficient. Various theories of electrolyte solutions such as (a) Debye-Huckel theory (b) Bromley equation (c) Pitzer theory are described in detail and corresponding equations for calculating activity coefficient of multicomponent electrolyte solutions are given. The Debye –Huckel theory is described briefly while the theory of Pitzer formalism is described in detail. This Pitzer theory may be regarded as extension of Bromley treatment by adding the terms for

(1) binary interactions of the ions of same sign
(2) ternary interaction involving two ions of the same sign and one of the opposite sign. The Pitzer treatment gives relatively compact and more convenient equations with fewer parameters and are capable of representing and predicting the thermodynamic properties such as activity coefficients, osmotic coefficients of single and multicomponent electrolytes solutions upto their saturation limits. A comprehensive literature survey on the thermodynamic properties of mixed electrolyte solutions related to the present form is given in detail. Finally, a brief note on the scope of the present work is included. at the end of this chapter.

The present work is aimed at (a) experimental determination of activity coefficients of mixed electrolytes solutions containing *NaCl in NaCl - $MgCl_2$ - Glycine - H_2O, NaCl - $CaCl_2$ - Glycine - H_2O, NaCl - $SrCl_2$ - Glycine - H_2O, NaCl - $MgCl_2$ – β- Alanine - H_2O, NaCl - $CaCl_2$ - β-Alanine - H_2O, NaCl - $SrCl_2$ – β-Alanine - H_2O, NaCl - $MgCl_2$- L-Valine - H_2O, NaCl - $CaCl_2$ - L-Valine*

- H_2O, *NaCl* - $SrCl_2$ - *L-Valine* - H_2O at various temperatures and concentrations; (b) evaluation of Pitzer ion interaction parameters and estimation of Harned coefficients from the experimental data on all the nine mixtures in order to find the osmotic coefficients and to investigate the validity and usefulness of the Pitzer equations and corresponding mixing parameters (S_θ & φ) in modeling the thermodynamic properties of these solutions; (c) calculating the activity coefficients in several environmental waters.

The second chapter starts with experimental section. In this chapter a description of sodium ion selective electrode, reagents used, preparation of Ag/AgCl reference electrode and preparation of solutions is given. The EMF's were measured using Keithly $5_{1/2}$ digit electrometer. The procedure employed to determine the activity coefficient of electrolyte in the mixed electrolyte solutions from the experimentally measured EMF's values is given in detail.

In third chapter, the experimental results are presented in two sections. Section-A of this chapter contains the results on the calibration run of the Na ion selective electrode at 25°C and at total ionic strength of 0.1 to 3.0 mol.kg^{-1} to evaluate the values of E_o and Nernst slope.

In section-B, experimentally measured emf's values and the calculated activity coefficients data of NaCl in various quaternary mixtures given above at 25°C, 35°C, 45°C and at total ionic strength of 0.1 to 3.0 mol.kg^{-1} are tabulated and listed in the form of tables.

The fourth chapter containing analytical discussion of the experimental results is presented and are discussed in three sections.

Sections-A, the experimental data of quaternary mixtures are discussed. The osmotic and Harned coefficients were calculated using the Pitzer ion interaction parameters estimated for these systems at constant total ionic strength of 0.1 to 3.0 mol. kg^{-1} at 25°C.

The experimentally determined activity coefficient data of NaCl in these mixtures were fitted to the Harned equations.

$$\log\gamma_A = \log\gamma^o_A - \alpha_{AB}y_B - \beta_{AB}y^2_B$$

Where α_{AB} and β_{AB} are Harned coefficients. When the plot of $\log\gamma_A$ v/s y_B is nearly linear for any system, then the β_{AB} value is very small and can be neglected, then the Harned equations can be written as

$$\log\gamma_A = \log\gamma^o_A - \alpha_{AB} y_B$$

These Harned coefficients α_{AB} and β_{AB} values which are function of the ionic strength and temperature are useful in calculating the γ_{NaCl} values in the mixtures of any given ionic strength fraction (y_B) i.e., at any given composition.

The activity coefficient data is further analyzed using the Pitzer equations for multicomponent electrolyte solutions and Pitzer interaction parameters viz; binary interaction parameter (S_θ) and ternary interaction parameter(φ) values are evaluated. These Pitzer parameters were next used to calculate the osmotic coefficient for all the mixtures studied. These mixing parameters are useful in determining the thermodynamic properties of multicomponent electrolyte solutions at any given ionic strengths.

The Pitzer equations used in the present work for calculating Osmotic coefficient (Φ) and activity coefficient (γ) for single electrolyte systems are as follows:

$$\phi - 1 = -\left|Z_M Z_X\right| A_\phi \left(\frac{\sqrt{I}}{1+b\sqrt{I}}\right) + m\left(\frac{2\upsilon_M\upsilon_X}{\upsilon}\right) B^{\phi}_{MX}$$

$$+ m^2\left\{\frac{2(\upsilon_M\upsilon_X)^{3/2}}{\upsilon}\right\} C^{\phi}_{MX}$$

$$\ln\gamma_{MX} = -\left|Z_M Z_X\right| A_\phi \left[\left(\frac{\sqrt{I}}{1+b\sqrt{I}}\right) + \frac{2}{b}\ln\left(1+b\sqrt{I}\right)\right]$$

$$+ m\left(\frac{2\upsilon_M\upsilon_X}{\upsilon}\right) B^{\gamma}_{MX} + \frac{3m^2}{2}\left\{\frac{2(\upsilon_M\upsilon_X)^{3/2}}{\upsilon}\right\} C^{\phi}_{MX}$$

Where $I = \frac{1}{2}\sum_i m_i z_i^2$ = ionic strength

In section-B, the environmental waters are studied to estimate the activity coefficients of the involved ions and electrolytes. Three (3) environmental waters studied in the present work are: (1) Patancheru nala, (2) Water of Musi river and (3) Water of Balanagar lake.

The analytical data obtained on these waters indicates that the major dissolved ions having significant concentration are four cations Na^+, K^+, Mg^{2+}, Ca^{2+} and four anions HCO_3^-, Cl^-, SO_4^{2-}, NO_3^- . The Pitzer equations and the necessary ion interaction parameters ($\beta^{(o)}$, $\beta^{(1)}$, C^Φ, S_θ and Ψ)

are used to calculate the ionic activity coefficients of the dissolved cations and anions. These dissolved ions plays a vital and cause several health problems and diseases when used as (1) drinking water for cattle and village labourers and (2) irrigation waters for crops. The calculations are presented to show that the ionic activity coefficients affect the values of Sodium Absorption Ratio (SAR).

In section-C, all the results obtained in the present work have been summarized in the form of graphs to reveal the trends in the activity coefficients. The effect of added cations, anions and amino acids on the activity coefficients of NaCl is discussed.

The trends in the activity coefficients values of NaCl in the quaternary systems could be explained on the basis of the crystallographic radii, charge densities and activity coefficients of the pure electrolytes.

The activity coefficients are increased by the addition of $MgCl_2$, $CaCl_2$, $SrCl_2$ to the NaCl and amino acid solution in the order

$$MgCl_2 > CaCl_2 > SrCl_2$$

The activity coefficients of NaCl in the quaternary systems studied shows that the activity coefficient also depend on the amino acid used.

Thus, the experimental data measured in the present work on several mixed electrolyte systems is analyzed using the Pitzer equations to demonstrate the usefulness of the thermodynamic properties of the aqueous electrolytes solutions in several fields of practical importance.

CONTENTS

CHAPTER-I

INTRODUCTION

The mean activity coefficient of one electrolyte in the presence of other electrolyte(s) are being determined with renewed interest now a days all over the world. Aqueous electrolyte solutions and their thermodynamic properties play an important role in understanding the behavior of amino acids[1-4], natural waters such as sea and lake water, environmental pollution waters, industrial solutions[5-7]. The specific ion interaction principle which postulated the existence of short range interactions among the ions of unlike charge was enunciated by Bronsted[8-10] and was applied to dilute solutions by Guggenheim[11-13]. Modification to this principle was suggested by Scatchard[14-15] who took into the consideration the interactions among the like charge ions as well. Scatchard et al[16] have subsequently extended and elaborated the Guggenheim equation in several ways by considering all possible interactions of ions in solutions leading to very complex formulae for activity coefficients and osmotic coefficients. Bromley[17] also, proposed single parameter equations for activity coefficients and osmotic coefficients. Pitzer and Bremer[18] extended the Guggenheim equations and developed a single and complex set of multicomponent electrolyte solutions. These Pitzer[19] equations have an electrostatic term of Debye-Huckel type plus a virial coefficients series.

Recently, the concentration and temperature dependence on thermodynamic properties of electrolyte solutions has been of much concern in different fields. Of all the thermodynamic properties, of these single and multicomponent electrolytes solutions the activity coefficients and osmotic coefficients received the maximum attention.

a) <u>General relations for Chemical Potentials, Activities and Activity coefficients</u>:

A Closed system that combines first and second laws gives the thermodynamic relationship

$$dE = TdS - PdV \qquad \ldots\ldots\ldots\ldots(1)$$

This implies that E is the internal energy and is a function of S and V. Sometimes we call S and V the 'natural variables' of E, T the Kelvin temperature, S the entropy, P the pressure and V the volume.

For an open system to which matter may be added or withdrawn one has,

$$dE = TdS-PdV+\mu_A dn_A+\mu_B dn_B+\mu_C dn_C+\ldots+ \mu_Z dn_Z \qquad \ldots\ldots\ldots\ldots(2)$$

Where n's represent the no: of moles of component A, B etc. and μ's represent the chemical potentials of various components.

The chemical potential of component ′C′ for eg: can be defined as follows,

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{n_B,T,P} \qquad \ldots\ldots\ldots\ldots (3)$$

$$\mu_B = \left(\frac{\partial G}{\partial n_B}\right)_{n_A,T,P} \qquad \ldots\ldots\ldots\ldots (4)$$

Where n_A and n_B are number moles of solvent and solute respectively.

In chemical thermodynamics, it is generally sufficient to study the variation of chemical potential with composition, because experiments can be readily designed where in the temperature and pressure are maintained constant.

The chemical potential of any component in a liquid solution can be represented by a relation.

$$\mu i = \mu_i^0 + RT \ln P_i \qquad \ldots\ldots\ldots\ldots (5)$$

Where P_i is the partial pressure or the fugacity of the component in the vapour, which is in equilibrium with the solution. The fugacity has units of pressure and is a function of pressure. It contains all the information's on the non-ideality of the gas.

For an ideal solution, the fugacity is same as pressure, hence the partial pressure or fugacity of any constituent is proportional to molefraction (X) of that constituent, and hence the above equation could be written as

$$\mu_i = \mu_i^0 + RT \ln X_i \qquad \ldots\ldots\ldots\ldots (6)$$

Where X_i is the concentration (molefraction) of component 'i' in the solution and μ_i^0 is the standard chemical potential and is independent of composition but dependents on temperature and pressure.

In ideal solution the solute particles does not have any interactions between themselves or with solvent particles, but in electrolyte solutions the long-range ion- ion interaction plays an important role at all concentration ranges.

In order to apply equation (6) for electrolyte solutions, an empirical correlation factor f_i was introduced in the concentration terms as

$$\mu_i = \mu_i^0 + RT \ln (X_i f_i) \qquad \ldots\ldots\ldots\ldots (7)$$

The product $X_i f_i$ is known as effective concentration, which is known as activity of the component i.

Thus,

$$a_i = X_i f_i \qquad \ldots\ldots\ldots\ldots (8)$$

These expressions for chemical potential all have the form of a reference standard state chemical potential plus RT times the logarithm of something related to pressure or concentration. This form turns out to be very important, so important that G.N. Lewis[20-21] used it to give the most general case of chemical potential as

$$\mu_i = \mu_i^0 + RT \ln a_i \qquad \ldots\ldots\ldots\ldots (9)$$

The quantity a_i is called the **"activity"** of component i and equation (9) should be regarded as the definition of activity.

Notice that the activity has no units.

In eq. (9) the activity a_i is in logarithmic form and hence it is apparent that the activity a_i of any substance can be expressed only in turns of ratio of two chemical potentials μ_i and μ_i^0.

Therefore choosing a reference state or standard state in which activity of given substance is arbitrarily taken as unity is essential.

In case of electrolyte solutions, the chemical potential of solute depends on concentration scale employed. The concentration scales that are in general use are, mole fraction (X_i, the ratio of no: of moles of i to the total no: of moles in solution), molarity (C_i, moles per liter of solution) and molality (no: of moles per 1000 grams of solvent).

In first method, the activity of solution, the reference state is equal to its mole fraction, hence

$a_i = a_x$.

Therefore the equation can be written as

$$\mu_i = \mu_x^0 + RT \ln (a_x) \qquad \ldots\ldots\ldots\ldots(10)$$

In second method, the activity of solution is equal to molarity of solute when concentration approaches to zero hence,

$a_i = a_c$

Therefore equation can be written as

$$\mu_i = \mu_c^0 + RT \ln (a_c) \qquad \ldots\ldots\ldots\ldots(11)$$

In third method, the activity of solute is equal to molality of solute in a solution in which the concentration of solute approaches to zero. Then

$a_i = a_m$

Therefore the equation can be written as

$$\mu_i = \mu_m^0 + RT \ln (a_m) \qquad \ldots\ldots\ldots\ldots(12)$$

The mole fraction scale is called rational system, where as the other two scales are called the practical units.

The activity coefficient of a species 'i' in the molal scale is written as

$$\mu_i = \mu_i^0 + RT \ln m_i(T_i) = \mu_i^0 + RT \ln a_i \qquad \ldots\ldots\ldots\ldots(13)$$

The quantity T_i is called the molal activity coefficient.

Consider an electrolyte solution, which is completely dissociated into ions. The total Gibbs free energy of a solution is given by the sum of the Gibbs free energy of solvent, the positive and negative ions.

Thus,

$$G = n_s G_s + n_+ \mu_+ + n_- \mu_- \quad \ldots\ldots\ldots\ldots(14)$$

The subscript s stands for solvent.

If each mole of an electrolyte dissociates into ν_+ positive and ν_- negative ions

Then,

$$n_+ = \nu_+ n \text{ and } n_- = \nu_- n$$

Where n is the number of moles of electrolyte in the solution.

Now above equation (14) can be rewritten as

$$G = n_s G_s + n (\nu_+ \mu_+ + \nu_- \mu_-) \quad \ldots\ldots\ldots\ldots(15)$$

If 'μ' is the chemical potential of electrolyte in the solution, then one can also write

$$G = n_s G_s + n\mu \quad \ldots\ldots\ldots\ldots(16)$$

Comparing the equation (15) and (16) we get

$$\mu = \nu_+ \mu_+ + \nu_- \mu_- \quad \ldots\ldots\ldots\ldots(17)$$

The total no: of moles of ions produced by one mole of an electrolyte (ν) is given by the relation

$$\nu = \nu_+ + \nu_- \quad \ldots\ldots\ldots\ldots(18)$$

The activity coefficient ν_+ and ν_- cannot be measured independently, because solutions must be electrically neutral. In other wards, we cannot make a solution, which has just positive or negative ions. We can't calculate the individual activity coefficient from theory, either. However, we can measure a "geometric mean" activity coefficient within limits and can calculate it from theory. We will show, how to do both of these things later. The actual form of the geometric mean depends on the no: of ions produced by the salt.

Then the mean ionic chemical potential $\mu_\pm$ is defined as

$$\nu \mu_\pm = \mu = \nu_+ \mu_+ + \nu_- \mu_- \quad \ldots\ldots\ldots\ldots(19)$$

Now one can represent various activities as

$\mu = \mu^0 + RT \ln a$ ……(20)

$\mu_{\pm} = \mu^0_{\pm} RT \ln a_{\pm}$ ……(21)

$\mu_+ = \mu^0_+ + RT \ln a_+$ ……(22)

$\mu_- = \mu^0_- + RT \ln a_-$ ……(23)

In these relations, a is the activity of the electrolyte, $a_{\pm}$ is the mean ionic activity and a_+, a_- are the individual ionic activities. Then one can also write the relations

$\nu \mu^0_{\pm} = \mu^0 = \nu_+ \mu^0_+ + \nu_- \mu^0_-$ ……(24)

and

$\mu^0 + RT \ln a = \nu \mu^0_{\pm} + \nu RT \ln a_{\pm}$ ……(25)

Subtracting equation (24) from equation (25) one gets

$a = a_{\pm}^{\nu}$ ……(26)

Then it is also evident that

$a_{\pm}^{\nu} = a_+^{\nu_+} + a_-^{\nu_-}$ ……(27)

Therefore, the mean ionic activity is the geometric mean of the individual ionic activities.

The various activity coefficients are now defined by relations

$a_{\pm} = \gamma_{\pm} m_{\pm}$ ……(28)

$a_+ = \gamma_+ m_+$ ……(29)

$a_- = \gamma_- m_-$ ……(30)

Where $\gamma_{\pm}$ is the mean ionic activity coefficient and $m_{\pm}$ is the mean ionic molality. Using the values of $a_{\pm}$, a_+ and a_ from equations (28), (29) and (30) in eq. (27)

we obtain

$a_{\pm}^{\nu} = \gamma_{\pm}^{\nu} m_{\pm}^{\nu} = \gamma_+^{\nu_+} \gamma_-^{\nu_-} m_+^{\nu_+} m_-^{\nu_-}$ ……(31)

Now the mean activity coefficient $\gamma_{\pm}$ and mean molality $m_{\pm}$ can be defined as

$$\gamma_{\pm}^{\nu} = \gamma_{+}^{\nu+} \gamma_{-}^{\nu-} \quad \text{.....(32)}$$

$$m_{\pm}^{\nu} = m_{+}^{\nu+} m_{-}^{\nu-} \quad \text{.....(33)}$$

These equations show that $\gamma_{\pm}$ and $m_{\pm}$ are also geometric means of the individual ionic quantities. The extent of deviation of solvent activity from ideality is measured in terms of Osmotic coefficient (ϕ), which is defined using the relation

$$\mu_A = \mu^0_A - \phi RT\left(\frac{\gamma_m W_A}{1000}\right) \quad \text{.....(34)}$$

and hence,

$$\ln a_A = \phi \quad \text{.....(35)}$$

Where W_A is the molecular weight of the solvent. For mixed electrolyte solution ν_m is replaced by $\sum m_i$, which is the sum of molalities of all the ions in the solution.

