

**ACTIVITY MEASUREMENTS IN AQUEOUS MIXED ELECTROLYTE SOLUTIONS OF  
NaCl In  $NaCl - MgCl_2 - \beta - ALANINE - H_2O$ .**

**Dr. A. Kiran Kumar\*<sup>1</sup> and Dr. A. Swaroopa Rani<sup>2</sup>**

<sup>1</sup>Department of Chemistry, University College of Technology (Autonomous),  
Osmania University, Hyderabad-500 007, Telangana, India.

\*Corresponding author E-mail Id: drakk2010@gmail.com

<sup>2</sup>Department of Biotechnology, Jawaharlal Nehru technological university (JNTUA),  
Pulivendula, 516390, A.P, India.

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## ABSTRACT

In this paper, we have calculated Raoultian standard reduction potentials ( $E^0$ ) for NaCl and also discussed about the experimental methodology and challenges associated with the employment of an electrochemical cell to determine the activity of species in salt systems. Finally, experimental activity data is found for NaCl in  $NaCl - MgCl_2 - \beta - Alanine - H_2O$ . In order to achieve fine control over the composition of the metals being reduced at the cathode, it is important to know the key properties used by the Nernst Equation-including standard reduction potentials ( $E^0$ ) and activity/activity coefficients for each species that can be reduced onto the cathode.

**Keywords:** EMF Measurements, Pitzer Model; Electrolyte solution; Activity coefficient; Glycine, Ionic Strength.

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## INTRODUCTION

One of the major challenges for molten salt electro refining systems is the presence of a very large number of species present in solution. These species dissolved in the molten salt electrolyte may interact and complex with each other and the base NaCl-MgCl<sub>2</sub> electrolyte. There is the additional concern of the concentration dependence of these properties. It is important to develop a clear understanding of the theoretical framework within which such properties should be calculated. For understanding of the activity and activity coefficients, there must be consistency in how they are calculated and used. In this paper, we will look into the applicable theory and thermodynamics that must be used to calculate such properties for various elements that may interest us. Using the presented theory, the standard reduction potentials ( $E^0$ ) for various electrolytes are calculated and presented.

Since the early eighties, densities, vapor pressures, solubility's, and activity coefficients of amino acids and peptides in various solvents have been correlated, measured, and calculated. The modeling of such systems requires the availability of precise experimental data. As literature data does not cover the solubility and activity coefficients of all amino acids and peptides in water, some of the new data will be presented in this study.

In the case of solubility's, the gravimetric method has already been applied and proven as a suitable tool for precise and fast determination of single-solute<sup>1</sup> and multisolute<sup>1,2</sup> solubility data. The measurement of water activity coefficients is also well established. The oldest procedure is the isopiestic method applied for example, explained earlier<sup>3</sup> to aqueous electrolyte systems. However, this method is extremely time consuming for small solute concentrations. This makes it inappropriate for the systems considered in this work as many amino acids are very little soluble in water. Furthermore, there exist some vapor-pressure measurements which also provide activity coefficients. They are performed as measurement of absolute vapor pressures or by vapor-pressure depressions with high certainty<sup>4</sup> and almost no limitations with respect to concentration, solute, or solvent. However, such measurements are as difficult as they are very sensitive (e.g., to the tempering the system or to the accuracy of weighing) and additionally expensive. Recently, vapor-pressure osmometry is more and more used as an alternative possibility for the determination of activity coefficients. Because of its simplicity and reliability it has already been applied to aqueous biomolecule solutions.<sup>5</sup> For the thermodynamic modeling of amino-acid and peptide solutions, two main types of models have been applied so far: Gibbs-energy (gE) models and equations of state (EOS). Previous studies<sup>6</sup> give an excellent overview of the thermodynamic models as well as EOS applied in the recent years to calculate activity coefficients and solubilities of amino acids in aqueous solutions. For example, et al.<sup>7</sup> used the UNIFAC model combined with a Pitzer-Debye-Hu<sup>o</sup>ckel theory to calculate activity coefficients in aqueous solutions containing amino acids, sugars, and inorganic salts. Earlier studies<sup>8</sup> applied the electrolyte NRTL model to describe amino-acid solubilities of Lalanine, L-serine, and L-threonine. Other studies shown<sup>9</sup> and previous studies<sup>10,11</sup> suggested the modified Wilson model for the calculation of activity coefficients and solubilities of several amino acids in aqueous solutions that may also contain electrolytes. Both groups compared their modeling results with other gE models like UNIQUAC or UNIFAC and perturbation models of varying complexity. The reported mean root square deviations indicate that perturbation models (equation of states) yield comparably good or even better results than gE models<sup>12,13</sup>.

