

# EVALUATION OF EXCESS GIBBS ENERGY VALUES OF SOME AQUEOUS SULPHATES, CHLORIDES AND NITRATES AT 298K USING THE EXTENSION OF LU AND MAURER MODEL

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## ABSTRACT

The model proposed by Lu and Maurer (1993) for aqueous electrolyte solutions is extended to calculate excess Gibbs energy values of some aqueous Sulphates, Chlorides and Nitrates whose mean activity and osmotic coefficient values are evaluated from Pitzer's model. All excess Gibbs energy values are negative in sign. Hence the system is tending to absorb energy from environmental source point and is performing work on the system to create internal physiochemical changes. The plots presented also revealed that this absorption of energy is progressively increasing. **Keywords:** Pitzer Model, Activity Coefficient, Osmotic Coefficient, Debye- Huckel Theory, Dielectric Constant, Eigen Tamm Ion Pair Mechanism (ETIPM).

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## INTRODUCTION

Due to their wide range of potential applications, room-temperature ionic liquids (RTILs) and their mixtures with polar and non-polar components are intensively investigated and significant progress is being made during the last decade<sup>1</sup>. Several new mechanisms like the Eigen and Tamm mechanism of Ion pair formation (that won the Nobel award in Chemistry), came to lime light. Major aims of all these studies are thermodynamic and transport properties in the ionic systems<sup>2</sup>. Detailed molecular- level information on the structure and happenings at ionic levels have become available from a variety of experiments, like the various spectroscopy, computer simulations, several types of studies like the Ultrasonic ,Viscometric , Densitometry and Electrochemical to mention a few<sup>3,4</sup>. M.Inhat observed that the Viscometric hydrations decreased more rapidly with temperature, and agreed reasonably well with the thermodynamic results at low temperatures<sup>5</sup>. Our understanding of molecular motions in RTILs and their mixtures is still rather limited, to interpret the experimental findings. Major reason for that is the intrinsic complexity of this dynamics which is heterogeneous, highly collective and characterized by strong coupling of translational and rotational contributions. The present study reported by the author, in a series of communications on solute solvent interactions, mainly revolves around the objective of pursuing further in this line. This paper deals mainly about the Gibbs energy, its excess value evaluations and related results.

## EXPERIMENTAL

### Excess Gibbs Energy

In principle, activity coefficient models are excess Gibbs energy models. The activity coefficient is related to the Molar Excess Gibbs Energy  $G^E$ , by:

$$RT \ln \tilde{a}_i = [\partial n G^E / \partial n_i]_{T,P, n_j} \quad (1)$$

In this equation, all the symbols have their conventional meaning. The excess Gibbs energy of a solution is the difference between the actual Gibbs energy and the Gibbs energy of the ideal solution at the same temperature  $T$ , pressure  $P$  and composition. As reviewed by Anderko et.al, a large variety of models starting with the D-H expression, for example the UNIQUAC and the NRTL models, using two different frame works, i.e., McMillan-Mayer (M-M) framework, and Lewis –Randal (L-R) framework, for the description of the excess Gibbs energy of mixtures of molecular components<sup>6-8</sup>. Also some electrolyte models are extended as models for the excess Gibbs energy calculation. Regardless of the specific model used to describe the individual thermodynamic properties as a function of factors like concentration, temperature; it should be necessary that, the relationships between the various functions must be thermodynamically consistent. So the Thermodynamic Parameter chosen for interpretation of the final result is to be evaluated with the application of the fundamental definition of the same.

### Lu and Maurer Model and its extension

Lu and Maurer developed a new model, that combines physical interactions with solvation equilibria<sup>9</sup>. Later this model was extended<sup>10</sup>. The parameters for this model were experimentally determined, for single aqueous electrolyte solutions, at 298K. The empirical temperature dependence of this model was carefully tested by the prediction of excess enthalpy from this  $G^E$  model, with the Gibbs-Helmholtz relation. This model describes excess Gibbs energy and related properties. It was assumed that the dissolution of strong electrolytes in water results in a mixture of water molecules, unsolvated and solvated ions. Physical interactions between all the species are taken into account by combining Debye-Huckel law with the UNIQUAC model.