At constant temperature and pressure, for a solution containing only one solute the Gibb's-Duhem equation is

$$n_A \, d\overline{G_A} = - n_B \, d\overline{G_B} \quad \text{.....(36)}$$

Where n_A and n_B are the no: of moles of solvent and solute respectively.

Multiplying each side by $\left(\frac{1000}{W_A n_A}\right)$ we get

$$\left(\frac{1000}{W_A}\right) d\overline{G_A} = - m\, d\overline{G_B} \quad \text{.....(37)}$$

Where ($\overline{G_B} = \overline{\mu_B}$)

For an aqueous electrolyte solution equation (20), (31) and (37) gives

$$-55.51 \, d\ln a_w = m\, d\overline{G_B}\ (RT) = \nu m\, d\ln(\gamma_{\pm} m) \quad \text{.....(38)}$$

From equation (37) we gets

$$\nu m\phi = -55.51 \ln a_w \quad \text{.....(39)}$$

Equation (39) on differentiating and subtracting in eq. (38) gives

$$(\phi\text{-}1)\ \frac{dm}{m} + d\phi = d\ln\gamma$$

This equation on integration gives

$$\ln\gamma = (\phi\text{-}1) + \int_0^m (\phi\text{-}1)\, d\ln m \qquad \ldots\ldots\ldots\ldots(40)$$

Alternatively one can write

$$\nu m\phi = -55.51\ \ln a_w = \int_0^m \nu m\, d\ln(\gamma m)$$

This gives

$$\phi = 1 + 1\backslash m \int_0^m m\, d\ln\gamma \qquad \ldots\ldots\ldots\ldots(41)$$

Using equation (40) and (41); one can convert the osmotic coefficient into activity coefficient and vice versa.

b) <u>Theories of Electrolyte Solutions:</u>

In electrolyte solutions, the solvated positive and negative ions are in constant motion. Also there are electrical attractions and repulsions between these ions. Therefore quantitative theory of an ionic solution requires a complete understanding of inter-ionic attractions, sizes of ions, the detailed structure and molecular properties of solvent as well as the ion-solvent interactions. The basic mathematical difficulty in the development of rigorous electrolyte solution theory is that, if the distributions of ions in an electrolyte solution are known then it is possible to calculate the electrical potential arising from this distribution, but the calculation of this distribution requires the use of electrical potential. The first attempt to solve this problem was made by Milner[22] in 1912 by a laborious method of numerical summation of interaction energies for all possible configurations of the system.

(1) Debye-Huckel Theory:

The ideal dilute solution is a solution where the solvent follows Raoults law, and solute follows Henry's law.

$y_i P = x_i H_i$

Where H_i is Henry's law constant for solute i.

In electrolyte solutions, the ion interacts strongly with each other and with the solvent through their electric charges. So deviation from ideality is important even at low concentrations. Also, the ions are not volatile at atmospheric pressure and ambient temperature, so a different approach is needed in order to formulate a limiting law for thermodynamic behavior of electrolyte solutions.

The Debye- Huckel theory was formulated by Debye and Huckel[23] in 1923 for electrolyte solutions. In this theory, the solvent is thought of a continuous dielectric medium, upon which the ion interactions are superimposed. An ion in the solution, termed the reference ion (i), is arbitrarily selected. All the calculation is then related to this one ion. The reference ion, with a charge e_i, will attract ions of opposite charges while repelling those of like charges. This results in the central ion being surrounded by an "ion cloud" which on average, have a higher charge density (ρ) of counter ions than the bulk solvent. For the laws of electro neutrality to obey, the overall charge of the ion cloud must be equal and the opposite to that of reference ion. The difference in the charges gives rise to a potential difference between the reference ion and surrounding ions (Ψ).

Therefore the expression for Ψ due to its ionic atmosphere is given by

$$\Psi_{Cloud} = -Z_i ek/D \qquad \text{.....(42)}$$

Then, the electrical free energy (G_{el}) of the solution was considered as the difference between the work done in changing all the ions in an electrical solution (i) at a given concentration and (ii) at infinite dilution.

Then,

$$G_{el} = -\frac{Ne^2k}{3D} \sum n_i Z_i^2 \qquad \text{.....(43)}$$

Where n_i represents the no: of moles of an ionic species of valence, z_i , D, the dielectric constant and

$$k=\left(\frac{8\Pi e^2}{DKT}.I\right)^{1/2} \qquad \ldots\ldots\ldots\ldots(44)$$

Debye-Huckel reciprocal length (1/k) is a measure of the radius of ionic atmosphere.

Debye-Huckel postulated that, if the ions of an electrolyte lost their charges, and becomes neutral particles, the solution would behave like ideal solution and obeys Henry's law. The departure from ideal behaviors is attributed to the mutual interaction of electrical charges carried by the ions, Hence,

$$\left(\frac{\partial G_{el}}{\partial n_i}\right)_{T,P} = \mu_{i\ (el)} = RT \ln \gamma_i \qquad \ldots\ldots\ldots\ldots(45)$$

$$\ln \gamma_i = \frac{Ne^2 kZ_i^{\ 2}}{2DkT} \qquad \ldots\ldots\ldots\ldots(46)$$

This is the original Debye- Huckel form for the activity coefficients of any single ionic species in an electrolyte solution. However this equation is generally used in the form

$$\log \gamma_{\pm} = -A\,|Z_+ Z_-|\,I^{1/2} \qquad \ldots\ldots\ldots\ldots(47)$$

Where

$\gamma_{\pm}$ = Mean ionic Activity coefficient.

I = Ionic strength, equal to

$$I=1/2 \sum c_i z_i^{\ 2}$$

$$A=\left(\frac{2\Pi N}{1000}\right)^{1/2}.\left(\frac{e^3}{2.303k^{\frac{3}{2}}}\right).\frac{1}{(DT)^{3/2}} \qquad \ldots\ldots\ldots\ldots(48)$$

= 0.509 at 25^0C for aqueous solution.

According to equation-47 the activity coefficient should decrease steadily with increasing ionic strength, where as actual values pass through a maximum and increase.

The Debye-Huckel theory provides an accurate representation of the behaviors of activity coefficients in dilute ionic solutions. It is however valid in the limit of very low concentrations (≤ 0.001), but not valid even at moderate ionic concentration (≥0.01) the major drawback of this theory is that, in this only long range interactions are being considered. It has no provision for more complicated short-range interactions. When the ions are more density packed in water, we need to consider the energetic of repulsion and attraction as well as the heterogeneous distribution of charges within individual hydration spheres.

To overcome this problem, an extended form of Debye-Huckel theory is proposed which includes the terms like, effect of finite size of ions.

By taking into consideration of above facts, the extended Debye-Huckel equation can be expressed as,

$$\log \gamma_{\pm} = - \frac{A \left| Z_{+} Z_{-} \right| I^{1/2}}{1+Ba\, I^{1/2}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(49)$$

Where 'a' is the effective diameter of the hydrated ion in centimeter, A and B are called Debye–Huckle constants, for activity coefficients. Z_+ and Z_- are the valence of the cation and anion respectively. The numerator in the above equation accounts for the electrostatic interactions white the denominator introduces a factor for the finite size of the ions.

The symbol 'a' in above equation is called "distance of closest approach" a term that tries to account for finite size of the ion in solution.

$$B = \left(\frac{k}{\sqrt{I}} \right)$$

$$= \left(\frac{8\Pi N e^2}{1000 D k T} \right)^{1/2} = \frac{50.29 x 10^8}{(DT)^{1/2}} \qquad \ldots\ldots\ldots\ldots(50)$$

'a' is dependent on size of ions introduced, but is usually considered constant.

Where 'e' is the electronic charge, D is dielectric constant, K the Boltzman constant,

T is the Kelvin temperature and N is the Avagardo number.

It is readily shown from above two equations, that at low ionic strength the Debye- Huckel equation reduces to the Debye- Huckle limiting law.

$$\log \gamma_{\pm} = -A \mid Z+Z- \mid I^{1/2} \qquad \ldots\ldots\ldots\ldots(51)$$

The Debye-Huckel equation and its limiting law proved successful in calculating the mean activity coefficient of electrolyte solution for all electrolyte types but only for solutions of very low ionic length. This limitation arises because Debye-Huckel limiting law is based on number of assumptions that are only correct at very high levels of dilution. The main assumption involved were

(a) The ions could be treated as point charges and

(b) Only long-range columbic forces operate between the ions. Ignoring the physical size of ions and the short range dispersive forces simplified the problem by allowing the forces between the ions to be calculated purely by the laws of electrostatics.

This supposition works well at low concentrations when the solute ion in the solutions is at considerable distance apart, but becomes increasingly inappropriate as the concentration increases. When the ions are in close proximity short range dispersion forces becomes dominant. Modifications to the extended Debye – Huckel theory has been made to extent its applicability to higher concentrations.

(2) <u>Bromley Equation</u>:

Bromley[24] presented a generalized analytical equation for the thermodynamic properties of single and multicomponent aqueous strong electrolyte solutions.

He suggested the equation

$$\log\gamma_{\pm} = \frac{-A_{\gamma}\sqrt{I}}{1+\sqrt{I}} + \beta M \qquad \ldots\ldots\ldots\ldots(52)$$

For 1-1 salts γ is a function of $I^{1/2}$ even at small ionic strengths.

Further, the β (taken as constant), may be approximated as the sum individual ions β values although the constant is only applicable to about 0.1 molal. After several trials the following equation was found to provide a good fit to most of the data on strongly ionized salts:

$$\log\gamma_{\pm} = \frac{-A_{\gamma}|Z_{+}Z_{-}|I^{1/2}}{1+\rho I^{1/2}} + \frac{(B_0 - B)I}{(1+aI)^{n}} + BI + CI^{2} \qquad \ldots\ldots\ldots\ldots(53)$$

A few determinations quickly indicated that the best integer value of 'n' was 2; which gave ρ values as ρ =1.0 ± 0.2 for 1-1, 2-1, 1-2, 2-2, 3-2 and 1-4 types of salts. The fit for all types of salts with ρ = 1.0 was reasonably satisfactory and was accepted. The ρ was also found to be temperature independent by using the data on aqueous sodium chloride from 0 to 100°C. The vales of 'a' is also near to unity but appears to decrease systematically with increase in valence number such that the product a | Z+Z- | ≈1.5. Individual values of this product ranged from 0.8 to 3.0. Fortunately, the data fit is not sensitive to the value of 'a'. Thus, a | Z+Z- | ≈ 1.5 was satisfactory upto 200°C. The value of 'C' was found to bear no consistent relation to 'B' value. The individual

values of 'C' had a nearly normal probability distribution about c=0. Accordingly, upto an ionic strength of 6m, 'C' was assigned the zero value. The best relation between B_0 and B was found at 25^0C to depend on | Z+Z- | as follows:

$$\frac{B_0 - B}{|Z_{+}Z_{-}|} = 0.06 + 0.6B \qquad \ldots\ldots\ldots\ldots(54)$$

This relationship was tested for the effect of temperature, using the data on sodium chloride, and was also found to be temperature independent in the range 0 to 100°C. The term involving B_0-B in equation (53), which represents a transition between the Debye- Huckel term and the linear term, contributed at most a few percent to the activity coefficient. Most of the above tests were made using activity coefficient data, but numerous individual tests were also made using osmotic coefficient data, enthalpies of solution, and heat capacities of aqueous sodium chloride between 80° and 200°C by Likke and Bromley[25] and reasonable agreement was obtained in all cases. Thus, the final single empirical constant equation for activity coefficients was found to be:

$$\log\gamma_{\pm} = \frac{-A_{\gamma}|Z_{+}Z_{-}|I^{1/2}}{1+\rho I^{1/2}} + \frac{(0.06+0.6B)|Z_{+}Z_{-}|I}{\left(1+1.5I/|Z_{+}Z_{-}|\right)^{2}} + BI \qquad \ldots\ldots\ldots\ldots(55)$$

Recently, the Bromley's equations for the mean activity coefficient ($\gamma_{\pm}$) and osmotic coefficient were expressed in terms of molalities by Partanen and Minkkinen[26], as:

$$\log \gamma_{\pm} = -A_{\gamma} m^{1/2}/(1+\rho I^{1/2})+Bm+[0.06(m^{o})^{-1}+0.6(B)]m/(1+am)^2 \qquad ...(56)$$

Where m^{o}=1mol.kg^{-1}. This equation contains only one parameter (B) that is dependent on the electrolyte. From this equation, the following equation can be derived for the osmotic coefficient.

$$\phi = 1- [A_{\gamma} \ln(10)/(\rho^3 m)][(1+\rho m^{1/2})-2 \ln(1+\rho m^{1/2})-1/(1+\rho m^{1/2})] + \ln(10)[0.06(m^{o})^{-1}+0.6B][(1+2am)/(1+am)^2- \ln(1+am)/am]/a + \ln(10)\, Bm/2 \qquad \ldots\ldots\ldots\ldots(57)$$

A complete set of 'B' values at 25^{0}C obtained using the method of least squares with ρ set equal to 1.0(kg.mol.$^{-1}$)$^{1/2}$, valid upto an ionic strength of 6m is tested by Bromley. Equation (57) is satisfactory for all strong electrolyte upto I= 6m over the temperature range of 0 to 100^{o}C, but it is not satisfactory for Sulfuric acid, the zinc and cadmium halides, etc., where ion- association is appreciable. The average maximum error in γ is 5.1% upto I= 6m.

(3) <u>Pitzer Equations</u>:

Pitzer and co-workers[27-33] developed an ion-interaction model for predicting the activity coefficients and other thermodynamics properties of single and mixed electrolyte solutions. In 1970's and early 1980's Pitzer model extended the Debye-Huckel theory using a virial expansion to account for ionic strength dependence of the short-range forces due to the binary and ternary ion interactions. This virial expansion approach accurately represents the composition dependence of the thermodynamic properties in the multicomponent electrolyte solutions to higher ionic strength. Moreover these equations need very few parameters to estimate the thermodynamic properties of both single and mixed electrolytes.

The Pitzer formalism starts with an equation for the excess free energy of a solution containing n_w kg of solvent and m_i, m_j, ... mol.kg^{-1} of solute species i, j,…. as

$$\frac{G^{ex}}{(n_W RT)} = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) + \sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk} \qquad \ldots(58)$$

Where f(I) is a function of the ionic strength I and depends on the properties of solvent and temparature.This takes care of effects of long range electrostatic forces. The expression selected for f(I) is

$$f(I) = - A_{\phi}\left(\frac{4I}{b}\right)\ln(1+bI^{1\backslash 2}) \qquad \ldots\ldots\ldots\ldots(59)$$

Where b is a fixed parameter and is given the value of 1.2 $kg^{1/2}\,mol^{-1/2}$ for all solutions and A_{ϕ} is the Debye- Huckel slope given by

$$A_{\phi} = 1/3\ (2\pi N_o d_W/1000)^{1/2}\ (e^2/4\pi\varepsilon_o DKT)^{3/2} \qquad \ldots\ldots\ldots\ldots(60)$$

D is the dielectric constant or relative permittivity, 'e' is the electronic charge and ε_o is the permultivity of free space. The second virial coefficient $\lambda_{ij}(I)$ is a function of ionic strength and takes care of effect of short-range forces between the species i and j. The term $\mu_{ijk}(I)$ is the triple ion- interaction parameter and it is also a function of Ionic strength but it is significant only at high ionic strengths.

The matrices $\lambda_{ij}(I)$ and $\mu_{ijk}(I)$ are symmetric, i.e.

$$\lambda_{ij}(I) = \lambda_{ji}(I)$$

$$\mu_{ijk} = \mu_{ikj} = \mu_{kij} = \mu_{kji} = \mu_{jki} = \mu_{jik}$$

The individual coefficients for ions cannot be measured directly. Therefore, measurable coefficients for electrically neutral combinations are defined by

$$B_{MX} = \lambda_{MX} + |Z_X/2Z_M|\lambda_{MM} + |Z_M/2Z_X|\lambda_{XX} \qquad \ldots\ldots\ldots\ldots(61)$$

$$\theta_{MN} = \lambda_{MN} - (Z_N/2Z_M)\lambda_{MM} - (Z_M/2Z_N)\lambda_{NN} \qquad \ldots\ldots\ldots\ldots(62)$$

Where M and N are ions of the same sign, and X is an ion of the opposite sign. The B terms can be evaluated from the electrolyte data, the θ terms arise only for mixtures and can be evaluated from the common ion mixtures. Since the λ depends on the ionic

strength, so do B and θ. The empirical expression of the same form were chosen for the ionic strength dependence of B and θ as follows:

$$\theta_{MN} = \theta^{(0)}_{MN} + (2\theta^{1}_{MN} / \alpha^2 I)\ \{ 1-(1+\alpha^2 I)\exp(-\alpha^2 I)\} \qquad \ldots\ldots\ldots(63)$$

Where the values of α is generally fixed as equal to $2.0 kg^{1/2}.mol^{-1/2}$. Further, it is convenient to write equation (58) in terms of the measurable coefficients B and θ and the corresponding third virtual coefficients C and Ψ as follows[34-35].

$$\begin{aligned} G^{ex}/n_W RT &= f(I) + 2 \sum_c \sum_a m_c m_a \{B_{ca} + (\sum_c M_c Z_c)\, C_{ca}\} \\ &+ \sum_c \sum_{c'} m_c m_{c'} \{\theta_{cc'} + \sum_a m_a \Psi_{cc'a} / 2\} \\ &+ \sum_a \sum_{a'} m_a m_{a'} \{\theta_{aa'} + \sum_c m_c \Psi_{caa'} / 2\} \qquad \ldots\ldots\ldots(64) \end{aligned}$$

Where the sums are over the various cations c, c′ and the various anions a, a′.

