# Development of a Modified Pitzer Model for Enhanced Accuracy in Strong Electrolyte Systems

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## Abstract

This paper focused on enhancing Pitzer equation and its application for calculating activity and osmotic coefficients. Proposed modification specifically addresses long-range term, as expressed by Debye-Hückel equation, which accounts for size of ions in aqueous solutions. Additionally, experimental data for osmotic and activity coefficients of 103 strong electrolyte systems, including 1-1, 1-2, 2-1, 2-2 and 3-1 electrolytes, as well as 27 ternary systems, were herein correlated. Results obtained from the modified model were compared with those from original Pitzer parameters and other existing models. Improved thermodynamic model demonstrated significant utility in efficiently computing activity and osmotic coefficients, offering an accurate representation of deviations from ideality in electrolyte solutions. Furthermore, the modified model enabled precise predictions of salt solubility in aqueous solutions containing multiple electrolytes.

***Keywords***: osmotic and activity coefficients; Pitzer model; strong electrolytes; thermodynamic modeling.

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## Introduction

Electrolyte solutions find applications across physical sciences, including chemistry, geology and material science. They play a crucial role in numerous engineering fields, especially in chemical, biochemical and hydrometallurgical applications. Moreover, they are essential in electrical and petrochemical engineering, as well as in water hydrolysis for hydrogen production. Efficiently managing and monitoring industrial processes involving electrolytic solutions demands either experimental data or a model capable of accurately regenerating data that describes non-ideal behavior in mixtures associated with these processes. Undoubtedly, opting to develop a model emerges as the most economically efficient approach.

Several models have been developed and presented in literature for aqueous solutions of electrolyte systems [1-21]. Most of them include a term expressing short-range interactions while utilizing Debye–Huckel equation [1] to account for long-range interactions. Well-known models employed in literature are Pitzer [8-11], Electrolyte–NRTL [12, 13], eUniquac [14-16], Pitzer-Simonson Clegg [17, 18], NRTL-NRF [19] and modified Wilson model for electrolytes [20, 21].

Pitzer model is widely employed to describe electrolytic aqueous solutions [8-11, 22-33]. Its expression utilizes Virial equation for short-range term and includes two non-linear parameters that are fixed (α and b), along with three other linear parameters $\beta^{(0)}$, $\beta^{(1)}$ and $C_{MX}^{\phi}$adjusted based on experimental data. Numerous studies discussed in literature aim to enhance this thermodynamic model [22-33].

Pitzer model has been recently investigated by [22], aiming to establish correlations between its parameters and thermodynamic properties of the solution. Authors analyzed both original and optimized parameters from osmotic coefficient data for simplified Pitzer models, excluding third virial coefficient. However, the paper, while appropriately addressing osmotic coefficient, lacks discussion on activity coefficient, limiting comprehensive understanding of chemical phenomena in aqueous solutions.

Pitzer interaction parameters have been re-estimated by [23] for 93 electrolyte systems 1-1 through least-squares analysis of experimental osmotic coefficient data at 25 °C. Authors have provided a table of Pitzer parameters and their associated standard errors, derived from published data. They have concluded that newly estimated Pitzer parameters consistently illustrate enhanced fits compared to published interaction parameters values, and quality of the fit consistently exceeds that attained with earlier parameters. They have deduced that differences between their estimated parameters and published values primarily center around (1) parameter, and relative standard error in (1) parameter depends on maximum molality.

Tests on Pitzer model have been conducted by [24, 25], treating coefficient b in Debye-Hückel equation as an unknown parameter. In these studies, modifications have been made to short-range contribution by omitting third virial parameter $C_{MX}^{\phi}$, and it has been concluded that optimal b values, differing from traditional 1.2, enhance precision in linear model.

Accuracy of Pitzer model in describing thermodynamic properties of aqueous electrolyte solutions has been assessed by [26], focusing on mean ionic activity coefficient using experimental data. While appropriately addressing activity coefficient, the paper unfortunately neglects osmotic coefficient, hindering a comprehensive understanding of chemical phenomena. Limited to type 1-1 electrolytes, it narrows its scope, omitting crucial information on other electrolyte systems, thereby restricting its relevance.

As universal parameter b is not a measurable quantity, its value is chosen to be 1.2, being theoretically linked to the distance at which significant ion-ion repulsion forces begin. The value of this parameter is determined based on average distance of approach from two ions of opposite charge, which is assumed to be the same for all ions in the system. This parameter is introduced by Debye-Hückel factor to account for the distance of closest approach, being considered as proportional to ion size. Debye-Hückel equation for estimating ionic activity coefficients has been revised and extended by [34], considering diameter of hydrated ions. A higher-order parameter extended Debye–Hückel equation has been used by [35-39] to describe osmotic coefficient and mean activity coefficients of uni-univalent electrolytes in water at 25 °C. Constant in Debye–Hückel equation related to the distance of closest approach is considered an unknown parameter, being adjusted for each single electrolyte system [24, 25, 35-39].