However the depression in the dielectric constant of the dielectric continuum of the solvent on the dissolution of the electrolyte does not figure in these calculations of Lu and Maurer<sup>11</sup>. Recently, application of our experimental data for this lowering of dielectric constant to the activity coefficient and Osmotic coefficient evaluations, gave concrete evidence of the Ion Pair formation of Eigen and Tamm mechanism<sup>12-13</sup>. Several experimental techniques support these findings, as was cited in the references therein. The Excess Gibbs energy values of the above mentioned electrolytes were evaluated by using the notation of Lu et.al., in terms of Osmotic coefficient  $\phi$  and activity coefficient  $\gamma_{\pm}$ . The relationship can be expressed as:

$$G^E = n_w m R T (1 - \phi + \ln \gamma_{\pm}) \quad (2)$$

In this equation, mean activity coefficient and osmotic coefficient values are determined from Pitzer's model<sup>14</sup>.

The relative enthalpy is related to  $G^E$  by -

$$L = -T^2 \left[ \frac{\partial G^E / T}{\partial T} \right]_{P,m} \quad (3)$$

The Apparent Relative Molar Enthalpy (ARME) that requires experimental data is given by-

$$\phi L = \frac{L}{n_w m} = v R T^2 \left[ \left( \frac{\partial \phi}{\partial T} \right) - \left( \frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{P,m} \right] \quad (4)$$

In all the above equations the notation of Prigogine, Defay and Xiaohua Lu and G. Maurer was used<sup>15</sup>.

A new excess Gibbs energy function to represent the deviations from ideality of binary electrolyte solutions was derived by Ali Haghtalab; the function consists of two contributions, the first due to long-range forces, represented by the Debye-Huckel theory, and the second due to short-range forces represented by the local composition concept<sup>16</sup>. The model is valid for the whole range of electrolyte concentrations, from dilute solutions up to saturation.

Haghtalab claims that the model consistently produces better results at higher concentration ranges in which other models deteriorate. One of the possible reasons is the implied ion pair formation mechanism, which is yet to be mathematically incorporated in to several equations, through several missing links one of whom is the dielectric property.