Thus Pitzer equations for the activity and osmotic coefficients were obtained from the appropriate derivatives of G^{ex} and are as follows[36].

$$\begin{aligned} \phi - 1 &= - \frac{G^{ex}/\partial n_w}{RT \sum_i m_i} \\ &= (\sum_i m_i)^{-1} \{(If' - f) + \sum_{ij} m_i m_j (\lambda_{ij} + I\lambda'_{ij}) + 2 \sum_{ijk} m_i m_j m_k \mu_{ijk}\} \qquad \ldots(65) \end{aligned}$$

$$\begin{aligned} \ln \gamma_i &= \frac{1}{RT} \frac{\partial G^{ex}}{\partial n_i} \\ &= \frac{Z_i^2}{2} f' + 2 \sum_j \lambda_{ij} m_j + \sum_{jk} m_j m_k \left(\frac{Z_i^2}{2} \lambda'_{jk} + 3\mu_{ijk}\right) \qquad \ldots\ldots\ldots(66) \end{aligned}$$

where $f' = \partial f / \partial I$, $\lambda'_{jk} = \partial \lambda_{jk} / \partial I$ and for various ions molalities $m_i = n_i / n_w$.

The above equation is for the activity coefficient of i^{th} component in an electrolyte solution. For a neutral electrolyte $M_{(\upsilon M)}\ X_{(\upsilon X)}$ in aqueous solution, the Pitzer equation for the activity coefficient is given as

$$\ln \gamma_{MX} = \upsilon^{-1}(\upsilon_M \ln\gamma_M + \upsilon_X \ln\gamma_X)$$

$$= \frac{|Z_M Z_X|}{2} f' + \frac{2}{\upsilon} \sum_j m_j (\upsilon_M \lambda_{Mj} + \upsilon_X \lambda_{Xj})$$

$$+ \sum_{jk} m_j m_k \{ \frac{|Z_M Z_X|}{2} \lambda'_{jk} + \frac{3}{\upsilon} (\upsilon_M \mu_{Mjk} + \upsilon_X \mu_{Xjk}) \} \quad \ldots\ldots\ldots\ldots(67)$$

The single electrolyte MX solution equation reduced to

$$\phi\text{-}1 = \frac{|Z_M Z_X|}{2} (f' - \frac{f}{i}) + \frac{m}{\upsilon} \{ 2 \upsilon_M \upsilon_X (\lambda_{MX} + I\lambda'_{MX})$$

$$+ \upsilon_M^2 (\lambda_{MM} + I\lambda'_{MN}) + \upsilon_X^2 (\lambda_{XX} + I \lambda'_{XX}) \}$$

$$+ \frac{6\upsilon_M \upsilon_X m^2}{\upsilon} (\upsilon_M \mu_{MMX} + \upsilon_X \mu_{MXX}) \quad \ldots\ldots\ldots\ldots(68)$$

$$\ln\gamma_{MX} = \frac{|Z_M Z_X|}{2} f' + \frac{m}{\upsilon} \{ 2\upsilon_M\upsilon_X(2\lambda_{MX} + I\lambda'_{MX})$$

$$+ \upsilon_M^2 (2\lambda_{MM} + I\lambda_{MN'}) + \upsilon_X^2 (2\lambda_{XX} + I \lambda'_{XX}) \}$$

$$+ \frac{9\upsilon_M \upsilon_X m^2}{\upsilon} (\upsilon_M \mu_{MMX} + \upsilon_X \mu_{MXX}). \quad \ldots\ldots\ldots\ldots(69)$$

Where $\upsilon = \upsilon_M + \upsilon_X$. The terms for triple ion interactions with all three ions of the same sign (υ_{MMM}, μ_{XXX}) have been taken as zeros since they are negligibly small. The properties of a single electrolyte solution are determined by the combinations ($\upsilon_M\upsilon_X \lambda_{MX} + \upsilon^2_M \lambda_{MM} + \upsilon^2_X \lambda_{XX}$) and ($\upsilon_M \mu_{MMX} + \upsilon_X \mu_{MXX}$). The following definition of the directly observable quantities is very convenient and has been retained.

$$B^{\phi}_{MX} (I) = \lambda_{MX} + I\lambda'_{MX} + (\upsilon_M / 2\upsilon_X) (\lambda_{MM} + I\lambda'_{MM})$$

$$+ (\upsilon_X / 2\upsilon_M) (\lambda_{XX} + I \lambda'_{XX}) \quad \ldots\ldots\ldots\ldots(70)$$

$$B^{\gamma}_{MX} (I) = 2\lambda_{MX} + I\lambda'_{MX} + (\upsilon_M / 2\upsilon_X)(2\lambda_{MM} + I\lambda_{MM'})$$

$$+ (\upsilon_X / 2\upsilon_M)(\lambda_{XX} + I \lambda'_{XX}). \quad \ldots\ldots\ldots\ldots(71)$$

$$B^{\gamma}_{MX}(I) = B^{\phi}_{MX}(I) + \left(\frac{1}{I}\right) \int_0^1 B^{\phi}_{MX}(X)dx \qquad \ldots\ldots\ldots\ldots(72)$$

$$C^{\phi}_{MX} = \{ 3/(\upsilon_M \upsilon_X)^{1/2} \} \{ \upsilon_M \mu_{MMX} + \upsilon_X \mu_{MXX}) \qquad \ldots\ldots\ldots\ldots(73)$$

$$C^{\gamma}_{MX} = \frac{3}{2} C^{\phi}_{MX} \qquad \ldots\ldots\ldots\ldots(74)$$

$$\theta_{MN} = \lambda_{MN} - (Z_N / 2Z_M) \lambda_{MM} - (Z_M / 2Z_N) \lambda_{NN} \qquad \ldots\ldots\ldots\ldots(75)$$

$$\theta'_{MN} = d\theta_{MN} / dI = \lambda'_{MN} - (Z_N / 2Z_M) \lambda'_{MM} - (Z_M / 2Z_N) \lambda'_{NN} \qquad \ldots(76)$$

$$\Psi_{MNX} = 6\mu_{MNX} - (3Z_N / Z_M) \mu_{MMX} - (3Z_M / Z_N) \mu_{NNX} \qquad \ldots(77)$$

Also, f^{ϕ} and f^{γ} are given by the equations:

$$f^{\phi} = \tfrac{1}{2}\{ f' - f / I \} \qquad \ldots\ldots\ldots\ldots(78)$$

$$f^{\gamma} = \tfrac{1}{2} f' \qquad \ldots\ldots\ldots\ldots(79)$$

The osmotic and activity coefficient equations for pure electrolyte solutions taken the form given below[37]:

$$\phi - 1 = - \left|Z_M Z_X\right| A_{\phi} + \left(\sqrt{I} \Big/ 1 + b\sqrt{I} \right) + m \left(\frac{2\upsilon_M \upsilon_X}{\upsilon}\right) B^{\phi}_{MX} + m^2 \left\{ \frac{2(\upsilon_M \upsilon_X)^{3/2}}{\upsilon} \right\} C^{\phi}_{MX} \qquad \ldots\ldots\ldots\ldots(80)$$

$$\ln\gamma_{MX} = -\left|Z_M Z_X\right| A_{\phi} \left[\left(\sqrt{I} \Big/ 1 + b\sqrt{I} \right) + \frac{2}{b} \ln\left(1 + b\sqrt{I}\right) \right] + m\left(\frac{2\upsilon_M \upsilon_X}{\upsilon}\right) B^{\gamma}_{MX} + \frac{3m^2}{2} \left\{ \frac{2(\upsilon_M \upsilon_X)^{3/2}}{\upsilon} \right\} C^{\phi}_{MX} \qquad \ldots\ldots\ldots\ldots(81)$$

Where $I = \tfrac{1}{2} \sum_i m_i z_i^2$ = ionic strength

A_ϕ is the Debye – Huckel constant for osmotic coefficient and is given by the equation:

$$A_\phi = \frac{1}{3}\left(\frac{2\Pi N D_W}{1000}\right)^{1/2}\left(\frac{e^2}{DkT}\right)^{\frac{3}{2}} = \frac{A_\gamma}{3} \qquad \ldots\ldots\ldots\ldots(82)$$

$$B^{\phi}_{MX} = \beta_{MX}{}^{(0)} + \beta^{1}_{MX}\exp(-\alpha I^{1/2}) \qquad \ldots\ldots\ldots\ldots(83)$$

$$B^{\gamma} = 2\beta^{(0)} + \frac{2\beta^{(1)}_{MX}}{\alpha^2 I}\left\{1-(1+\alpha I^{1/2}-\frac{1}{2}\alpha^2 I)\exp(-\alpha I^{1/2})\right\} \qquad \ldots\ldots\ldots\ldots(84)$$

Where α = 2.0 $kg^{1/2}\ mol^{-1/2}$; b = 1.2 $kg^{1/2}\ mol^{-1/2}$

The $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$ and $C^{(\phi)}_{MX}$ are adjustable parameters and for pure electrolytes these $\beta^{(0)}_{MX}$ and $\beta^{(1)}_{MX}$define the second virial coefficients, which describe the interactions between

the pairs of oppositely charged ions. The third virtual coefficient $C^{(\phi)}_{MX}$ is for triple ion interaction and is important only at high concentrations i.e., greater than 2.0 $mol.kg^{-1}$.

The Pitzer general equations for the calculation of the osmotic and activity coefficients of any mixed electrolyte solutions are follows:

$$\phi - 1 = \frac{2}{\sum m_i}\{-A_\phi\frac{I^{3/2}}{1+b\sqrt{I}} + \sum_c\sum_a m_c m_a\left(B^{\phi}_{ca} + ZC_{ca}\right) + \sum_{c<}\sum_{c'} m_c m_{c'}(\theta^{\phi}_{cc'} + \sum_a m_a\psi_{cca'}) + \sum_{a<}\sum_{a'} m_a m_{a'}(\theta^{\phi}_{aa'} + \sum_c m_c\psi_{aa'c})\} \qquad \ldots\ldots\ldots\ldots(85)$$

$$\ln\gamma_M = Z^2_M\ F + \sum_a m_a(2B_{Ma} + ZC_{Ma}) + \sum_c m_c(2\theta_{Mc} + \sum_a m_a\psi_{Mca}) + \sum_{a<}\sum_{a'} m_a m_{a'}\psi_{Maa'} + |Z_M|\sum_c\sum_a m_c m_a C_{ca} \qquad \ldots\ldots\ldots\ldots(86)$$

$$\ln\gamma_X = Z_M^2\, F + \sum_c m_c(2B_{Xc} + ZC_{Xc}) + \sum_a m_a(2\theta_{Xa} + \sum_c m_c\psi_{Xca})$$

$$\sum_{c<}\sum_{c'} m_c m_{c'}\psi_{cc'X} + |Z_M|\sum_c\sum_a m_c m_a C_{ca} \qquad \ldots\ldots\ldots\ldots(87)$$

In these equations

$$F = -A_\phi \left\{ \left(\sqrt{I} \Big/ 1 + b\sqrt{I} \right) + \frac{2}{b} \ln\left(1 + b\sqrt{I}\right) \right\}$$

$$+ \sum_c \sum_a m_c m_a B'_{ca} + \sum_{c<c'} m_c m_{c'} \theta'_{cc'} + \sum_{a<a'} m_a m_{a'} \theta'_{aa'} \qquad \ldots(88a)$$

$$Z = \sum m_i |Z_i| \qquad \ldots(88b)$$

$$B^\phi_{ca} = B_{ca} + I B'_{ca}$$

$$= \beta^{(0)}_{ca} + \beta^{(1)}_{ca} \exp(-\alpha\sqrt{I}) \qquad \ldots(88c)$$

$$\theta^\phi_{cc'} = \theta_{cc'} + I\theta'_{cc'} \qquad \ldots(88d)$$

$$B_{ca} = \beta^{(0)}_{ca} + \beta^{(1)}_{ca}\, g(X) \qquad \ldots(88e)$$

$$B'_{ca} = \beta^{(1)}_{ca}\, g'(X)/I \qquad \ldots(88f)$$

$$C_{MX} = C^\phi_{MX} / 2(|Z_M Z_X|)^{1/2} \qquad \ldots(88g)$$

$$g(X) = 2\{1-(1+X)\exp(-X)\}/X^2 \qquad \ldots(88h)$$

$$g'(X) = -2\{1-(1+X+X^2/2)\exp(-X)\}/X^2 \qquad \ldots(88i)$$

For a wide variety of 1-1, 2-1 and 3-1 electrolytes, above equations fit the experimental data very well with

$X = \alpha\sqrt{I}$; $\alpha = 2$ and $b = 1.2$ kg ^{½} . mol$^{-1/2}$

If the two electrolytes are symmetric this can be expressed in terms of the molarity 'm' of the common ion and the solute mole fraction 'y' of NX. Thus for MX-NX mixtures, the activity and osmotic coefficient equation are:

$$\phi - 1 = Z^2 f^\phi + m\{(1-y)B^\phi_{MX} + yB^\phi_{NX} + y(1-y)(\theta_{MN} + I\theta'_{MN})\}$$

$$+ m^2\{(1-y)C^\phi_{MX} + y\,C^\phi_{NX} + y(1-y)\,\Psi_{MNX}\} \qquad \ldots(89)$$

$$\ln\gamma_{MX} = Z^2 f^{\gamma} + m\{B^{\gamma}_{MX} + y\,(B^{\Psi}_{NX} - B^{\phi}_{MX} + \theta_{MN}) + y(1-y)I\theta'_{MN})\}$$
$$+ m^2\,\{C^{\gamma}_{MX} + y(C^{\phi}_{NX} - C^{\phi}_{MX} + 0.5\,\Psi_{MNX})$$
$$+ 0.5y\,(1-y)\Psi_{MNX}\} \qquad \ldots\ldots\ldots\ldots(90)$$

$$\ln\gamma_{NX} = Z^2 f^{\gamma} + m\{B^{\gamma}_{NX} + (1-y)\,(B^{\Psi}_{MX} - + \theta_{MN}) + y(1-y)I\theta'_{MN}\}$$
$$+ m^2\,\{C^{\gamma}_{NX} + (1-y)\,(C^{\phi}_{MX} - C^{\phi}_{NX} + 0.5\,\Psi_{MNX})$$
$$+ 0.5\,y(1-y)\Psi_{MNX}\} \qquad \ldots\ldots\ldots\ldots(91)$$

where B^{γ}_{MX} is given in equation - 84

and $C^{\gamma}_{MX} = 1.5\,C^{\phi}_{NX}$ $\ldots\ldots\ldots\ldots(91a)$

The quantities θ and Ψ arises for mixtures only, in constant to the other terms which can be determined by the properties of the pure MX and NX solutions. For the mixture MX-NY where there is no common ion, the Pitzer equations are:

$$\phi - 1 = Z^2 f^{\phi} + m\{y(1-y)(B^{\phi}_{MY} + B^{\phi}_{NX} + \theta_{MN} + I\theta'_{MN} + \theta_{XY} + I\theta'_{NY})$$
$$+ (1-y)^2 B^{\phi}_{MX} + y^2 B^{\phi}_{NY}\} + m^2\{(1-y)^2 C^{\phi}_{MX} + y^2\,C^{\phi}_{NY}$$
$$+ y\,(1-y)(C^{\phi}_{MY} + C^{\phi}_{NX}) + y(1-y)^2\,(\Psi_{MNX} + \Psi_{MXY})$$
$$+ y^2\,(1-y)\,(\Psi_{MNY} + \Psi_{NXY}) \qquad \ldots\ldots\ldots\ldots(92)$$

$$\ln\gamma_{MX} = Z^2 f^{\gamma} + m\{(1-y^2)B^{\gamma}_{MX} + y(\theta_{MN} + \theta_{XY})$$
$$+ y\,(1-y)(B^{\phi}_{MY} + B^{\phi}_{NX} - 2\,B^{\phi}_{MX} + I\theta'_{MN} + I\theta'_{XY}$$
$$+ y^2\,(B^{\gamma}_{MY} - B^{\phi}_{MY} + B^{\gamma}_{NX} - B^{\phi}_{NX} + 2B^{\phi}_{NY} - B^{\gamma}_{NY})\}$$
$$+ m^2\,\{(1-y)^2\,C^{\gamma}_{MX} + y(1-y)(\Psi_{MNX} + \Psi_{MXY} + C^{\phi}_{MX} + C^{\phi}_{NX} + C^{\phi}_{MY})$$
$$+ 1/2\,y^2\,(\Psi_{MNY} + \Psi_{NXY} + C^{\phi}_{MY} + C^{\phi}_{NX} + C^{\phi}_{NY})\} \qquad \ldots\ldots\ldots\ldots(93)$$

The expression for $\ln\gamma_{NY}$ may be obtained from the equation for γ_{MX} by replacing M by N, X by Y, and y by (1-y). It may be noted that these equations can be written for any electrolyte mixture containing any number of components.

For ternary systems, the terms φ_{ij} and Ψ_{ijk} arises. They are expected to be small because like charged ions repel one another and therefore, will be rarely close enough to have significant short-range interactions. Also, from above equation, one notes that these terms are differences between small quantities. Nevertheless, these small terms are needed in many cases to yield quantitative agreement with experimental data at moderate and high molalities.