## MATERIALS AND REAGENTS

The amino acids  $\beta$ - Alanine (Sigma, 99%), NaCl (Sigma, 99%) and MgCl<sub>2</sub> (Sigma, 99%), were used without further purification. For the calibration of the vapor-pressure osmometer, a Sodium Chloride solution (NaCl Merck > 99.5 %) was applied. All solutions were prepared gravimetrically by weighing with an accuracy of 0.01 mg. Water from the Millipore purification system was used for the preparation of all aqueous solutions.

## EXPERIMENTAL SET-UP

### SELECTION OF REFERENCE ELECTRODE

The selection of an appropriate reference electrode is critical to reliable and reproducible cell EMF measurements. While potentials are usually calculated (as in Table I) relative to the Cl<sup>-</sup>/Cl<sub>2</sub> reference electrode, using these electrodes for measurements is difficult and impractical. The most commonly used experimental reference electrode is the Ag/AgCl reference electrode with concentrations of silver chloride fixed at a value ranging from 1 to 5 mole % AgCl with the balance being the electrolyte (LiCl-KCl). If higher concentrations of AgCl are used, the liquid junction potential can become significant and cause meaningful errors in physical measurements.

## WORKING ELECTRODE

The working electrode can be an inert rod (Mo or W). When using an inert working electrode, a reducing current is run to deposit some of the analyte metal onto this rod. After the current is stopped, the OCP can be measured for a short period of time (few seconds) as the deposited metal corrodes off. Such measurements are not necessarily 'equilibrium' measurements. Better measurements can be obtained by using a source of the metal analyte (a small rod of analyte metal) as the working electrode. This gives more stable and reproducible measurements.

Tests were performed for NaCl in NaCl - MgCl<sub>2</sub> - β- Alanine - H<sub>2</sub>O at 35 °C of interest for this paper. All of the experiments were performed in an argon atmosphere glovebox (< 0.1 ppm O<sub>2</sub>, <0.1ppm H<sub>2</sub>O). A two electrode electrochemical cell was used to make the cell EMF measurements. The working electrodes were pure metals placed in a perforated stainless steel basket. A 5 mole % Ag/AgCl reference electrodes were used. Experiments were performed at several concentrations that were progressively incremented upwards. The standard state potentials used were calculated.

## MEASUREMENT OF ACTIVITY COEFFICIENTS.

The measuring cell of the Osmomat contains two thermistors placed in a tempered closed, water-saturated atmosphere. With the help of a syringe, the thermistors are wetted, one with water and the other one with the solute solution of interest. Being at the same solvent pressure, the temperature difference between the two droplets is detected. This value can be converted into the osmotic coefficient or the solvent activity coefficient. Before carrying out the measurements, the Osmomat was calibrated with sodium chloride solutions between 0.05 and 1.2 mol/kg using reference values from literature. After that the experiments for the amino acids were performed at 300C. For each solution the measurements were repeated until a constant temperature difference could be observed. Afterward, at stable results, the measuring signal of five measurements at equal concentration were recorded and averaged. After measurement, the calibration was controlled again to exclude any baseline drifts of the apparatus. This procedure was repeated for all measured concentrations allowing for a maximum uncertainty of (2% in experimental osmotic coefficients).