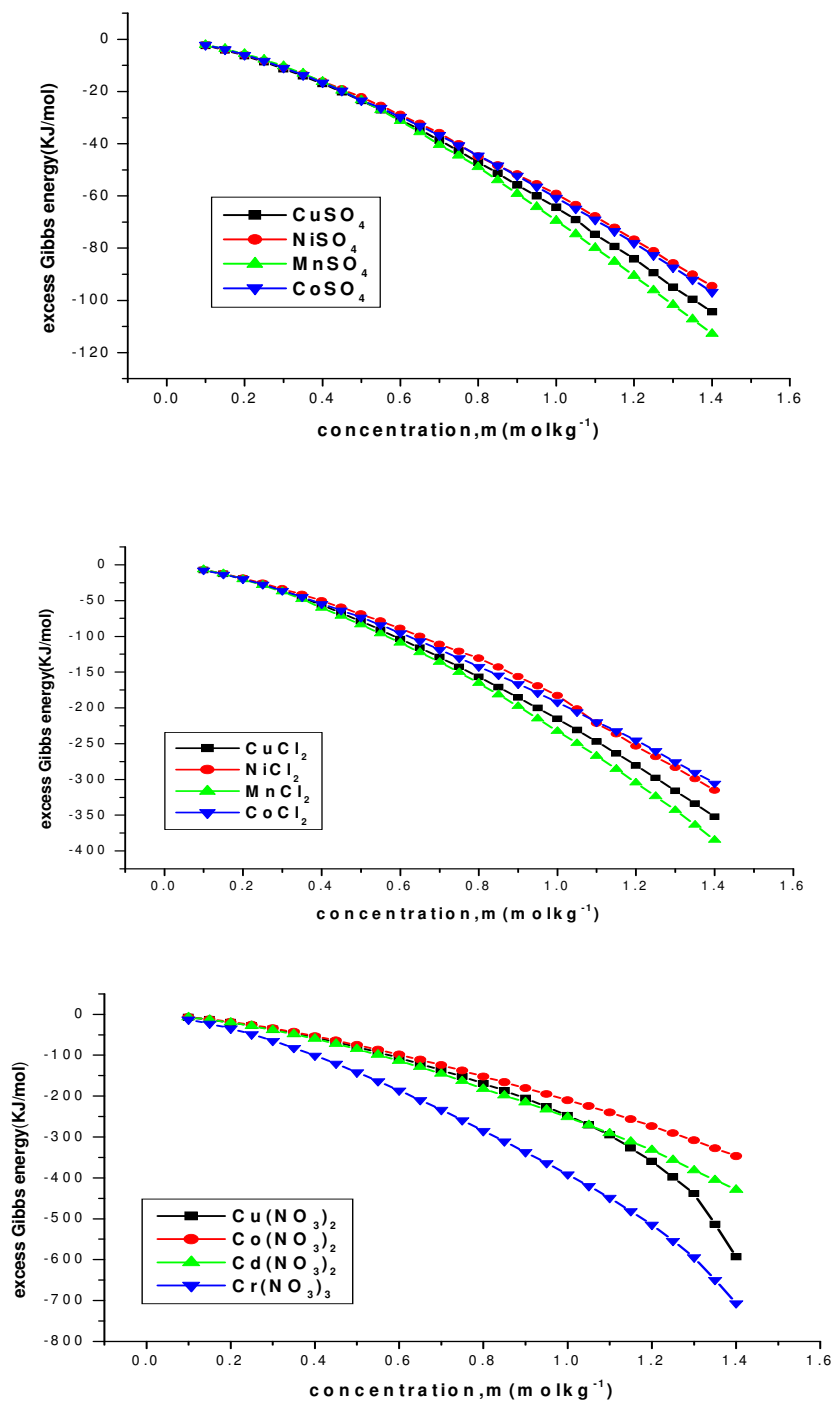


Fig.-1

According to Chen et. al., the excess Gibbs energy of an aqueous electrolyte solution may be expressed as the sum of a contribution due to long-range coulombic interactions and a contribution due to short-range interactions causing local order<sup>17</sup>.

The contribution due to long-range coulombic interactions for the molar excess Gibbs energy of an individual single ion of species 'j' can be obtained by the charging process adopted by Fowler and

Guggenheim and the excess Gibbs energy due to the short-range effects arises from molecule-molecule, molecule-ion and ion-ion interactions at high concentrations<sup>18</sup>.

According to Chen et.al, the ionic liquid system is likely to be made up of three types of cells i.e., Cation Central Cell, Anion Central Cell, and Solvent Central Cell. For an open phase in which matter is able to enter or leave, and where surface and force fields effects are negligible, differential Gibbs energy can be written as-

$$dG = -SdT + VdP + \sum_j \mu_j dn_j \quad (5)$$

Where S and V are the entropy and volume of the system and  $n_j$  denote the number of moles of species j present in the phase. This is the fundamental relation for 'G'. The partial molar Gibbs energy cannot be measured directly.

## RESULTS AND DISCUSSION

Xiaohua Lu et.al, attempted to predict activity coefficients and Enthalpies simultaneously. This model was developed by combining ionic salvation equilibriums and physical interaction forces. It is shown that by using the parameters correlated from single electrolyte aqueous systems; the activity coefficients in mixed electrolyte aqueous solutions can be accurately predicted up to the solubility limit, for example, at very high ionic strength. Even though the thermodynamic properties of 2-2 electrolytes are initially assumed to be independent of discrete chemical species of ion pairs, Spectroscopic and ultrasonic measurements reveal the existence of inner shell ion pairs. The activity coefficient and osmotic coefficient data evaluated from Pitzer model for above chosen electrolytes were used in the present model to calculate excess Gibbs energy values. The evaluated data is presented as graphs drawn between concentration (m) on abscissa and excess Gibbs energy values ( $-G^E$ ) on ordinate. All values are negative in sign. The following conclusions can be drawn from these observations.

The Negative Excess Gibbs Energy ( $-G^E$ ), implies that, Change produced in  $[G = F + pV; dG = -SdT + Vdp + \mu dn]$  is negative.

Hence the system is tending to absorb, energy from environmental source point and is performing work on the system to create internal physiochemical changes. This generates some or all of the involved parameters of its defining equation to undergo a change. Thus Entropy, Enthalpy, and Chemical potential are the basic parameters which generate measurable parameters that facilitate in this study. However every experimental technique used need not detect the physiochemical consequences always. The plots presented will only reveal that there is absorption of the energy which is progressively increasing. Obviously this absorbed excess energy is put to use in the mechanism of ETIPM.

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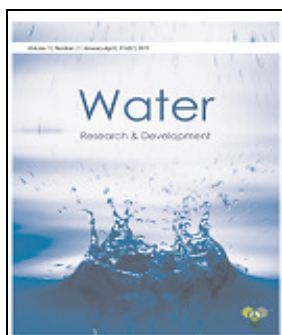
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