The mixed electrolyte, term θ_{ij} arise for any ternary mixture and is given by the following equations.

$$\theta_{ij} = S\theta_{ij} + E\,\theta_{ij} \qquad \ldots\ldots\ldots\ldots(94)$$

$$\theta'_{ij} = E\,\theta'_{ij} \qquad \ldots\ldots\ldots\ldots(95)$$

$$\theta^{\phi}_{ij} = S\theta_{ij} + E\,\theta_{ij} + I\,E\,\theta'_{ij} \qquad \ldots\ldots\ldots\ldots(96)$$

The $S\theta_{ij}$ term arises due to the short ranges forces. The terms $E\theta_{ij}$ and $E\theta'_{ij}$ account for the electrostatic unsymmetrical mixing effects. Pitter derived equations for calculating $E\theta_{ij}$ and $E\,\theta'_{ij}$ as:

$$E\theta_{ij} = \frac{|Z_i\ Z_j|}{4I}\ \{J(X_{ij}) - 0.5\ J(X_{ii}) - 0.5J(X_{JJ})\} \qquad \ldots\ldots\ldots\ldots(97)$$

$$E\theta'_{ij} = \frac{|Z_i\ Z_j|}{8I^2}\ \{J'(X_{ij}) - 0.5\ J'(X_{ii}) - 0.5J'(X_{JJ})\} - \frac{E\theta_{ij}}{I} \qquad \ldots\ldots\ldots\ldots(98)$$

Where $X_{ij} = 6Z_iZ_jA_\phi\sqrt{I}$, for ions i and j. the $E\theta_{ij}$ and $E\theta'_{ij}$ are the functions of ionic strength, the terms J(X) and J′(X) are given as

$$J(X) = X\ \{4+c1x^{-C_2}\exp(-c_3\,x\,c^4)\}^{-1} \qquad \ldots\ldots\ldots\ldots(99)$$

$$J'(X) = \frac{1}{\{4 + c_1x^{-c_2}\ \exp(-c_3xc_4)\}} + \frac{c_1x^{c_2}(c_2 + c_3c_4x^{c_4})\exp(c_3x^{c_4})}{\{4 + c_1x^{-c_2}\ \exp(-c_3xc_4)\}^2} \qquad \ldots(100)$$

Where $c_1 = 4.581$; $c_2 = 0.7237$; $c_3 = 0.0120$; $c_4 = 0.528$. These E_θ and $E\theta'$ depend only on the charges of the ions i and j and the total ionic strength.

Also, $E_\theta(I)$ and $E_\theta(I)$ are zero when the ions i and j are of equal charges.

c) Experimental Techniques for the Determination of Activity Coefficients:

The activity coefficients in mixed electrolyte solutions can be determined by any experimental technique, which measures directly or indirectly the chemical potential of the solute or the solvent. In these methods such as (i) Isopiestic (ii) Freezing point depression (Cryoscopy) (iii) Boiling point elevation (ebullioscopy) and (iv) osmotic pressure (vapor pressure) method the activity of the solvent is measured. The solvent activities are then used to calculate the activity coefficients of the solute using the Gibbs- Duhem equations. The isopiestic method can be conveniently used to estimate the solvent activities at high concentrations i.e., $m>0.2$ mol.kg^{-1} but in the range of low concentrations upto 0.01 mol.kg^{-1} the cryoscopic method is generally reliable. At high temperatures the vapour pressure and boiling point elevation methods are advantageous down to 0.1 mol.kg^{-1}. The various direct methods of measuring the activity coefficients of the electrolytes include (i) EMF method (potentiometry) (ii) solubility (iii) distribution coefficients and (iv) diffusion coefficient measurements. Among all these methods the EMF method (potentiometry) is a very accurate[38-41] and convenient method for directly estimating the activity coefficients of electrolytes in aqueous solutions. But, EMF method is limited only to systems for which reversible electrodes are available. This problem has been mostly overcome in recent years due to the availability of a variety of ion selective electrodes.

In single or mixed electrolyte solutions, the activity of a salt can be measured by using one electrode reversible to cation and another electrode reversible to anion. The examples of electrodes, reversible to cations are hydrogen electrode, metal amalgam electrode, glass electrode and ion- selective electrodes such as solid-state membrane electrodes, liquid ion exchange electrodes. The calomel electrode, silver- silver chloride electrode, ion selective electrodes such as solid membrane electrode and liquid ion exchange electrodes, etc, are examples of anion reversible electrodes.

In a multicomponent solution, the activity of salt can be measured by using a electrode reversible to M^+ ion and another electrode reversible to X^- ion.

The cell

"M electrode" | MX, H_2O etc.| "X- electrode", has a potential given by

$$E = E_o - \frac{RT}{nF} \ln(m_M m_X \gamma^2_{\pm}) \qquad \ldots\ldots\ldots\ldots(101)$$

Where, n is number of electrons, m_M and m_X are molal concentrations of ions M^+ and X^- ; $\gamma_{\pm}$ is the mean activity coefficient of the salt; R is the gas constant (8.314 J/mol/K): T is the absolute temperature, F is the faraday (96,500 coulombs) and Eo is the standard electrode potential, determined by measurements in solutions of known MX activity or by extrapolation to infinite dilution.

Above equation (101) can also be written as

$$\gamma^2_{\pm} = 1/ m_M m_X \exp (E - Eo) nF/RT \qquad \ldots\ldots\ldots\ldots(102)$$

Hence, the mean activity coefficients ($\gamma_{\pm}$) of the electrolyte MX can be estimated by using eq (102) if the cell EMFs (E) are measured at several molalities of MX.

The most accurate electrochemical systems (eg. hydrogen silver chloride) given results reproducible to ± 0.02 mV, corresponding to an error of about 2 in the fourth decimal place of log γ, or ± 0.05% in γ itself. The accuracy is limited by the accuracy, with which solution concentration can be determined, by the accuracy of temperature control, and by the noise inherent in electrical measurement. Other system gives less accurate data, but even an accuracy of ±1 mV will give γ to within ±2.5%, which is sufficient to test the theoretical equations and predict the thermodynamic behavior of electrolyte solutions.

Eissenman et al[42-43] developed NAS (11-18) electrode for Na^+ determination, (the number denotes the percentages Na and Al) by a systematic study of the selectivity coefficients of the special glasses towards the alkali metal ions. The membrane potential set up on a glass

membrane results from ion exchange between the solution and the membrane[44-45]. When the membrane is in contact with the solution, the water molecules penetrate the membrane and form a hydrated layer about 50 to 1000A^o thick.

To obtain reliable and reproducible EMF data, the ion selection electrodes are to be calibrated[46-47] and their selectivity property estimated[42, 48-50]. Studies of aqueous sodium chloride using the Na ion selection electrode have seen frequent[51-57] and the results obtained are in satisfactory agreement with data obtained by other methods[58-60].

The various multicomponent system studied using sodium ion-selective glass electrode are $NaCl-CaCl_2-H_2O$[61], $NaCl-Dl-Threonine-H_2O$[62], $NaNO_3-Dl-Threonine-H_2O$[62], $NaCl-MgCl_2-H_2O$[63], $NaCl-SrCl_2-H_2O$[39] etc. In all these cases the results are generally in good agreement with isopiestic studies[64-65].

i) Hydrogen Electrode

The hydrogen electrode [Pt, H_2/H^+] is reversible to hydrogen ions and its standard EMF is defined as zero at all temperatures. The expression for its potential can be written as

$$E = E^o + \frac{RT}{2F} \ln \frac{(a_{H^+})^2}{P_{H_2}} \qquad \text{.....(103)}$$

Where $E_o = 0$ (standard convention) and P_{H_2} = partial pressure of hydrogen gas. The hydrogen electrode is useful in aqueous solution over a wide range of pH. Harned and co-workers[66-69] used this electrode in a variety of alkali hydroxide solutions up to 4 mol.kg^{-1}. They also determined the activity coefficients of HCl in a number of electrolyte mixtures, using the so called Harned cell shown below:

H_2, Pt | H+, Cl-, … | H+, Cl-, … | Ag, AgCl

The liquid junction potential of this cell is very low[70-71] i.e., less than 0.01mV and is generally neglected. The EMF of this cell is given by the relation

$$E = E^{o} - \frac{RT}{nF} \ln (m_H m_{Cl} \gamma_{\pm}^2 / pH^{1/2}) \quad \ldots\ldots\ldots\ldots(104)$$

However, the hydrogen electrode has the following drawbacks such as (i) hydrogen electrode fails in neutral solutions (ii) oxygen gas affects its potential and (iii) the solute- solvent interactions also lead to erroneous results.

Therefore, these hydrogen electrodes are being supplanted these days by more accurate and easy to handle ion selective electrodes.

ii) Metal-Amalgam Electrodes:

The metal amalgam electrodes have been used with considerable success to determine the activity coefficients alkali and alkaline earth halide salts such as sodium chloride[72], potassium chloride[73], barium chloride[74] and strontium chloride[75].

The metal amalgam cells of the type

$$Ag, AgCl \mid NaCl_{(m)} \mid NaX\ Hg \mid NaCl_{(0.1)} \mid Ag, AgCl$$

The activity coefficients of many typical electrolytes have been determined in both dilute and concentrated solutions. Some results[76] have been reported for calcium sulphate also. The following cell was used by Lamer and Parks[77] to estimate the activity of $CdSO_4$ over the entire concentration range:

$$Cd_X\text{-}Hg \mid CdSO_{4(M)} \mid PbSO_{4(S)} \mid Pb_X\text{-}Hg$$

The alkali-amalgam electrodes have the drawback, that it is extremely cumbersome to determine the exact composition of the amalgam. The alkaline earth amalgam electrodes suffer because of their very small exchange currents resulting from the necessity for a two electron transfer and more negative electrode potentials. Therefore, these amalgam electrodes are being supplanted these days by more accurate and easy to handle ion- selective electrodes.

iii) Ion Selective Electrodes

Ion selective electrodes[78-84] are recently developed and widely used now a days for determining the activity coefficients. The chief advantage of determinations with ion selective electrodes is that direct potentiometry can be employed. Further, improvement in accuracy and precision is attained by using the titrimetric method, which recently becomes quite sophisticated due to the introduction of newer methods of the endpoint detection and automation of the titration procedures. In all these methods, the electrodes response time, drift and the temperature coefficient are the important factors. In these aspects, the ion- selective electrodes have several advantages. Thus, they (a) do not affect the solution studied, (b) are portable, (c) are suitable either for direct determinations or as sensors in titration and (d) are not very expensive. The ion-selective electrode consists of a membrane which is in contact, on one side (internally) with a solution containing the ions for which the electrodes is selective and suitable reference electrode, and on the other side with the test solution in which a second reference electrode is immersed. The potential of an ion- selective electrode in an electrode solution containing 's' kinds of ions of charges z_i is generally represented by the equation

$$\Delta E_J = \frac{RT}{Z_i F} \ln \frac{a_J(1) + \sum_{i=1}^{s} \left\{ K_{Jk}^{Pot}\ a_i(1) \right\}^{1/Z_i}}{a_J(2) + \sum_{i=1}^{s} \left\{ K_{JK}^{Pot}\ a_i(2) \right\}^{1/Z_i}} \qquad \text{.....(105)}$$

This equation is valid for an ion- exchanger (solid-state) membrane with a fixed concentration of active sites (anionic). Let two kinds of univalent captions, J^+ and K^+ be present in the solutions on both sides of the membrane. Also, let these ions simultaneously enter the membrane and associate with the anionic centers or ' counterions' then, an ion exchange reaction taken place between the ions in solution and in the membrane

$$J^+(S) + K^+(m) = J^+(m) + K^+(S)$$

Where 'S' denotes the ions in the electrode solution, and 'm' those in the membrane.

$a_J(1)$ and $a_K(1)$ are the activities of ions J^+ and K^+ in solution 1.

$a_J(2)$ and a_K (2) are the activities of ions J^+ and K^+ in solution 2.

K^{Pot}_{JK} is the selectivity coefficient of the electrode for the ion J^+ with respect to the ion K^+.

Generally, for an ion-selective electrode, the concentrations of the internal solution (1) is kept constant and the concentration of solution (2) i.e., test solution only is varied. Then the above equation could be written as

$$E_{ISE(i)} = E_{0(ISE)} \frac{RT}{Z_i F} \ln\{a_i + \sum_{j=1}^{s} K_{ij}^{Pot} \quad (a_j)^{Z_i/Z_j}\} \qquad \ldots\ldots\ldots\ldots(106)$$

Where,

$E_{ISE(i)}$ = e.m.f. of the ion- selective electrode for the i-ion when immersed in a solution containing i–ions.

a_i = activity of I^- ion in the test solution

K_{ij}^{Pot} = selectivity coefficient for j-ions with respect to i-ion selective electrode.

a_j = concentration of j- ion in test solution

$E_{o(ISE)}$ = standard potential of the ion- selective electrode.

Generally, it is not possible to determine or fix exact values for the standard potentials of ion selective electrodes, due to the presence of several arbitrary parameters such as liquid junction potentials. Therefore, these ion- selective electrodes[79] are first standardized using the solution of known concentration and activity. The values of the selectivity coefficients (K_{ij}) also should be estimated before using them to find the activities in a test solution.

A brief survey of literature covering the thermodynamic properties such as activity coefficients, osmotic coefficients, enthalpies of dilution, etc., of aqueous electrolyte solutions relevant to the present work is given below.

i) Single Salt solutions:

Sodium Chloride:- Harned[85] studied the activity coefficients of aqueous sodium chloride by vapour pressure method at 25°C over a concentration range of 0.1003 to 6.12mol.kg^{-1}. Scatchard and Prentiss[86] determined the activity coefficients of *NaCl* from 0.001 to 1.1 m at 25°C by cryoscopic method. Scatchard[87] reviewed the activity coefficients data of aqueous sodium chloride at 25°C over the concentration range of 0.001 to 5.2 mol.kg^{-1}. Caramazza[88] estimated the activity coefficients of *NaCl* using sodium amalgam electrode over a temperature ranges of 0 to 50°C. Mac Innes and Brown[89] used the concentration cells with transference and determined the activity coefficients of *NaCl* at 25°C and concentration range 0.004984 to 0.09953N. Shedlovsky[90] estimated the γ values at 25°C and concentration range 0.001 to 0.1 mol.kg^{-1}. Janz and Gordon[91] in the temperature range 15 to 45°C and over the concentration range 0.03 to 0.1 mol.kg^{-1}. Sodium ion-selective electrode and silver-silver chloride electrodes were used to estimate the activity coefficient of *NaCl* over 0.01 to 1 mol.kg and at 15, 25, 38 and 50°C by Truesdell[81]:

Na	NaCl (m)	Ag/AgCl electrode
Ion-selective	+	or
electrode	MCl_2	Cl^- ion-selective
	+	electrode
H_2O		

Harned and Owen[67] critically evaluated the results of electrochemical cell emf measurements to determine the activity coefficients of aqueous *NaCl*. Smith and Hirtle[92] used the boiling point elevation method to determine the activity and osmotic coefficients of aqueous *NaCl* solutions over the concentration range 0.1 to 4.0 mol.kg^{-1} and temperature range 0 to 100°C. Isopiestic studies were made by Robinson[93] over the concentration range 0.1 to 0.6 mol.kg^{-1} at 25°C. The activity coefficient data of *NaCl* at 25°C and from 0.001 to 6.146mol.kg^{-1} were reported by Hammer and Wu[94]. Makhov et al[95]., studied the activity coefficients of individual ions viz., Na^+ and Cl^- from 25°C to 80°C and concentration range 0.01 to 3.0 mol.kg^{-1}. The vapor pressure

measurements were carried out by Gibbered et al[96], to determine the osmotic coefficients of *NaCl* from 25 to 100°C and concentration range 1.0 to 6.0 mol.kg^{-1}. Gardner[97] determined the activity coefficients from 125 to 270°C at 0.5 mol.kg^{-1}. Lindsay and Liu[98] estimated the activity coefficients from 125 to 270°C at 0.5 mol.kg-1. The activity coefficient of aqueous NaCl was estimated over temperature range 0-300°C and concentration range 6.096 to 10.413 mol.kg^{-1} and osmotic coefficients over 0-300°C by Silvester and Pitzer[99]. The osmotic coefficients of aqueous *NaCl* from 293.15 to 363.15 K over the concentration range from 1 to 5.5mol.kg^{-1} were determined by Hubert et al.[100]. The osmotic coefficients of aqueous NaCl were determined using the lowering of vapor pressure measurements over the concentration range 0.1 to 1.0 mol.kg^{-1} at 25°C intervals from 125 to 300°C by Lindsay and Liu[98]. The vapor pressures of saturated aqueous solutions of *NaCl* were measured at temperatures ranging from 227 to 323 K by Apelblat and Korin[101].