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

The cell

“M electrode” | MX, H<sub>2</sub>O etc. | “X- electrode”, has a potential given by

$$E = E_0 - \frac{RT}{nF} \ln (m_M m_X \gamma_{\pm}^2)$$

Where, n is number of electrons, m<sub>M</sub> and m<sub>X</sub> are molal concentrations of ions M<sup>+</sup> and X<sup>-</sup>; γ<sub>±</sub> 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 E<sub>0</sub> is the standard electrode potential, determined by measurements in solutions of known MX activity or by extrapolation to infinite dilution.

Above equation can also be written as :

$$\gamma_{\pm}^2 = 1/ m_M m_X \exp (E - E_0) nF/RT$$

## RESULT AND DISCUSSION

*Table-1: Activity coefficients of NaCl in the NaCl-MgCl<sub>2</sub>-Alanine-H<sub>2</sub>O System at 25°C*

Conc. NaCl mol.kg <sup>-1</sup>	Conc. MgCl <sub>2</sub> mol.kg <sup>-1</sup>	Conc. Alanine mol.kg <sup>-1</sup>	EmF Volts.	y <sub>B</sub>	log <sub>γ</sub> NaCl	γ NaCl
<b>I = 0.5</b>						
0.5000	0.0000	0.0000	0.1593	0.0000	-0.0923	0.8085
0.4490	0.0170	0.0170	0.1558	0.1019	-0.0925	0.8082
0.4074	0.0309	0.0309	0.1528	0.1854	-0.0927	0.8078
0.3729	0.0424	0.0424	0.1500	0.2542	-0.0929	0.8074
0.3438	0.0521	0.0521	0.1475	0.3124	-0.0930	0.8072
0.3189	0.0604	0.0604	0.1452	0.3622	-0.0932	0.8069
0.2973	0.0676	0.0676	0.1430	0.4000	-0.0933	0.8067
0.2785	0.0738	0.0738	0.1410	0.4430	-0.0934	0.8065
0.2619	0.0794	0.0794	0.1392	0.4760	-0.0935	0.8065
0.2472	0.0843	0.0843	0.1375	0.5054	-0.0935	0.8065
0.2341	0.0886	0.0886	0.1358	0.5318	-0.0936	0.8061
0.2223	0.0926	0.0926	0.1343	0.5555	-0.0937	0.8059
0.0477	0.1508	0.1508	0.0915	0.9046	-0.0945	0.8045
0.0870	0.1377	0.1377	0.1077	0.8261	-0.0943	0.8048
0.1201	0.1266	0.1266	0.1166	0.7599	-0.0942	0.8050
0.1482	0.1173	0.1173	0.1226	0.7070	-0.0940	0.8053
0.1725	0.1092	0.1092	0.1269	0.6550	-0.0940	0.8053
0.1936	0.1021	0.1021	0.1303	0.6127	-0.0938	0.8057
0.2122	0.0959	0.0959	0.1329	0.5780	-0.0937	0.8059
0.2287	0.0904	0.0904	0.1351	0.5427	-0.0936	0.8061
<b>I = 1.0</b>						
1.0000	0.0000	0.0000	0.1911	0.0000	-0.0915	0.8101
0.8938	0.0354	0.0354	0.1876	0.1062	-0.0916	0.8099
0.8080	0.0640	0.0640	0.1845	0.1920	-0.0919	0.8093
0.7372	0.0874	0.0874	0.1817	0.2628	-0.0921	0.8089
0.6778	0.1074	0.1074	0.1792	0.3222	-0.0922	0.8087
0.6273	0.1242	0.1242	0.1768	0.3727	-0.0924	0.8083
0.5838	0.1387	0.1387	0.1747	0.4162	-0.0924	0.8083
0.5459	0.1514	0.1514	0.1727	0.4541	-0.0926	0.8079
0.5126	0.1625	0.1625	0.1708	0.4874	-0.0927	0.8077
0.4832	0.1723	0.1723	0.1691	0.5168	-0.0927	0.8077
0.4570	0.1810	0.1810	0.1675	0.5430	-0.0928	0.8075
0.4334	0.1889	0.1889	0.1659	0.5666	-0.0928	0.8075
0.0939	0.3020	0.3020	0.1239	0.9061	-0.0929	0.8073
0.1716	0.2761	0.2761	0.1400	0.8284	-0.0929	0.8073
0.2371	0.2543	0.2543	0.1489	0.7629	-0.0930	0.8072
0.2929	0.2357	0.2357	0.1548	0.7071	-0.0932	0.8069
0.3412	0.2196	0.2196	0.1591	0.6588	-0.0933	0.8067
0.3833	0.2056	0.2056	0.1624	0.6167	-0.0934	0.8065
0.4203	0.1932	0.1932	0.1651	0.5797	-0.0934	0.8065
0.4531	0.1823	0.1823	0.1672	0.5469	-0.0936	0.8061