The enthalpies of dilution of aqueous *NaCl* solutions were measured by Fortier et al.,[102] at 298.15K. Sanahuja and Cesari[103] studied the enthalpies of aqueous NaCl at 303.15, 308.15 and 313.15K and concentrations from 0.005 to 0.12 mol. Kg.$^{-1}$; Archer[104] from 76 to 225°C and concentration range 0.01 to 3.0m; Smith, Cone and Van Hook[105] at 298.15 K and Mayrath and Wood[106] over the temperature range 348.15 to 472.95 K. The enthalpies and heat capacities of aqueous *NaCl* solutions were estimated for concentration unto 5.5m and temperatures upto 300°C by Rogers and Pitzer[107]. The heats of dilution were studied by Pratt[108] over the concentration range of 0.2 N to 3.2 N; Wust and Lange[109] at 25°C over the entire solubility range; Guggenheim and Prue[110] at 25°C and concentration range 0.1 to 0.00625 mol.kg^{-1}. The partial molal heat contents and heat capacities of aqueous *NaCl* solutions were determined from 0 to 40°C and from 0.05 to 4.0 mol. Kg^{-1} by Harned and Cook[111]; Gardner et al[112]., estimated from 100 to 200°C and Cobble, Murray and Sen[113] upto 300°C. Clarke and Glow[114] evaluated the thermodynamics functions for aqueous *NaCl* from equilibrium and Calorimetric measurements below 154°C. Vaslow[115] measured the heats of dilution of aqueous *NaCl* solution at 25°C over the concentration range 1.0 to 1.5 mol.kg^{-1}. Perron, Fortier and Desnoyers[116] measured the apparent molar heat capacities of aqueous *NaCl* with a flow micro calorimeter at 274.65 to 318.15K over the concentration the range 0.10 to 3m. Millero[117] estimated the partial molar volumes of aqueous *NaCl* over the concentration range 0.01 to 1.0m over the temperature range

0 to 55^{0}C. Rogers and Duffy[118] estimated the heat capacities of aqueous NaCl from 1 to 6mol. kg^{-1} upto 598K at 20Mpa and 523K unto 36MPa. The heat capacities of aqueous *NaCl* were measured at 0.0150mol.kg^{-1} over the temperature range 604 to 718K at 32 MPa by White et al.,[119]. Woolley[120] estimated the heat capacities of aqueous *NaCl* over the temperature range 283.15 to 393.15K at 0.35MPa. The apparent molar heat capacities of aqueous *NaCl* were estimated over the concentration range 0.05 to 3.0 mol.kg^{-1}, the temperature range 350 to 600K and at pressures 2 to 18 Mpa by Gates et al[121]. Busey, Holmes and Mesmer[122] estimated the ermodynamic properties of aqueous *NaCl* over the concentration range 0.1 to 5 mol.kg^{-1} and the temperature range 323 to 673 K. Pitzer, Peiper and Busey[32] reviewed the thermodynamic properties of aqueous *NaCl* such as the activity and osmotic coefficients, the enthalpy and the heat capacity at constant saturation pressure $\leq$ P $\leq$ 1K bar and the temperature 273 K $\leq$ T $\leq$ 573K over the concentration range 0 $\leq$ m $\leq$ 6.0 mol.kg^{-1}.

Strontium Chloride: - Lucasse[75] estimated the activity coefficients of aqueous *$SrCl_2$* from emf of the cells without transference over the concentration range 0.029 to 3.0 mol.kg^{-1} at 25^{o}C. Longhi et al.[123], studied over the concentration range 0.04 to 0.24 mol.kg^{-1} at 25^{o}C. Isopiestic measurements were made by Downes[124] at 25^{0}C over the concentration range 0.12 to 2.2 mol.kg^{-1} and Stokes[125] at 0.078 to 4.0 mol.kg^{-1}; Robinson[126] estimated over the concentration range 0.12 to 2.26 mol.kg^{-1}. Holmes and Mesmer[127] isopiestically estimated the activity coefficient of aqueous *$SrCl_2$* over the temperature range 382.96 to 473.61 K from 0.6 to 6.5 mol.kg^{-1} and from 273.15 to 523.15 K over the saturation pressure to 40MPa and the concentration range 0.1 to 4.0 mol kg^{-1}. Rard and Miller[128] estimated the osmotic coefficient of aqueous strontium chloride solutions at 25^{o}C. The activity and osmotic coefficient of aqueous *$SrCl_2$* were estimated over the concentration range 0.5 to 8.6 mol.kg^{-1} in the temperature range of 303.15 to 345.15 K by Patil et al.,[129]. Morss and Williams[130] measured the enthalpy of solution of *$SrCl_2$* in H_2O and in 1 mol.dm^{-3} HCl solution to find the values of enthalpy of formation of *$SrCl_2$*: ΔH_f^o $SrCl_2$, c, 298.15K) = -832.7$\pm$0.09kJmol^{-1} and enthalpy of formation of Sr^{2+} ions in water: $\Delta H_f^o(Sr^{2+}$, aq, 298.15K) = -549.7 $\pm$ 0.9KJmol^{-1}. Leung and Millero[131] estimated the enthalpies of aqueous strontium chloride solutions at 30^{o}C. The apparent molar heat capacities of aqueous *$SrCl_2$* solutions at 25 to 100^{o}C over the concentration range 0.03 to 2.0 mol.kg^{-1} at a pressure 0.6 MPa were evaluated by Saluja and Leblanc[132]. Desnoyers et al[133-134] estimated the heat capacities of

aqueous strontium chloride solutions at 25°C; and Karapet 'Yants et al[135]., at 25 to 100°C over the concentration range 0.3 to 2.0 mol.kg^{-1}. The thermodynamic properties of aqueous $SrCl_2$ solutions were evaluated by Pitzer et al.,[136]., and obtained the temperature dependent equations valid from 25 to 200°C for the heat capacities.

Calcium Chloride:- The activity coefficients of aqueous $CaCl_2$ solutions were estimated from the emf's of concentration cells with transference over the concentration range 0.003 to 0.075 mol.kg^{-1} and the temperature range 15 to 35^{0}C by McLeod and Gordon[137]. The activity coefficients of $CaCl_2$ were studied upto saturation limit 25°C by Hess and tellinek[138]. The calcium amalgam electrodes were used by Mussini and Pagella[139], in the concentration range 0.006 to 0.1 mol kg^{-1}. Individual ion activity coefficients were determined in aqueous $CaCl_2$ at 25^{0}C over the concentration range 0.001-3.0m using an emf method by Rabinovich et al.,[140]. Platford[141] estimated the osmotic coefficients of aqueous $CaCl_2$ at 0^{0}C and Childs and Platford[142] studied at 15^{0}C. Rard and Spedding[143] measured the osmotic coefficients of the aqueous $CaCl_2$ at 25^{0}C and concentration between 2.6 and 8.8mol.kg^{-1}. Robinson and Lim[144] estimated the osmotic coefficient of aqueous $CaCl_2$ at 25^{0}C. Bechtold and Newton[145] measured vapor pressure to calculate the osmotic coefficients of aqueous $CaCl_2$ solutions from 0.3 to7.0mol.kg^{-1} at 35 and 45^{0}C. Jakli and VanHook[146] reported the osmotic coefficients between 0 and 90°C over the concentration range 5.418 to 7.8761 mol.kg^{-1}. The osmotic coefficients of aqueous $CaCl_2$ were isopiestically estimated by Duckett et al.,[147] at 50^{0}C over the concentration range 3.0 to 12.0mol.kg^{-1}; by Holmes, Baes and Mesmer[148] over the temperature range 443.92 to 524.12K and the concentration range 0.4 to 1.75 mol. kg^{-1}. The activity and the osmotic coefficients of aqueous $CaCl_2$ solutions were estimated isopiestically at 25^{0}C over the concentration range 0.005 to 9.0mol.kg^{-1} by Rard et al.,[149] and Gilchrist and Calvert[150] measured at 45^{0}C upto an ionic strength of 9m. The osmotic coefficients and activity coefficients of aqueous $CaCl_2$ were evaluated over the concentration range 0.1 to 30.0mol.kg^{-1} and the temperature range 298.15 to 523.15K by Pitzer and Oakes[151] at saturation pressures.

Hakuta et al.,[152] studied the elevation of boiling points of aqueous $CaCl_2$ solutions over the concentration range 1.64 to 3.0mol.kg^{-1}. The enthalpies of dilution of aqueous $CaCl_2$ solutions were measured by Perchon and Thourey[153] at 25^{0}C upto a concentration of 3.0mol.kg^{-1} and Leung and Millero[154] at 30^{0}C . The enthalpies of dilution of aqueous $CaCl_2$ were measured upto a

minimum molality of $1.7x10^{-3}$ $mol.kg^{-1}$ using a liquid flow micro calorimeter at temperatures upto 673K by Simonson, Busy and Mesmer[155]. Lilich et al.,[156] studied the heats of dilution of aqueous $CaCl_2$ solutions from 0 to 50°C upto concentration of 5.4 and 11.9 $mol.kg^{-1}$. Richards and Dole[157] measured the heats of dilution of calcium chloride solutions at 20 and 25°C. The apparent molar heat capacities of aqueous calcium chloride solutions were measured over 25 to 100°C and the concentration range 0.03 to 0.98$mol.kg^{-1}$ at a pressure 0.6 Mpa by Saluja and LeBlanc[132]. Perron et al[158] reported the apparent molar heat capacities at 25°C. The heat Capacities of $CaCl_2$ were measured over the temperature range 306.21 to 602.68K at constant pressure of 17.5Mpa by White et al[159] and Soboleva et al[160] , studied at weight percentages 5.31 to 4.73 over the temperature range of 423 to 623K. Vasilev et al.,[161] measured the specific heats of aqueous calcium chloride solutions at 25°C. Similarly, the specific heats were measured by Rutskov[162] at 25, 50 and 75°C.

Magnesium Chloride: Activity coefficients of aqueous magnesium chloride were estimated by Geissler[163] using the concentrations cells with transference;

Hg (I),Hg_2Cl_2 (S)$|$$MgCl_2(C_1)$ $\|$ $MgCl_2$ (C_2) $|$ $HgCl_2$(S), Hg(I) the isopiestic measurements at 25°C were reported by Robinson and Stokes[164] at molalities of 0.1 to
2.0m; Robinson and Brower[165] at 0.4 to 2.0m; Saad, Padova and Marcus[166] at 0.4 to 2.0 and Platford[167] 0.08 to 2.7m. Mesmer et al[168] estimated the osmotic coefficients of magnesium chloride isopiestically over the ranges 1 to 6m and 382 to 474K. Snipes et al[169]., measured the heat of dilution over the ranges 0.005 to 2.0m and 40 to 80°C. The heat capacities of aqueous magnesium chloride were measured at 25°C. Eigen and Wicke[170] measured activity coefficients at 10 to 130°C, Likke and Bromley[171] at 80 to 200°C; Saluja and Leblanc[132] at 298.15 to 373.15K. Phutela, Pitzer and Saluja[172] combined the thermal data from literature with activity data of Rard and Miller[173] to predict the thermodynamic properties of aqueous magnesium chloride solutions over the temperature range of 298.15 to 473 K.

d) <u>Scope of work</u>

A current problem in the field of electrolyte solutions is the prediction of thermodynamic properties of mixed electrolyte solutions from the properties of single electrolyte solutions. Activity coefficients are of primary importance in describing accurately the thermodynamic

behavior of aqueous mixed electrolyte solutions. The lack of accurate activity coefficient data causes large errors in calculating the solubility's of aqueous multicomponent ionic solutions at high ionic strengths.

Thus, a detailed experimental research is taken all over the world on aqueous electrolyte solutions, over a wide range of concentrations and temperatures to determine and tabulate the database on thermodynamic properties such as activity coefficients, osmotic coefficients, heat capacities etc., of single and multi component electrolyte solutions. However a comprehensive data is not yet available on mixed electrolyte solutions of NaCl with amino acids such as Glycine, Alanine and Valine.

The present work aims at

(i) Experimentally determining the activity coefficients of aqueous NaCl in several quaternary electrolyte mixtures.

(ii) Interpreting the thermodynamic behavior of mixed electrolyte solution data in terms of Pitzer formalism.

(iii) Using Pitzer interaction parameters for predicting the thermodynamic properties of multicomponent electrolyte solutions.

The activity coefficients of aqueous *NaCl* in the following quaternary systems were studied by an emf method using sodium ion selective electrode.

1) NaCl- $MgCl_2$-Glycine-H_2O
2) NaCl-$CaCl_2$-Glycine-H_2O
3) NaCl-$SrCl_2$-Glycine-H_2O

The system containing glycine as one of the constituents were studied at constant total ionic strengths of 0.5, 1.0, 2.0 and 3.0mol.kg^{-1} and at 25^{o}C, 35^{o}C and 45^{o}C.

4) NaCl- $MgCl_2$-β-alanne-H_2O
5) NaCl-$CaCl_2$-β-alanne-H_2O
6) NaCl-$SrCl_2$-β-alanne-H_2O

In this case, the systems were studied at ionic strengths of 0.5, 1.0, 1.5 and 2.0 mol.kg^{-1} and at temperatures of 25^{o}C, 35^{o}C and 45^{o}C.

The following systems were studied

7) NaCl- $MgCl_2$-Valine-H_2O
8) NaCl-$CaCl_2$-Valine-H_2O
9) NaCl-$SrCl_2$-Valine-H_2O.

at ionic strengths of I = 0.1, 0.2, 0.3 and 0.4 $mol.kg^{-1}$ and at 25°C, 35°C and 45°C.

The literature data on single electrolyte solutions involved in above mixtures viz., NaCl, $MgCl_2$, $CaCl_2$, $SrCl_2$ and amino acids glycine, β -alanine and valine were reviewed and activity coefficients and osmotic coefficients are tabulated at 25°C, 35°C and 45°C.

The experimentallly determined activity coefficients data for NaCl were interpreted using Harned and Pitzer equations. The predictive capability of Pitzer ion interaction parameters (S_Θ) and (Ψ) has been demonstrated by

(i) Analyzing the activity coefficient data of multicomponent electrolyte solutions like quaternary systems.

(ii) By calculating the activity coefficients of dissolved ions in environmental waters.

CHAPTER-II

EXPERIMENTAL

The experimental part consisted of the following aspects:

1. Electrodes
2. Equipment
3. Chemicals
4. Conductivity water
5. Preparation of solutions
6. Method of Measuring potentials
7. Treatment of Data
8. Error Limits

Electrodes:

The sodium ion selective electrode (Elico, India) was used to measure the activities of sodium ions in the salt solutions. The *Ag/AgCl* reference electrodes were prepared by the thermal methods[70]. The Ag_2O was freshly precipitated by adding a solution of NaOH to a vigorously stirred solution of $AgNO_3$ (one half equivalent of analar $AgNO_3$ in 750 ml of water). The precipitate was thoroughly washed to completely remove the water soluble impurities and traces of *NaOH*. The silver chlorate was prepared by mixing equal portions of sodium chlorate (10N) and silver nitrate (10N) solutions preheated to 85^0C and then slowly cooling to 0^oC. The Silver Chlorate crystals were separated by decantation, washed repeatedly and recrystallized. A mixture of 90% silver oxide and 10% of sliver chlorate paste was applied to the platinum spiral wire of an electrode. The pasted electrodes were heated first slowly to 100^0C for vaporizing water and then finally at the decomposition temperature of 650^0C, at which it was maintained for a period of about seven minutes. At least five to six electrodes were prepared in each batch. Three to four of *Ag/AgCl* electrodes were found to be stable and gave reproducible Emfs. These reference electrodes were allowed to stand in 0.01m KCl solution so that their potentials could settle down for about a week before using them.

Equipment

The Emfs of the cell were measured using Keithley 51/2 digit electrometer/ multimeters (Model-DMM-191). The electrodes were connected to a high impedance ($\cong 10^{12}\Omega$) unit gain amplifier. The output of this amplifier was measured by the Keithley electrometer. The accuracy of emf measurements was up to ±0.01 mV. The initial measurements were carried out using a digital pH meter with Emf mode (Digisun Electronics, India; Model DI 707) for establishing the experimental conditions to get stable and reproducible results. Finally the cell Emfs were measured on the Keithley digital electrometer.

Chemicals

All the chemicals/ regents i.e., sodium chloride (Merck), glycine (S.D.fine., India), magnesium chloride (Merck or BDH), calcium chloride (Merck), strontium chloride (S.D. fineChem., India), alanine (S.D.Chem., India) and valine (Merck), were of analytical grade. All salts were dried at 120^{o}C in an oven just before use to get moisture free salts. The concentration of stock solutions was checked using the standard analytical titration methods.

Conductivity Water

The laboratory filtered tap water was passed through a mixed bed ion- exchange resin unit (IA&C: India). The deionised water was distilled twice over alkaline permanganate in an aged all glass still. The deionised, doubly distilled water so obtained had a specific conductance of $\leq 1.0X10^{-6}$ ohm^{-1} cm^{-1}

Preparation of solutions

The conductivity water was used for preparation of stock solutions. The stock solutions were prepared by weight in the molal scale at various total ionic strengths. All titrations and dilutions were made using weight burettes. Owalabor balance of capacity 1000 gms, with an accuracy of ±0.01 gms and a semi micro analytical (electrical) balance of 100gms capacity, with an accuracy of ±0.0001 gm were used in the preparation of stock solutions and weighing of experimental solutions.

Method of Measuring Potentials

The cell arrangement consisted of a sodium ion- selective electrode and a silver chloride reference electrode, immersed in the experimental electrolyte solution (MX and NY_2) placed in a double walled glass cell having a glass lid. The lid had the provision for inserting the electrodes and thermometer. The temperature was maintained constant by circulating thermostat water within ± 0.01°C. The cell arrangement was as follows.

Na	NaX (m)	Ag/AgCl electrode
Ion-selective	+	or
electrode	NX_2	Cl^- ion-selective
	+	electrode
	$Z + H_2O$	

Where

X =Cl^-

N= Ca^{+2}, Sr^{+2}, Mg^{+2}

Z= amino acid

The electrodes were kept immersed in a 0.01 mol/kg *NaCl* or *KCl* solution while not in use. The sodium ion- selective electrode was calibrated at every ionic strength studied. The Emfs recorded in this calibration run were plotted against $\log a_{NaCl}$ values to evaluate the E_o and Nernst slope (k) values. The electrodes were allowed to stand in the pure electrolyte solution for about 40 to 50 minutes prior to the first reading in order to attain the equilibrium. Successive readings were taken at 10-minute intervals. At every ionic strength a set of four experiments are carried out. In the first set, pure *NaCl* was taken in the double-walled glass cell and conductance water was added in successive aliquots using a weight burette. The potential differences were noted after each addition and equilibration. The set of results were used to calibrate the electrodes (cf. table-1 in Chapter-III).

In the second set, pure *NaCl* solution was taken in the double walled-glass vessel and the second salt solution was added in successive aliquots. The third set was made by starting with pure second salt solution and adding *NaCl* solution in successive aliquots. The overlapping portion between the second and third set was used to test the reproducibility and accuracy of the measurements. In the fourth set pure second salt solution was taken in the cell and the Emfs were noted after adding conductance water in aliquots. This set of results was used to calculate the selectivity coefficient (cf. Tables 2-3 in chapter-III) of the Na-ion selective electrode towards the metal ion in second salt solution. All the sets were repeated at least twice or thrice to get consistent and reproducible results.

Treatment of Data

The emfs of sodium ion-selective electrode vs the *Ag/AgCl* electrode in MX-NY_2 solution is given by the relation.

$$E_{MX-NY_2} = E_0 + k \log (a_M a_X + K a_N^{1\backslash 2} a_X + K' a_N^{1/2} a_Y + K'' a_M a_Y) \quad \ldots(107)$$

The K′ and K′′ terms are omitted because the cell is reversible to ′X′ ion only. The K term could be neglected in the final calculation because the emfs recorded in the fourth set (≅ - 40mV) are very low as compared to the emfs obtained (≅125mV) in the 1st, 2nd and 3rd sets. Thus equation-107 first reduces to

$$E_{MX-NY_2} = E_0 + k \log (a_M a_X + K a_N^{1\backslash 2} a_X) \quad \ldots\ldots\ldots\ldots(108)$$

Where k′ is the Nernst slope i.e., k= 2.303 RT/nF, K is the selectivity coefficient of the ion selective electrodes the N^{2+} ions and E_o is the emf due to the MX solution at unit activity. In pure MX solution a_N =0 and therefore equation-108 becomes

$$E_{MX} = E_0 + k \log a_M a_X \quad \ldots\ldots\ldots\ldots(109)$$

In pure NY solution $a_M = 0$ and thus,

$$E_{NY} = E_0 + k \log K a_N^{1/2} a_Y \quad \ldots\ldots\ldots\ldots(110)$$

$$K^2 = \frac{1}{a^3_{NY_2}} . \exp[4.606 (E_{NY_2} - E_0)/k] \quad \ldots\ldots\ldots\ldots(111)$$

or

$$K^2 = \left(\frac{1}{a^3_{NY_2}}\right).\ 10^{\frac{2(E_{NY_2}-E_0)}{k}} \qquad \ldots\ldots\ldots\ldots(112)$$

For the calibration run in the first set at each ionic strength, the Emfs of the aqueous *NaCl* solutions were measured. These Emfs were fitted to equation-109 and the E_o and K values were estimated using a least squares procedure. The emfs of pure NY_2 solution in second set were measured and substituted in equation-112 to find selectivity coefficient (K) values. The pure electrolytes activity coefficients of *NaCl* were taken from literature. The selectivity coefficient (K) values for all seconds salt solutions and the all the ionic strengths studied were in the range of 10^{-5} to 10^{-4}. Therefore, the second term with in brackets on the RHS of equation-108 was neglected. Thus, cell emf values for the MX-NY_2-H_2O mixtures are given by the relation

$$E_{MX-NY_2} = E_0 + k \log a_M\, a_X \qquad \ldots\ldots\ldots\ldots(113)$$

But

$$a_M = m_A\, \gamma_{\pm} \qquad \ldots\ldots\ldots\ldots(114)$$

and

$$a_X = m_A\, \gamma_{\pm} \qquad \ldots\ldots\ldots\ldots(115)$$

Where $\gamma_{\pm}$ is the mean ionic activity coefficient of MX and m_A is the concentration of MX. Substituting these relations in equations in equation-113, we get

$$E_{MX-NY_2} = E_0 + k \log \{\, a_M\, m_A\, \gamma^2_{\pm}\,\} \qquad \ldots\ldots\ldots\ldots(116)$$

or

$$\gamma^2_{\pm} = (\,1/m_M m_X)\, \exp\,\{\,2.303\,(E_{MX-NY_2})/k\} \qquad \ldots\ldots\ldots\ldots(117)$$

Since $m_M = m_A$ and $m_X = m_A$

Hence, the mean activity coefficient of NaCl could be determined by substituting the emfs of the cell with MX-NY_2 mixture, i.e., E_{MX-NY_2} in equation-117. The $\gamma_{\pm}$ values were determined at all the ionic strengths studied and at different values of the ionic strength fraction of the second salt (y_B) were,

$$y_B = 3\, m_{NY_2} / (m_{MX} + 3 m_{NY_2}) \qquad \ldots\ldots\ldots\ldots(118)$$

and

$$y_A = 1 - y_B \qquad \ldots\ldots\ldots\ldots(119)$$

or

$$y_A + y_B = 1 \qquad \text{……(120)}$$

Error Limits

The errors in arious quantities were estimated using the standard procedures .The error in EMF values is 0.1mV to 0.01MV and the error in concentration is 0.01%. These error limits lead to an error in $\gamma = \pm 0.0001$. The error in the Pitzer parameters
(S_θ and ψ) is about 1% or less.

CHAPTER-III

DISCUSSION

Activity and osmotic coefficients are of basic importance in understanding and describing the thermodynamic behavior of the muilticomponent electrolyte solutions. All the water that we generally come across e.g., seawater industrial solutions, biological fluids, geo-thermal brines is nothing but the mixed electrolyte solutions. These waters are existing under a wide variety of temperature and pressure conditions. Therefore, we should know the thermodynamic properties of the mixed electrolyte solutions over a wide range of temperatures, pressures and pH values. Such a wide grid of thermodynamic data will help us to tackle the problems in environmental pollution control, soil and agricultural chemistry and life determining processes involving biological fluids.

Eleven elements are absolutely essential for the all-biological systems, which include plants, animals human beings[174-175]. These eleven elements are hydrogen, oxygen, carbon, nitrogen, sodium, potassium, calcium, magnesium, phosphorus, sulphur, and chlorine. Of these, the four elements hydrogen, oxygen, carbon and nitrogen make upto 99% of the total number of atoms present in the human body.

In living system these essential elements are consistently present in appropriate proportions and the deficiency of any element will cause disease, metabolic anomalies, and deformations in shape and retardation in growth.

The very large percentages of hydrogen and oxygen in living systems come from then high water content of these systems. Next in importance and abundance are carbon and nitrogen. These H, O, C, and N are the four basic elements of the organic structures i.e., RNA, DNA, proteins and metabolites of the living species. The only solvent of biological systems in which all the life chemistry occurs is WATER. Therefore, only those elements and chemical species, which are compatible and solute in aqueous media, are found in biological species.

The three elements sodium, potassium and chlorine are very essential components of life. Only these three elements have simple electrolytic functions and are present in living systems mostly in the form of free hydrated ions viz., Na^{+}_{aq}, K^{+}_{aq} and $Cl^{-}_{aq.}$ These ions have two types of

functions: one type is related to their concentrations and the other type is related to their mobility. The primary functions[176] of these mineral ions in the body are that (i) they play a major role in maintaining normal osmotic pressure relations through out the body, (ii) the maintenances of the normal state of acid- base balance and water balance and (iii) contraction in muscle and conduction in nerve in order to maintain muscle and nerve irritability at proper level. In blood plasma Sodium and Potassium chlorides have the functions of (i) Keeping the globulins in physical solutions and (ii) Maintaining the proper viscosity of blood by regulating the degree of hydrolysis of plasma proteins.

Important functions of the ions and amino acids which are important to present work are described below:

Calcium:

Calcium (Ca) is absolutely essential for living organisms. The vital functions of calcium in human body are:

1. Calcium and phosphorous are responsible for the formation of bones and teeth. With out bone development, there cannot be any growth. Hence Ca is essential for the growth of life.
2. The Ca^{+2} ion is directly related to muscle contraction. In the absence of calcium all types of muscles lose their ability to contract. However, in excess of calcium the isolated heart stops due to contraction. Calcium also controls the mechanical stability of cell walls and cell membranes. The membrane permeability is generally decreased by calcium and this effect balances the opposite action of Na and K.
3. The blood clotting process requires Ca^{++} ion. The normal level of blood calcium in humans ranges from 9-11 mg per100ml of serum. A 70kg man has about 300 mg of calcium in blood serum. About one half of this serum calcium is protein-bound, and remainder is in a diffusible state. This diffusible part is known as the ultra ‘filterable’ or the ‘ionized’ blood calcium. The level of blood calcium is strictly maintained with in very narrow limits.
4. Calcium is intimately associated with fertilization, cell division and hormonal activities.
5. In the controls over metabolic pathways, always there is a calcium dependent step. For example in photosynthesis, the calcium is involved in the controlling step of di-oxygen release.

The calcium is so much important for human life; the recommended dietary intake of Calcium is 0.8gm per day for men and women. During pregnancy it is 1.3gm and during lactation it is 2.0gm per day.

The deficiency of calcium causes the diseases such as bone deformities, tetany and Osteoporesis. However, the excess of Calcium causes cataracts, gall stones and atherosclerosis.

Magnesium:

Magnesium is very essential for the human life. Blood serum contains 2-3 mg percent of magnesium and the erythrocytes slightly more. The bone contains about 1.5 percent $Mg_3(PO_4)_2$. Soft tissues contain 3-5 times as much magnesium as calcium. A large number of enzymes concerned with metabolic processes involving fats, proteins and carbohydrates require Mg^{++} as an activating ion. In plants magnesium is the key element in chlorophyll which is responsible for photosynthesis.

Low level of blood magnesium, like low levels of calcium produces tetany. Excess plasma magnesium decreases muscles and nerve irritability at very high level i.e., 20mg percent in blood induces the nerve and muscle anaesthesia.

Chloride:

The chlorine is present to an extent of about 200 gm in adult human body. Most of this chlorine is present as free Cl^- ions in body fluids. This chloride ion in combination with Na^+, K^+, Mg^{+2}, Ca^{+2} ion etc. is useful for the transmission of messages in nerves and production of metabolic energy[177].

Glycine:

Glycine is an amino acid that is necessary for central nervous system function, and is essential for the synthesis of nucleic acids, bile acids, and other nonessential amino acids in the body. This amino acid slows the degeneration of muscles by supplying creatine, which is found in muscle tissue, and is used in the construction of DNA and RNA. Glycine also improves glycogen storage, which works to free up glucose for energy needs.

High concentrations of Glycine are found in the skin and connective tissues and helps repair damaged tissues and promotes healing. Glycine supplementation can be used to help prevent epileptic seizures. It has also been used to treat bipolar or manic depression and hyperactivity. Having the right amount of Glycine in your body will boost your energy level naturally.

Exceeding the recommended dosage of Glycine can lead to fatigue; however, there is no evidence to suggest toxicity from taking high doses of Glycine, though as a precaution, people with kidney or liver disease should not take high doses of Glycine.

Alanine:

Alanine is a nonessential amino acid, it is one of the 20 most common natural amino acids. Alanine is not essential to the human diet, since it can be synthesized from other cellular metabolites. Alanine is manufactured from other amino acids in the liver. Its side chain is a nonpolar, hydrophobic methyl group. Alanine is one of the simplest of the amino acids and is involved in the energy-producing breakdown of glucose. L-alanine is created in muscle cells from glutamate in a process called transamination. Alanine comes from the breakdown of DNA or the dipeptides, anserine and carnosine, and the conversion of pyruvate, a compound in carbohydrate metabolism. In the liver, alanine is transformed into pyruvate.

Alanine functions and uses:

Alanine is used by the body to build proteins. Alanine is vital for the production of protein, essential for proper function of the central nervous system and helps form neurotransmitters. Alanine is necessary for the promotion of proper blood glucose levels from dietary protein. Alanine is abundant in human muscle tissue. Alanine is readily converted to glucose when blood sugar levels fall and amino acids are liberated from muscle tissue to provide energy. During exercise the muscles release alanine into the bloodstream in direct proportion to the intensity of the exertion. The alanine is then is converted into glucose and released into the blood plasma. Alanine may help keep blood sugar levels stable during exercise. Glucose can be made from alanine in the liver or muscles when energy is needed, and thus it may help maintain the blood sugar level. Low levels of blood sugar have been linked with fatigue during exertion.

Alanine stimulates lymphocyte production and may help people who have immune suppression. Alanine strengthens the immune system by producing antibodies. This amino acid is known to be involved in the metabolism of the vitamin pyridoxine, and also tryptophan. Alanine is present in prostate fluid, and it may play a role in supporting prostate health. Alanine is one of the most widely used in protein construction. Only the l-alanine participates in the biosynthesis of proteins. This contributes to the desirable features of the fiber-strength, resistance to stretching, and flexibility.

Dietary sources of alanine:

Alanine is a nonessential amino acid, which means that it is manufactured from other amino acids in the liver. Alanine is manufactured in the body from pyruvate. Alanine can also be manufactured from branched chain amino acids such as valine, leucine, and isoleucine.

Because the body easily constructs alanine from other sources, it is difficult to become deficient in alanine. Deficiencies of a nonessential amino acid will not occur if a well-balanced diet is consume because the intake of proper foods will allow the body to produce exactly the amount of amino acid required to function optimally. Vitamin B6 deficiency will cause an alanine deficiency. Alanine deficiency has been seen in hypoglycemia, and alanine supplementation may be helpful in treating this condition.

People with kidney or liver disease should not consume high intakes of amino acid.

Valine:

Valine is an essential amino acid and an essential protein building block. It is a source of fuel for cells, and supports muscle recovery after physical exercise. It also aids in wound healing and the growth of new tissue. This amino acid is also a branched-chain amino acid that cannot be produced by the body. Valine can be found in many meats, dairy products, eggs, and in lesser amounts in grains, legumes, and nuts. .

Taking Valine supplements after a serious injury and after exercising heavily can aid in muscle repair. This amino acid is also helpful in treating muscle wasting, twitching and tremors, hepatic encephalopathy, and brain damage related to alcohol abuse. It enhances energy, increases endurance, lowers elevated blood sugar levels and increases growth hormone production. Using Valine supplements also helps maintain the nitrogen balance in the body and can correct severe amino acid deficiencies caused by drug addiction.

Valine deficiency is not likely if you have an adequate amount of protein in the diet. Lacking adequate amounts of this amino acid could stunt growth, cause neuropathic obstacles, and anemia. Consuming high levels of Valine may, over time, lead to symptoms such as a crawling sensation in the skin and hallucinations.

In the present work, the activity coefficients of NaCl were experimentally determined in the following aqueous quaternary mixtures; *NaCl-$MgCl_2$-Glycine-H_2O, NaCl-$CaCl_2$-Glycine-*

H_2O, NaCl-$SrCl_2$-Glycine-H_2O, NaCl-$MgCl_2$-β-Alanine-H_2O, NaCl-$CaCl_2$-β-Alanine-H_2O, NaCl-$SrCl_2$-β-Alanine-H_2O, NaCl-$MgCl_2$-Valine-H_2O, NaCl-$CaCl_2$-Valine-H_2O, NaCl-$SrCl_2$-Valine-H_2O using emf method at ionic strengths range of 0.1to 3.0 m and 25^0C, 35^0C, 45^0C temperatures

The activity coefficients in some model aqueous electrolyte mixtures have been estimated using Pitzer equations for

(i) Several quaternary mixtures.

(ii) Waters, which are relevant to environmental pollution studies.

Section –A

The multi-component electrolyte solutions are analogous to the natural brines encountered in water pollution control, oceanography and petroleum drilling. Aqueous solutions of multi-component electrolyte solutions are analogous to the natural brines encountered in water pollution control, oceanography and petroleum drilling. Although considerable information is available on activity coefficients of single electrolyte solutions, similar data is lacking on the mixed electrolyte solutions.

In present work, the activity coefficients of NaCl were experimentally determined. This activity coefficient data of each system is analyzed to calculate (i) Harned Coefficients (ii) osmotic coefficients.

The experimentally determined activity coefficient data of NaCl in mixed electrolyte solutions studied were conveniently expressed by Harned equations[67] which describe the variation of activity coefficients with composition at constant total ionic strengths.

The Harned equations are given below:

$$\log\gamma_A = \log\gamma^o_A - \alpha_{AB}y_B - \beta_{AB}y^2_B \qquad \text{……(121)}$$

Where

γ_A = Activity coefficient of NaCl in the mixture.

γ^o_A = Activity coefficient of pure NaCl solution of the same ionic strength as the total ionic strength of the mixture.

y_B = Ionic strength fraction of the second salt in the mixture and α_{AB} and β_{AB} is Harned coefficients.

α_{AB} and β_{AB} are Harned coefficients.

These Harned coefficients measure the effect of an added electrolyte on the activity coefficient of another electrolyte. These coefficients α_{AB} and β_{AB} depend partly on the electrostatic properties of the individual electrolytes and partly on the magnitude of the interactions between the (two like charged) ions in mixed electrolyte solutions. These coefficients are functions of molality, temperature, pressure and system specific. Thus the Harned coefficients determined for a given system is of not much importance for any other system.

In case the $\log\gamma_A$ v/s y_B plot is nearly linear for any system, then the β_{AB} value is very small and can be neglected, then the Harned equations can be rewritten as

$$\log\gamma_A = \log\gamma^o_A - \alpha_{AB} y_B \qquad \ldots\ldots\ldots\ldots(122)$$

The activity coefficient data were fitted to Harned equations (122) using least square program. The Harned coefficients can be estimated for all the mixtures studied and the results are listed for each one of the system studied.

The experimental activity coefficient data were also analyzed using the Pitzer equations and the Binary (S_θ) and Ternary (Ψ) interaction parameters were evaluated. These mixing parameters are considered to be ionic strength independent. These mixing parameters evaluated for quaternary systems are useful in predicting the thermodynamic properties of multicomponent electrolyte solutions.