Contd.....

Conc. NaCl mol.kg <sup>-1</sup>	Conc. MgCl <sub>2</sub> mol.kg <sup>-1</sup>	Conc. Alanine mol.kg <sup>-1</sup>	EmF Volts.	y <sub>B</sub>	log <sub>y</sub> NaCl	γ NaCl
<b>I = 1.5</b>						
1.5000	0.0000	0.0000	0.2240	0.0000	-0.0909	0.8111
1.7805	0.0732	0.0732	0.2205	0.0880	-0.0910	0.8109
1.6045	0.1318	0.1318	0.2173	0.1789	-0.0912	0.8106
1.4601	0.1800	0.1800	0.2145	0.2444	-0.0914	0.8102
1.3396	0.2201	0.2201	0.2120	0.3023	-0.0916	0.8098
1.2374	0.2542	0.2542	0.2097	0.3461	-0.0918	0.8095
1.1497	0.2834	0.2834	0.2076	0.3932	-0.0919	0.8093
1.0737	0.3088	0.3088	0.2056	0.4316	-0.0920	0.8091
1.0070	0.3310	0.3310	0.2038	0.4672	-0.0921	0.8089
0.9482	0.3506	0.3506	0.2021	0.4955	-0.0921	0.8089
0.8958	0.3681	0.3681	0.2004	0.5194	-0.0922	0.8087
0.8490	0.3837	0.3837	0.1989	0.8927	-0.0931	0.8070
0.1861	0.6046	0.6046	0.1579	0.8162	-0.0929	0.8074
0.3405	0.5532	0.5532	0.1739	0.8297	-0.0927	0.8077
0.4707	0.5098	0.5098	0.1826	0.7460	-0.0926	0.8079
0.5820	0.4727	0.4727	0.1884	0.6980	-0.0925	0.8081
0.6781	0.4406	0.4406	0.1927	0.6429	-0.0924	0.8083
0.7621	0.4126	0.4126	0.1959	0.6030	-0.0923	0.8085
0.8360	0.3830	0.3830	0.1985	0.5720	-0.0922	0.8077
0.9016	0.3661	0.3661	0.2006	0.5412	-0.0922	0.8077
<b>I = 2.0</b>						
2.0000	0.0000	0.0000	0.2444	0.0000	-0.0902	0.8125
2.6759	0.1080	0.1080	0.2410	0.1019	-0.0904	0.8120
2.4149	0.1950	0.1950	0.2379	0.1854	-0.0906	0.8116
2.2004	0.2665	0.2665	0.2352	0.2542	-0.0908	0.8113
2.0208	0.3264	0.3264	0.2328	0.3124	-0.0909	0.8111
1.8684	0.3772	0.3772	0.2305	0.3622	-0.0911	0.8107
1.7373	0.4209	0.4209	0.2285	0.4000	-0.0912	0.8105
1.6234	0.4589	0.4589	0.2266	0.4430	-0.0914	0.8102
1.5236	0.4921	0.4921	0.2248	0.4760	-0.0915	0.8100
1.4353	0.5216	0.5216	0.2231	0.5054	-0.0916	0.8098
1.3567	0.5478	0.5478	0.2216	0.5555	-0.0917	0.8096
1.2862	0.5713	0.5713	0.2201	0.5713	-0.0926	0.8080
0.2829	0.9057	0.9057	0.1798	0.9046	-0.0924	0.8084
0.5170	0.8277	0.8277	0.1956	0.8261	-0.0922	0.8087
0.7140	0.7620	0.7620	0.2042	0.7620	-0.0921	0.8089
0.8821	0.7060	0.7060	0.2098	0.7599	-0.0919	0.8093
1.0271	0.6576	0.6576	0.2140	0.7070	-0.0918	0.8095
1.1535	0.6155	0.6155	0.2171	0.6550	-0.0918	0.8095
1.2647	0.5784	0.5784	0.2196	0.6127	-0.0917	0.8097
1.3633	0.5456	0.5456	0.2217	0.5780	-0.0917	0.8097