In multicomponent electrolyte solutions the activity coefficients of individual cations (γ_M) and anions (γ_X) can be described by the Pitzer equations given below:

$$\ln\gamma_M = Z_M^2 \, F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c (2\theta_{Mc} + \sum_a m_a \psi_{Mca}) +$$

$$\sum_{a<} \sum_{a'} m_a m_{a'} \psi_{Maa'} + |Z_M| \sum_c \sum_a m_c m_a C_{ca} \qquad \ldots\ldots..(123)$$

$$\ln\gamma_X = Z_M^2 F + \sum_c m_c(2B_{Xc} + ZC_{Xc}) + \sum_a m_a(2\theta_{Xa} + \sum_c m_c\psi_{Xca})$$
$$\sum_{c<}\sum_{c'} m_c m_{c'}\psi_{cc'X} + |Z_M|\sum_c\sum_a m_c m_a C_{ca} \qquad \ldots\ldots\ldots(124)$$

Where m_c is the molality of the cation with charge Z_M and m_a is the molality of the anion with the charge Z_X.

In these equations

$$F = -A_\phi \left\{\left(\sqrt{I}/(1+b\sqrt{I})\right) + \frac{2}{b}\ln(1+b\sqrt{I})\right\}$$
$$+ \sum_c\sum_a m_c m_a B'_{ca} + \sum_{c<c'} m_c m_{c'} \theta'_{cc'} + \sum_{a<a'} m_a m_{a'} \theta' aa' \qquad \ldots.(125)$$

$$Z = \sum m_i |Z_i|$$

$$C_{MX} = C^{\phi}_{MX} / 2(|Z_M Z_X|)^{1/2}$$

and

$$A_\varphi = \frac{1}{3}\cdot\frac{2\Pi N_o d}{\sqrt{1000}}\cdot\frac{e^2}{(DKT)^{3/2}}$$

The Pitzer equations for osmotic coefficients in the given mixture are as follows:

$$\phi - 1 = \frac{2}{\sum m_i}\{-A_\phi \frac{I^{3/2}}{1+b\sqrt{I}} + \sum_c\sum_a m_c m_a\left(B^{\phi}_{ca} + ZC_{ca}\right) +$$
$$\sum_{c<}\sum_{c'} m_c m_{c'}(\theta^{\phi}_{cc'} + \sum_a m_a\psi_{cca'}) +$$
$$\sum_{a<}\sum_{a'} m_a m_{a'}(\theta^{\phi}_{aa'} + \sum_c m_c\psi_{aa'c})\}$$
$$\ldots\ldots\ldots(126)$$

From these general equations one can write the equation for the activity coefficient of any component salt in a given mixture, however complex it may be. The results obtained for the quaternary mixtures studied in this work are discussed below.

1) NaCl-$MgCl_2$-Glycine-H_2O :

The experimentally determined activity coefficient data of NaCl in *NaCl-$MgCl_2$-Glycine-H_2O* system at ionic strengths of 0.5, 1.0, 2.0, 3.0 mol.kg^{-1} at 25^{o}C, 35 ^{o}C and 45 ^{o}C are listed in tables 2,3 and 4.

The logγ_A v/s $y_{B\ at}$ 25^{o}C are plotted in Figure-2. The activity coefficient data at each ionic strength were fitted to the Harned equation (122) by a least square program in order to get Harned coefficients (α_{AB} and β_{AB}), and these values with corresponding RMSD values are listed in Table-29

Table: 29

Harned coefficients for the System

NaCl- $MgCl_2$-Glycine-H_2O at 25^{o}C.

I	α_{AB}	β_{AB}	RMSDx10^5
0.5	0.0235	-0.0010	2.76
1.0	0.0432	-0.0030	2.70
2.0	0.0870	-0.0116	3.17
3.0	0.1386	-0.0243	3.86

These activity coefficients data of NaCl in the quaternary mixture *NaCl- $MgCl_2$-Glycine-H_2O* could also be theoretically calculated using the Pitzer equations (123, 124) given below by substituting the relevant binary and ternary mixing parameters.

The required Pitzer equation is as follows:

$$\begin{aligned} \ln\gamma_{Na} = \quad & F + m_{Cl}(2B_{NaCl}+ZC_{NaCl}) + m_{Z+Z-}(2BNa_{Z+Z-}+ZC_{Na\ Z+Z-}) \\ & + m_{Mg}(2\theta_{NaMg}+m_{Cl}\Psi_{NaMgCl}+m_{Z+Z-}\Psi_{NaMgZ+Z-}) \\ & + m_{Z+Z-}(2\theta_{NaZ+Z-}+m_{Cl}\Psi_{Na\ Z+Z-Cl}+m_{Z+Z-}\Psi_{Na\ Z+Z-Cl}) \\ & + m_{Cl}m_{Z+Z-}\Psi_{NaCl\ Z+Z-}+m_{Na}m_{ClCNaCl} \\ & + m_{Na}m_{Z+Z-}C_{Na\ Z+Z-}+m_{Mg}m_{Cl}C_{MgCl}+m_{Mg}m_{Z+Z-}C_{Mg\ Z+Z-} \end{aligned}$$

$$+ m_{Z+Z-}\, m_{Cl} C_{Z+Z-Cl} + m_{Mg} m_{Z+Z-}\, C_{Mg\,Z+Z-}$$

.....(127)

$$\ln\gamma_{Cl} = F + m_{Na}(2B_{NaCl} + ZC_{NaCl})$$
$$+ m_{Mg}((2B_{MgCl} + ZC_{MgCl}) + m_{Z+Z-}(2B_{Z+Z-Cl} + ZC_{Z+Z-Cl})$$
$$+ m_{Z+Z-}(2\theta_{Z+Z-Cl} + m_{Na}\Psi_{NaCl\,Z+Z-} + m_{Mg}\Psi_{MgCl\,Z+Z-}$$
$$+ m_{Z+Z-}\Psi_{Z+Z-ClMg})$$
$$+ m_{Na}m_{Mg}\Psi_{NaMgCl} + m_{Na}m_{Z+Z-}\Psi_{Z+Z-Cl} + m_{Mg}m_{Cl}C_{MgCl}$$
$$+ m_{Na}m_{Cl}C_{NaCl} + m_{Na}m_{Z+Z-} + C_{Na\,Z+Z-} + m_{Mg}m_{Cl}C_{MgCl}$$
$$+ m_{Mg}m_{Z+Z-}C_{Mg\,Z+Z-} + m_{Z+Z-}m_{Cl}C_{Z+Z-Cl}$$

……(128)

where

$$F = -A_{\phi}\left\{\left(\frac{\sqrt{I}}{1+b\sqrt{I}}\right) + \frac{2}{b}\ln(1+b\sqrt{I})\right\}$$
$$+ m_{Na}m_{Cl}B`_{NaCl} + m_{Na}m_{Z+Z-}B`_{Na\,Z+Z-}$$
$$+ m_{Mg}m_{Cl}B`_{MgCl} + m_{Mg}m_{Z+Z-}B`_{Mg\,Z+Z-}$$
$$+ m_{Z+Z-Cl}B`_{Z+Z-Cl}$$
$$+ m_{Na}m_{Mg}\theta`_{NaMg} + m_{Na}M_{Z+Z-}\Theta`_{Na\,Z+Z-}$$
$$+ m_{Mg}m_{Z+Z-}\theta`_{Mg\,Z+Z-} + m_{Cl}m_{Z+Z-}\Theta`_{Cl\,Z+Z-}$$

……(129)

The values for Pitzer parameters required in the above equations are listed below.

Parameters

$S_{\theta\,Na-Mg} = 0.0701$ $\quad\quad$ $\Psi_{Na-Mg-Cl} = -0.0124$

$S_{\theta\,Na-A.A} = -0.0103$ $\quad\quad$ $\Psi_{Na-Mg-A.A} = -0.0043$

$S_{\theta Mg-A.A} = -0.0102$

$S_{\theta\,Cl-A.A} = -0.0045$

By substituting these Pitzer interaction parameters in Pitzer equations (127, 128) the activity coefficients of NaCl in this quaternary system were calculated and compared with the experimental values obtained in the present work. The calculated values were in good agreement with experimental values with an RMSD value of 3.45×10^{-4}

This shows that the Pitzer parameters listed above are able to fit the experimental data satisfactorily and also indicates applicability of Pitzer equations to quaternary systems as well.
The osmotic coefficients of the quaternary mixture *NaCl- $MgCl_2$-Glycine-H_2O* were calculated by substituting the Pitzer interaction parameters listed above in the Pitzer equations given below:

$$\varphi\text{-}1 = \frac{2}{\sum m_i}\{-\frac{A\phi I^{3/2}}{1+b\sqrt{I}} + m_{NaCl}(B^{\varphi}_{NaCl}+ZC_{NaCl})$$
$$+ m_{Na}m_{Z+Z-}(B^{\varphi}_{Na\ Z+Z-}+ZC_{Na\ Z+Z-})$$
$$+ m_{Mg}m_{Cl}(B^{\varphi}_{MgCl2}+ZC_{MgCL2})$$
$$+ m_{Mg}m_{Z+Z-}(B^{\varphi}_{MgZ+Z-}+ZC_{MgZ+Z-})$$
$$+ m_{Na}m_{Mg}(\theta^{\varphi}_{NaMg}+m_{Cl}\Psi_{NaMgCl}+m_{Z+Z-}\Psi_{NaMg\ Z+Z-}$$
$$+ m_{Na}m_{Z+Z-}(\theta^{\varphi}_{Na\ Z+Z-}+m_{Cl}\Psi_{NaCl\ Z+Z-}+m_{Z+Z-}\Psi_{NaMg\ Z+Z-}$$
$$+ m_{Mg}m_{Z+Z-}(\theta^{\varphi}_{Mg\ Z+Z-}+m_{Cl}\Psi_{Mg\ Z+Z-Cl}+m_{Z+Z-}\Psi_{Mg\ Z+Z-Na}$$
$$+ m_{Z+Z-}m_{Cl}(\theta^{\varphi}_{Z+Z-}+m_{Na}\Psi_{Cl\ Z+Z-Na}+m_{Mg}\Psi_{Cl\ Z+Z-Mg}$$
$$+ m_{Z+Z-}\Psi_{Cl\ Z+Z-Na}$$
$$\text{……(130)}$$

Where $\theta^{\varphi}ij = S\theta_{ij} + E\theta_{ij} + IE\theta`_{ij}$

The Osmotic coefficients were also calculated and data is summarized in the Table 30.

Table: 30

Osmotic coefficient for the system

NaCl-$MgCl_2$-Glycine-H_2O system at 25°C.

y_B	I= 0.5	I=1.0	I=2.0	I=3.0
0.0	0.9220	0.9363	0.9839	1.0445
0.1	0.9163	0.9260	0.9634	1.0123
0.2	0.9103	0.9151	0.9422	0.9796
0.3	0.9039	0.9034	0.9201	0.9464
0.4	0.8970	0.8911	0.8971	0.9126
0.5	0.8898	0.8780	0.8733	0.8783
0.6	0.8821	0.8643	0.8487	0.8435
0.7	0.8740	0.8499	0.8231	0.8081
0.8	0.8655	0.8348	0.7967	0.7720
0.9	0.8566	0.8191	0.7694	0.7354
1.0	0.8473	0.8026	0.7412	0.6981

2) NaCl- $CaCl_2$-Glycine-H_2O:

The experimentally determined activity coefficient data of NaCl in *NaCl-$CaCl_2$-Glycine-H_2O* system at total ionic strength of 0.5, 1.0, 2.0, 3.0 mol.kg^{-1} at 25°C, 35 °C, 45 °C are listed in tables 5,6 and 7.

The logγ_A v/s $y_{B\ at}$ 25°C are plotted in figure 3. The activity coefficient data at each ionic strength were fitted to the Harned equation (122) by a least square program in order to get Harned coefficients (α_{AB} and β_{AB}), and these values with corresponding RMSD values are listed in Table 31.

Table: 31

Harned coefficients for the system

NaCl- $CaCl_2$-Glycine-H_2O at 25°C.

I	α_{AB}	β_{AB}	RMSDx10^5
0.5	0.0012	0.0002	4.59
1.0	0.0041	-0.0007	2.76
2.0	0.0158	-0.0036	3.49
3.0	0.0351	-0.0074	3.76

The Pitzer equation for calculating the activity coefficients of NaCl in this mixture are similar to equation(123, 124) given earlier.

For this system the required Pitzer mixing parameters values are given below:

Parameters

$S_{\theta\ Na\text{-}Ca}$ = 0.0700

$S_{\theta\ Ca\text{-}A.A}$ = 0.0164

$S_{\theta Na\text{-}A.A}$ = -0.0011

$S_{\theta\ Cl\text{-}A.A}$ = -0.0004

$\Psi_{Na\text{-}Ca\text{-}Cl}$ = - 0.0114

$\Psi_{Na\text{-}Ca\text{-}A.A}$= - 0.0117

The activity coefficients of NaCl in this system were calculated by substituting these Pitzer ion-interaction parameters. These calculated activity coefficient values are in good agreement with experimental values with an RMSD = $4.56x10^{-4}$.

The osmotic coefficients of the quaternary mixture *$NaCl$-$CaCl_2$-Glycine-H_2O* were calculated by substituting the Pitzer interaction parameters listed above in the Pitzer equations (130) similar to shown above.

The osmotic coefficients were also calculated and the values are tabulated in table 32.

Table: 32

Osmotic coefficient for the NaCl-$CaCl_2$-Glycine –H_2O system at 25°C.

y_B	I= 0.5	I=1.0	I=2.0	I=3.0
0.0	0.9220	0.9363	0.9839	1.0445
0.1	0.9216	0.9355	0.9808	1.0378
0.2	0.9213	0.9346	0.9779	1.0315
0.3	0.9209	0.9337	0.9751	1.0256
0.4	0.9205	0.9327	0.9724	1.0201
0.5	0.9200	0.9318	0.9698	1.0150
0.6	0.9195	0.9308	0.9674	1.0103
0.7	0.9190	0.9298	0.9650	1.0060
0.8	0.9184	0.9287	0.9628	1.0021
0.9	0.9178	0.9276	0.9606	0.9987
1.0	0.9172	0.9266	0.9586	0.9957

3) NaCl-$SrCl_2$-Glycine-H_2O:

The experimentally determined activity coefficient data of NaCl in NaCl-*$CaCl_2$-Glycine-H_2O* system at total ionic strength of 0.5, 1.0, 2.0, 3.0 mol.kg^{-1} at 25°C, 35 °C, 45 °C are listed in tables 8,9and 10.

The logγ_A v/s $y_{B\ at}$ 25°C are plotted in figure 4. The γ data at each ionic strength were fitted to the Harned equation and Harned coefficients (α_{AB} and β_{AB}) were evaluated and these values with corresponding RMSD values are listed in Table 33.

Table: 33

Harned coefficients for the system

NaCl- $SrCl_2$-Glycine-H_2O at 25°C.

I	α_{AB}	β_{AB}	RMSDx10^5
0.5	0.0012	0.0002	4.25
1.0	0.0034	-0.0006	3.61
2.0	0.0098	-0.0036	2.99
3.0	0.0154	-0.0085	3.12

The Pitzer equation for calculating the activity coefficient of NaCl in this mixture are similar to equation(123, 124) given earlier. For this system the required Pitzer mixing parameters values are given below:

Parameters

$S_{\theta\ Na\text{-}Sr}$ = 0.0700

$S_{\theta\ Sr\text{-}A.A}$ = -0.0121

$S_{\theta Na\text{-}A.A}$ = -0.0011

$S_{\theta\ Cl\text{-}A.A}$ = -0.0014

$\Psi_{Na\text{-}Sr\text{-}Cl}$ = - 0.0070

$\Psi_{Na\text{-}Ca\text{-}A.A}$= - 0.0076

The activity coefficients of NaCl in this system were calculated by substituting these Pitzer ion-interaction parameters. These calculated activity coefficient values are in good agreement with experimental values with an RMSD = $4.56x10^{-4}$.

The osmotic coefficients were also calculated and the values are tabulated in table 34.

Table: 34

Osmotic coefficients of the NaCl-$SrCl_2$-Glycine –H_2O system at 25°C.

y_B	I= 0.5	I=1.0	I=2.0	I=3.0
0.0	0.9007	0.8990	0.9136	0.9374
0.1	0.9003	0.8980	0.9112	0.9333
0.2	0.8999	0.8971	0.9090	0.9297
0.3	0.8995	0.8961	0.9069	0.9265
0.4	0.8990	0.8951	0.9050	0.9239
0.5	0.8985	0.8941	0.9032	0.9217
0.6	0.8980	0.8930	0.9016	0.9200
0.7	0.8974	0.8920	0.9001	0.9189
0.8	0.8969	0.8909	0.8987	0.9182
0.9	0.8962	0.8899	0.8975	0.9180
1.0	0.8956	0.8888	0.8965	0.9183

4) NaCl- $MgCl_2$-β-Alanine-H_2O:

The experimentally determined activity coefficient data of NaCl in *NaCl- $MgCl_2$-β-alanine-H_2O* system at total ionic strength of 0.5, 1.0, 1.5, 2.0 mol.kg^{-1} at 25°C, 35 °C, 45 °C are listed in tables 11,12 and 13.

The $\log \gamma_A$ v/s y_B at 25°C are plotted in figure 5. The activity coefficient data at each ionic strength were fitted to the Harned equation (122) by a least square program in order to get Harned coefficients (α_{AB} and β_{AB}), and these values with corresponding RMSD values are listed in Table 35.

Table: 35

Harned coefficients for the

NaCl- $MgCl_2$-β-alanine -H_2O system at 25°C.

I	α_{AB}	β_{AB}	RMSDx10^5
0.5	-0.1823	-0.0139	6.880
1.0	-0.1749	-0.0323	6.116
1.5	-0.1465	-0.0554	13.314
2.0	-0.1023	-0.0751	15.023

The Pitzer equation for calculating the activity coefficient of NaCl in this mixture are similar to equation(123, 124) given earlier. For this system the required Pitzer mixing parameters values are given below.

Parameters

$S_{\theta\ Na\text{-}Mg}$ = 0.0700

$S_{\theta\ Na\text{-}A.A}$ = -0.0011

$S_{\theta Mg\text{-}A.A}$ = -0.0111

$S_{\theta\ Cl\text{-}A.A}$ = -0.0004

$\Psi_{Na\text{-}Mg\text{-}Cl}$ = - 0.0112

$\Psi_{Na\text{-}Mg\text{-}A.A}$= - 0.0014

By substituting these interaction parameters in Pitzer equations the activity coefficients of NaCl in this quaternary mixture were calculated and the values are in good agreement with experimental values with an RMSD value = $3.91x10^{-4}$

The osmotic coefficients were also calculated and data are summarized in table 36.

Table:36

Osmotic coefficient for the

NaCl-$MgCl_2$-β-alanine –H_2O system at 25°C

y_B	I= 0.5	I=1.0	I=1.5	I=2.0
0.0	0.8966	0.9363	0.9839	1.0446
0.1	0.8911	0.9309	0.9759	1.0327
0.2	0.8876	0.9254	0.9685	1.0223
0.3	0.8821	0.9198	0.9614	1.0131
0.4	0.8769	0.9140	0.9547	1.0051
0.5	0.8711	0.9079	0.9482	0.9981
0.6	0.8661	0.9016	0.9418	0.9920
0.7	0.8601	0.8949	0.9353	0.9864
0.8	0.8550	0.8872	0.9284	0.9811
0.9	0.8491	0.8788	0.9209	0.9756
1.0	0.8436	0.8693	0.9123	0.9683

5) NaCl-$CaCl_2$-β-Alanine-H_2O:

The experimentally determined activity coefficient data of NaCl in *NaCl- $CaCl_2$-β-alanine-H_2O* system at total ionic strength of 0.5, 1.0, 1.5, 2.0 mol.kg^{-1} at 25°C are listed in tables14, 15 and 16.

The logγ_A v/s $y_{B\ at}$ 25°C are plotted in figure 6. The activity coefficient data at each ionic strength were fitted to the Harned equation (122) by a least square program in order to get Harned coefficients (α_{AB} and β_{AB}), and these values with corresponding RMSD values are listed in Table 37.

Table:37

Harned coefficients for the system

NaCl- $CaCl_2$-β-alanine-H_2O at 25°C.

I	α_{AB}	β_{AB}	RMSD x10^5
0.5	-0.1823	-0.0189	11.009
1.0	-0.1749	-0.0400	7.925
1.5	-0.1465	-0.0649	3.429
2.0	-0.1023	-0.0821	0.013

The Pitzer equation for calculating the activity coefficient of NaCl in this mixture are similar to equations given earlier. For this system the required Pitzer mixing parameters values are given below.

Parameters

$S_{\theta\ Na\text{-}Ca}$ = 0.0700

$S_{\theta\ Ca\text{-}A.A}$ = 0.0170

$S_{\theta\ Na\text{-}A.A}$ = -0.0511

$S_{\theta\ Cl\text{-}A.A}$ = -0.0081

$\Psi_{Na\text{-}Ca\text{-}Cl}$ = - 0.0141

$\Psi_{Na\text{-}Ca\text{-}A.A}$= - 0.0131

By substituting these interaction parameters in Pitzer equation (123, 124) the activity coefficients of NaCl in this quaternary mixture were calculated and the values are in good agreement with experimental values with an RMSD value = $3.58x10^{-4}$

The osmotic coefficients were also calculated and the values are tabulated in table 38.

Table:38

Osmotic coefficient for the

NaCl-$CaCl_2$-β-alanine–H_2O system at 25°C

y_B	I= 0.5	I=1.0	I=1.5	I=2.0
0.0	0.8966	0.9363	0.9839	1.0446
0.1	0.8932	0.9304	0.9752	1.0319
0.2	0.8827	0.9245	0.9669	1.0200
0.3	0.8769	0.9184	0.9587	1.0089
0.4	0.8723	0.9123	0.9506	0.9984
0.5	0.8678	0.9060	0.9426	0.9884
0.6	0.8631	0.8995	0.9346	0.9789
0.7	0.8558	0.8928	0.9264	0.9697
0.8	0.8509	0.8856	0.9179	0.9607
0.9	0.8453	0.8779	0.9090	0.9515
1.0	0.8378	0.8696	0.8992	0.9419

6) NaCl- $SrCl_2$-β-Alanine-H_2O:

The experimentally determined activity coefficient data of NaCl in *NaCl- $SrCl_2$-β-Alanine -H_2O* system at total ionic strength of 0.5, 1.0, 1.5, 2.0 mol.kg^{-1} at 25°C, 35 °C, 45 °C are listed in table 17,18 and 19.

The logγ_A v/s $y_{B\ at}$ 25°C are plotted in figure-7. The activity coefficient data at each ionic strength were fitted to the Harned equation (122) by a least square program in order to get Harned coefficients (α_{AB} and β_{AB}), and these values with corresponding RMSD values are listed in Table 39.

Table: 39

Harned coefficients for the

NaCl- $SrCl_2$-β-Alanine -H_2O system at 25°C.

I	α_{AB}	β_{AB}	RMSDx10^5
0.5	-0.1823	-0.0223	14.209
1.0	-0.1749	-0.0429	9.006
1.5	-0.1465	-0.0764	6.300
2.0	-0.1023	-0.0911	3.152

The Pitzer equation for calculating the activity coefficient of NaCl in this mixture are similar to equation(123, 124) given earlier. For this system the required Pitzer mixing parameters values are given below:

Parameters

$S_{\theta\ Na\text{-}Sr}$ = 0.0700 $\quad\quad$ $\Psi_{Na\text{-}Sr\text{-}Cl}$ = - 0.0070

$S_{\theta\ Sr\text{-}A.A}$ = -0.0191 $\quad\quad$ $\Psi_{Na\text{-}Ca\text{-}A.A}$= - 0.0053

$S_{\theta Na\text{-}A.A}$ = -0.0500

$S_{\theta\ Cl\text{-}A.A}$ = -0.0012

The activity coefficients of NaCl in this system were calculated by substituting these Pitzer ion-interaction parameters. These calculated activity coefficient values are in good agreement with experimental values with an RMSD = $4.56x10^{-4}$.

The osmotic coefficients were also calculated and the values are tabulated in table 40.

Table: 40

Osmotic coefficient for the NaCl- $SrCl_2$-β-Alanine -H_2O system at 25°C

y_B	I= 0.5	I=1.0	I=1.5	I=2.0
0.0	0.8966	0.9363	0.9839	1.0446
0.1	0.8911	0.9309	0.9759	1.0327
0.2	0.8876	0.9254	0.9685	1.0223
0.3	0.8821	0.9198	0.9614	1.0131
0.4	0.8769	0.9140	0.9547	1.0051
0.5	0.8711	0.9079	0.9482	0.9981
0.6	0.8661	0.9016	0.9418	0.9920
0.7	0.8601	0.8949	0.9353	0.9864
0.8	0.8550	0.8872	0.9284	0.9811
0.9	0.8491	0.8788	0.9209	0.9756
1.0	0.8436	0.8693	0.9123	0.9683

7) NaCl- $MgCl_2$-Valine -H_2O:

The experimentally determined activity coefficient data of NaCl in *NaCl- $MgCl_2$-Valine-H_2O* system at total ionic strength of 0.1, 0.2, 0.3, 0.4 mol.kg^{-1} at 25°C, 35 °C, 45 °C are listed in table 20,21 and 22

The logγ_A v/s $y_{B\ at}$ 25°C are plotted in figure 8. The activity coefficient data at each ionic strength were fitted to the Harned equation (122) by a least square program in order to get Harned coefficients (α_{AB} and β_{AB}), and these values with corresponding RMSD values are listed in Table 41.

Table: 41

Harned coefficients for the NaCl- $MgCl_2$-Valine-H_2O system at 25°C.

I	α_{AB}	β_{AB}	RMSDx10^{-5}
0.1	-0.0166	-0.0027	3.52
0.2	-0.0131	-0.0099	3.57
0.3	-0.0201	-0.0225	1.80
0.4	-0.0296	-0.0378	0.97

The Pitzer equation for calculating the activity coefficient of NaCl in this mixture are similar to equation(122) given earlier. For this system the required Pitzer mixing parameters values are given below:

Parameters

$S_{\theta\ Na\text{-}Mg}$ = 0.0700

$S_{\theta\ Na\text{-}A.A}$ = -0.0051

$S_{\theta Mg\text{-}A.A}$ = -0.0160

$S_{\theta\ Cl\text{-}A.A}$ = -0.0090

$\Psi_{Na\text{-}Mg\text{-}Cl}$ = - 0.0121

$\Psi_{Na\text{-}Mg\text{-}A.A}$ = - 0.0071

By substituting these interaction parameters in Pitzer equation (122, 124) the activity coefficients of NaCl in this quaternary mixture were calculated and the values are in good agreement with experimental values with an RMSD value = 5.36x10^{-3}.

The osmotic coefficients were also calculated and data are summarized in table 42.

Table: 42

Osmotic coefficient for the NaCl-$MgCl_2$-Valine–H_2O system at 25°C

y_B	I= 0.1	I=0.2	I=0.3	I=0.4
0.0	0.9363	0.9839	1.0193	1.0446
0.1	0.9348	0.9834	1.0187	1.0435
0.2	0.9328	0.9830	1.0153	1.0443
0.3	0.9303	0.9825	1.0121	1.0435
0.4	0.9272	0.9818	1.0107	1.0446
0.5	0.9234	0.9807	1.0009	1.0459
0.6	0.9186	0.9790	1.0907	1.0476
0.7	0.9126	0.9766	1.1121	1.0494
0.8	0.9050	0.9731	1.1140	1.0510
0.9	0.8955	0.9680	1.1173	1.0521
1.0	0.8833	0.9608	1.1303	1.0522

8) NaCl- $CaCl_2$-Valine-H_2O:

The experimentally determined activity coefficient data of NaCl in *NaCl- $CaCl_2$-Valine-H_2O* system at total ionic strength of 0.1, 0.2, 0.3, 0.4 mol.kg^{-1} at 25°C, 35 °C, 45 °C are listed in table 23,24 and 25 .

The logγ_A v/s $y_{B\ at}$ 25°C are plotted in figure 9. The γ data at each ionic strength were fitted to the Harned equation and Harned coefficients (α_{AB} and β_{AB}) were evaluated and these values with corresponding RMSD values are listed in Table 43.

Table: 43

Harned coefficients for the NaCl-$CaCl_2$-Valine-H_2O system at 25°C

I	α_{AB}	β_{AB}	RMSDx10^{-5}
0.1	0.0177	-0.0025	7.93
0.2	-0.0094	-0.0101	2.50
0.3	-0.0174	-0.0230	2.63
0.4	-0.0251	-0.0319	1.73

The Pitzer equation for calculating the activity coefficient of NaCl in this mixture are similar to equation(123, 124) given earlier. For this system the required Pitzer mixing parameters values are given below:

Parameters

$S_{\theta\ Na\text{-}Ca}$ = 0.0700 $\quad\quad$ $\Psi_{Na\text{-}Ca\text{-}Cl}$ = - 0.0141

$S_{\theta\ Ca\text{-}A.A}$ = 0.0132 $\quad\quad$ $\Psi_{Na\text{-}Ca\text{-}A.A}$= - 0.0131

$S_{\theta Na\text{-}A.A}$ = -0.0090

$S_{\theta\ Cl\text{-}A.A}$ = -0.0060

The activity coefficients of NaCl in this system were calculated by substituting these Pitzer ion-interaction parameters. These calculated activity coefficient values are in good agreement with experimental values with an RMSD = 5.09x10^{-3}.

The osmotic coefficients were also calculated and the values are tabulated in table 44.

Table: 44

Osmotic coefficient for the

NaCl-$CaCl_2$-Valine–H_2O system at 25°C

y_B	I= 0.1	I=0.2	I=0.3	I=0.4
0.0	0.9363	0.9839	1.0193	1.0446
0.1	0.9347	0.9839	1.0182	1.0450
0.2	0.9327	0.9838	1.0176	1.0458
0.3	0.9302	0.9834	1.0155	1.0469
0.4	0.9270	0.9827	1.0139	1.0480
0.5	0.9232	0.9815	1.0121	1.0493
0.6	0.9184	0.9797	1.0112	1.0504
0.7	0.9125	0.9770	1.0105	1.0512
0.8	0.9051	0.9733	1.0099	1.0516
0.9	0.8959	0.9680	1.0071	1.0511
1.0	0.8842	0.9606	1.0053	1.0493

9) NaCl-$SrCl_2$-Valine-H_2O:

The experimentally determined activity coefficient data of NaCl in *NaCl- $SrCl_2$-Valine-H_2O* system at total ionic strength of 0.5, 1.0, 2.0, 3.0 mol.kg^{-1} at 25°C, 35 °C, 45 °C are listed in tables 26, 27 and 28.

The logγ_A v/s $y_{B\ at}$ 25°C are plotted in figure 10. The γ data at each ionic strength were fitted to the Harned equation and Harned coefficients (α_{AB} and β_{AB}) were evaluated and these values with corresponding RMSD values are listed in Table 45.

Table: 45

Harned coefficients for the

NaCl- $SrCl_2$-Valine-H_2O system at 25°C.

I	α_{AB}	β_{AB}	RMSDx10^{-5}
0.1	-0.0269	-0.0023	3.37
0.2	-0.2151	-0.0097	3.43
0.3	-0.0208	-0.0230	3.47
0.4	-0.0431	-0.0331	3.62

The Pitzer equation for calculating the activity coefficient of NaCl in this mixture are similar to equation(123) given earlier. For this system the required Pitzer mixing parameters values are given below:

Parameters

$S_{\theta\ Na\text{-}Sr}$ = 0.0700

$S_{\theta\ Sr\text{-}A.A}$ = -0.0150

$S_{\theta Na\text{-}A.A}$ = -0.0017

$S_{\theta\ Cl\text{-}A.A}$ = -0.0081

$\Psi_{Na\text{-}Sr\text{-}Cl}$ = - 0.0070

$\Psi_{Na\text{-}Ca\text{-}A.A}$= - 0.0046

The activity coefficients of NaCl in this system were calculated by substituting these Pitzer ion-interaction parameters. These calculated activity coefficient values are in good agreement with experimental values with an RMSD = 3.16x10^{-3}.

The osmotic coefficients were also calculated and the values are tabulated in table 46.

Table: 46

Osmotic coefficient for the NaCl-$SrCl_2$-Valine –H_2O system at 25°C.

y_B	I= 0.1	I=0.2	I=0.3	I=0.4
0.0	0.9363	0.9839	1.0192	1.0445
0.1	0.9349	0.9844	1.0185	1.0459
0.2	0.9331	0.9850	1.0179	1.0478
0.3	0.9308	0.9850	1.0167	1.0500
0.4	0.9279	0.9849	1.0158	1.0526
0.5	0.9243	0.9845	1.0151	1.0554
0.6	0.9197	0.9834	1.0143	1.0583
0.7	0.9139	0.9815	1.0135	1.0612
0.8	0.9067	0.9785	1.0129	1.0637
0.9	0.8975	0.9740	1.0107	1.0656
1.0	0.8859	0.9675	1.0075	1.0665

The thermodynamic properties of electrolyte solutions, viz., activity coefficients, osmotic coefficients, etc., are depend on the nature, size and charge of the involved cations and anions as well as the properties of the solvent. In the present work

Nine quaternary systems viz.,

(i) *NaCl - $MgCl_2$ – Glycine - H_2O.*

(ii) *NaCl - $CaCl_2$ – Glycine - H_2O.*

(iii) *NaCl - $SrCl_2$ - Glycine - H_2O.*

(iv) *NaCl - $MgCl_2$ - Alanine - H_2O.*

(v) *NaCl - $CaCl_2$ - Alanine - H_2O.*

(vi) *NaCl - $SrCl_2$ – Alanine - H_2O.*

(vii) *NaCl - $MgCl_2$ - L-Valine - H_2O.*

(viii) *NaCl - $CaCl_2$ - L-Valine - H_2O.*

(ix) *NaCl - $SrCl_2$ - L-Valine - H_2O.*

Were studied by emf method and the activity coefficients, osmotic coefficients were studied in these mixed electrolyte solutions.

In the quaternary systems studied, the activity coefficients of NaCl are increased by the addition of $MgCl_2$, $CaCl_2$, and $SrCl_2$.

This increasing effect is in the order

$$MgCl_2 > CaCl_2 > SrCl_2.$$

These trends in the activity coefficients of the mixed electrolyte solutions studied in the present work could be explained as follows:

An examination of the activity coefficients of the single salt solutions reveal that the activity coefficients of aqueous alkaline earth metal chlorides are in the order

$$MgCl_2 > CaCl_2 > SrCl_2$$

This is in the order of increasing crystallographic radii i.e., $Mg^{+2} = 0.65$ A, $Ca^{+2} = 0.99$A and $Sr^{+2} = 1.13$A. An ion with a smaller radius will have a higher charge density and therefore a greater tendency to hydrate. The hydration increases γ values in two ways:

(i) It increases the 'effective mean diameter' of the Debye-Huckel theory and

(ii) It removes water from the role of the solvent and makes it a part of the solvated ion so that the effective concentration of the solution is increased.

These trends in the activity coefficients of pure electrolyte solutions clearly explains all the trends observed in γ values of the mixed electrolyte solutions studied in the present work.

The discussion presented in section-A to C clearly indicates that the Pitzer single electrolyte parameters $\beta^{(o)}$, $\beta^{(1)}$ and C^{ϕ} and Pitzer interaction parameters (S_{θ} and Ψ) are useful in predicting the thermodynamic properties of the multicomponent electrolyte solutions.

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