### Treatment of Data

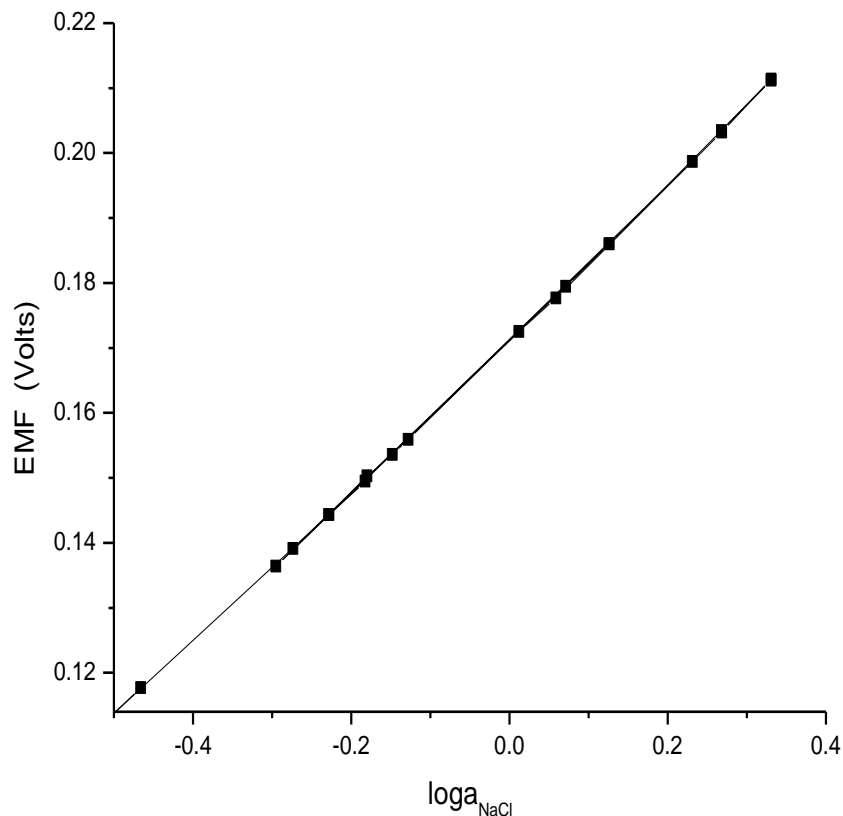
The EMF of sodium ion-selective electrode vs the  $Ag/AgCl$  electrode in  $MX-NY_2$  solution is given by the relation:

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

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 ( $\cong -40mV$ ) are very low as compared to the emfs obtained ( $\cong 125mV$ ) in the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> sets. Thus equation reduces to:

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

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  $E_0$  is the EMF due to the  $MX$  solution at unit activity. For the calibration run in the first set at each ionic strength, the Emf of the aqueous  $NaCl$  solutions were measured. The pure electrolytes activity coefficients of  $NaCl$  were taken from literature. The selectivity coefficient ( $K$ ) values for all second salt solutions and the all the ionic strengths studied were in the range of  $10^{-5}$  to  $10^{-4}$ .



**Fig-1** Variation of  $\log a_{NaCl}$  in the system  $NaCl-H_2O$  at  $25^\circ C$

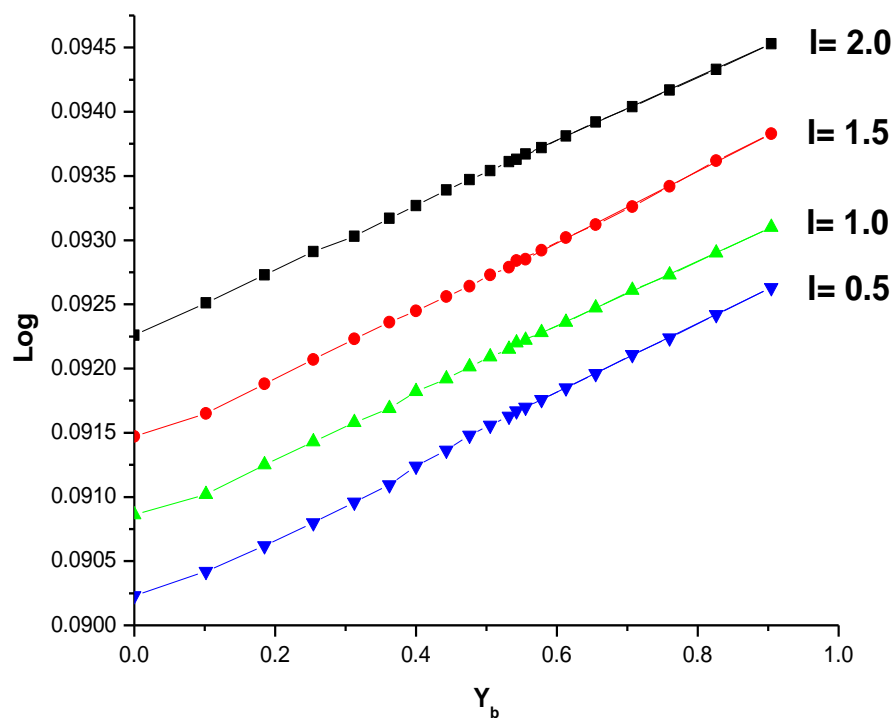
The experimentally determined activity coefficient data of NaCl in these mixtures were fitted to the Harned equations.

$$\log\gamma_A = \log\gamma_A^0 - \alpha_{AB}y_B - \beta_{AB}y_B^2$$

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

$$\log\gamma_A = \log\gamma_A^0 - \alpha_{AB}y_B$$

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



**Fig.-2 Variation of  $-\log NaCl$  with  $y_{MgCl_2}$  at  $25^\circ C$  in the system  $NaCl-MgCl_2-Alanine-H_2O$ .**

The activity coefficient data is further analyzed using the Pitzer equations for multicomponent electrolyte solutions and Pitzer interaction parameters viz; binary interaction parameter ( $S\theta$ ) and ternary interaction parameter ( $\phi$ ) values are evaluated. The results obtained in the present work have been summarized 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 will be explained on the basis of the crystallographic radii, charge densities and activity coefficients of the pure electrolytes. The activity coefficients of NaCl in the quaternary systems studied shows that the activity coefficient also depends 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 electrolyte solutions in several fields of practical importance.

## CONCLUSION

The trends in the activity coefficient values of NaCl in different quaternary systems is explained on the basis of crystallographic radii, charge densities and activity coefficients of pure electrolytes. The effect of added cations and anions on activity coefficient of NaCl is discussed. The analytical data obtained indicated that the majored dissolved ions having significant concentration are 4 ions  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$  and anions like  $\text{Cl}^-$ .

The Pitzer equations and necessary ion interaction parameters were used to calculate the ionic activity coefficients of dissolved cations and anions.

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

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