The aim of the present study was to modify long-range term of Pitzer model by incorporating considerations for ion size. Effective diameter of hydrated ion has been integrated, as outlined by [34]. Parameter optimization process for modified model involved using experimental data from various sources [35-41], at a temperature of 298.15 K.

## Thermodynamic model framework

Excess Gibbs energy equation given by Pitzer model [8-11] for a solution containing $n_w$ kg of solvent and $n_i$, $n_j$,... moles of solute species i, j,... is expressed as follows:

$$\frac{G^{ex}}{RT} = n_w f_{D-H}(I) + \frac{1}{n_w}\sum_{ij}\lambda_{ij}(I) n_i n_j + \frac{1}{n_w^2}\sum_{ijk}\mu_{ijk}(I) n_i n_j n_k \qquad (1)$$

where $\lambda_{ij}(I)$ and $\mu_{ijk}$ represent short-range binary and ternary interaction parameters, respectively, which parameters are analogous to second and third virial coefficients. I is ionic strength given as:

$$I = \frac{1}{2}\sum_i m_i z_i^2 \qquad (2)$$

where $m_i$ and $z_i$ are the molality and the charge of ion i, respectively.

In 1923, Debye and Hückel [1] have proposed a foundational theory concerning strong electrolytes, fully dissociated in the solvent, applied to highly diluted solutions. The theory addressed interionic attraction, emphasizing electrostatic forces between oppositely charged ions, leading to organized ion distribution and crucial potential energy considerations. Hückel has later refined the theory by introducing a term accounting for decreased dielectric constant due to increased concentration, addressing short-range effects in ion-solvent and ion-ion interactions. Several studies proposed modifications to Debye–Hückel equation [24, 25, 35-39], so as to enhance its applicability across various concentrations. Adjustments typically involve key parameters like Debye-Hückel constant (A) and factor b (distance of closest approach). Some authors arbitrarily set Debye-Hückel parameter at 1.2, while others, like in the works reported by [24, 25], argue for variations based on solute-solvent systems, challenging conventional value, especially at higher concentrations. Constant b considers hydrated ion radius, commonly assumed to be 3.04 Å [42] or 4.0 Å [43]. However, different studies suggest a range from 2.5 to 11 Å [34] or 3.5 to 6.2 Å [44]. In this work, Debye-Huckel equation was modified to accommodate ion size, expressing it as the mean between anion and cation contributions:

$$f_{D-H}(I) = -\sum_{i=c,a}\left[\nu_i \frac{4A_\phi I}{B\cdot r_i}\ln\left(1+B\cdot r_i I^{1/2}\right)\right]\Big/\nu \qquad (3)$$

where $A_\phi$ is Debye-Huckel constant (0.39095 at 298.15 K), $r_i$ is hydrated radius, $\nu_i$ is number of ion i per molecule of electrolyte and $\nu = \nu_c + \nu_a$. B is a constant ($B=\sqrt{\frac{8\cdot\pi\cdot e^2\cdot N_a\cdot\rho_0}{1000\cdot\varepsilon\cdot K_b\cdot T}}$), ε is dielectric costant, $N_a$ is Avogadro number, $K_b$ is Boltzmann constant, e is electronic charge, $\rho_0$ is solvent density and T is temperature in K. Value of B is equal to 0.3287 [45, 46]. Activity and osmotic coefficients were obtained by derivation of excess Gibbs energy given by Eq. (1):

$$\phi - 1 = -\frac{1}{\sum_I m_i}\left(\frac{\partial\left(G^{ex}/RT\right)}{\partial n_w}\right) \qquad (4)$$

$$\ln(\gamma_i) = \left(\frac{\partial\left(G^{ex}/RT\right)}{\partial n_i}\right) \qquad (5)$$

Several simplifications were employed when developing original Pitzer model [8]. Expressions detailing osmotic coefficient of single electrolytes are provided as follows:

$$\phi - 1 = z_M z_X f^{\phi}_{D-H} + 2m\left(\frac{\nu_M \nu_X}{\nu}\right)\beta^{\phi}_{MX} + 2m^2\left(\frac{\left(\nu_M \nu_X\right)^{3/2}}{\nu}\right)C^{\phi}_{MX} \qquad (6)$$

$$\ln(\gamma_{MX}) = z_M z_X f^{\gamma}_{D-H} + 2m\left(\frac{\nu_M \nu_X}{\nu}\right)\beta^{\gamma}_{MX} + 2m^2\left(\frac{\left(\nu_M \nu_X\right)^{3/2}}{\nu}\right)C^{\gamma}_{MX} \qquad (7)$$

where terms $f^{\phi}_{D-H}$ and $f^{\gamma}_{D-H}$ are:

$$f^{\phi}_{D-H} = \frac{1}{2}\left[f'_{D-H} - \left(\frac{f_{D-H}}{I}\right)\right] = \frac{-A_\varphi\sqrt{I}}{\nu}\left(\frac{\nu_M}{1+\beta\cdot r_M\sqrt{I}} + \frac{\nu_X}{1+\beta\cdot r_X\sqrt{I}}\right) \qquad (8)$$

$$f^{\gamma}_{D-H}=\frac{1}{2}f^{'}_{D-H}=-\frac{A_{\varphi}}{\nu}\left[\begin{array}{l}\nu_M\left(\dfrac{\sqrt{I}}{1+\beta\cdot r_M\sqrt{I}}+\dfrac{2}{\beta\cdot r_M}\ln\left(1+\beta\cdot r_M\sqrt{I}\right)\right)\\+\nu_X\left(\dfrac{\sqrt{I}}{1+\beta\cdot r_X\sqrt{I}}+\dfrac{2}{\beta\cdot r_X}\ln\left(1+\beta\cdot r_X\sqrt{I}\right)\right)\end{array}\right] \tag{9}$$

Second Virial coefficient, $B_{MX}$, is empirically determined and influenced by ionic strength. Pitzer [8] has formulated a model for electrolytes, introducing specific interaction parameters, $\beta^{(0)}$ and $\beta^{(1)}$, where $\alpha_1$ is associated with $\beta^{(1)}$ and equals 2.0 $kg^{1/2}/mol^{-1/2}$. These parameters correspond to second Virial coefficient, $B_{MX}$, along with $C_{\phi}$, which corresponds to third Virial coefficient, $C_{MX}$. Values for these parameters have been determined by [9] for various electrolytes, and optimized by using data from literature [47]. Finally, $B_{MX}$ parameter was calculated as follows:

$$\beta^{\phi}_{MX}=\beta^{(0)}_{MX}+\beta^{(1)}_{MX}\exp\left(-\alpha_1\sqrt{I}\right) \tag{10}$$

$$\beta^{\gamma}_{MX}=2\beta^{(0)}_{MX}+\frac{2\beta^{(1)}_{MX}}{\alpha_1^2 I}\left[1-\left(1+\alpha_1\sqrt{I}-\frac{1}{2}\alpha_1^2 I\right)\exp\left(-\alpha_1\sqrt{I}\right)\right] \tag{11}$$

In 1974, [9] have introduced a parameter with an associated parameter, $\alpha_2$, equal to 12 $kg^{1/2}/mol^{-1/2}$ for type 2-2 electrolytes. In this context, $\alpha_1$ is set at 1.4 $kg^{1/2}/mol^{-1/2}$ to replicate the behavior of these electrolytes at molalities below 0.1 $mol/kg^{-1}$.

$$\beta^{\phi}_{MX}=\beta^{(0)}_{MX}+\beta^{(1)}_{MX}\exp\left(-\alpha_1\sqrt{I}\right)+\beta^{(2)}_{MX}\exp\left(-\alpha_2\sqrt{I}\right) \tag{12}$$

$$\begin{aligned}\beta^{\gamma}_{MX}=2\beta^{(0)}_{MX}&+\frac{2\beta^{(1)}_{MX}}{\alpha_1^2 I}\left[1-\left(1+\alpha_1\sqrt{I}-\frac{1}{2}\alpha_1^2 I\right)\exp\left(-\alpha_1\sqrt{I}\right)\right]\\&+\frac{2\beta^{(2)}_{MX}}{\alpha_2^2 I}\left[1-\left(1+\alpha_2\sqrt{I}-\frac{1}{2}\alpha_2^2 I\right)\exp\left(-\alpha_2\sqrt{I}\right)\right]\end{aligned} \tag{13}$$

Third virial coefficient, $C^{\phi}_{MX}$, contributes to computation of osmotic coefficient and activity coefficient, although it is independent of ionic strength. $C^{\gamma}_{MX}$ is calculated using the following relation:

$$C^{\gamma}_{MX}=\frac{3}{2}C^{\phi}_{MX} \tag{14}$$

Eqs. (6-14) represent expressions for osmotic and activity coefficients in modified Pitzer model. The model requires three binary interaction parameters $\beta^{(0)}$, $\beta^{(1)}$ and $C^{\phi}_{MX}$ at room temperature for single electrolyte systems, 1:1, 1:2, 2:1, and 1:3, and four parameters, $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and $C^{\phi}_{MX}$, for single electrolyte systems 2:2. Hydrated radii of ion, which are involved in modified Debye-Huckel expression, were taken from [34] and are presented in Table 1. To determine interaction parameters on single salt systems, a nonlinear least squares method employing

Particle Swarm Optimization (PSO) algorithm [48,49] is utilized. This approach fits the model to experimental values of ionic activity ($\gamma_{\pm}$) and osmotic coefficients ($\phi$) at a given temperature. Optimization process minimizes sum of squared deviations from experimental data, as defined by objective function $F\left(\beta^{(0)},\beta^{(1)},\beta^{(2)},C^{\phi}_{MX}\right)$:

$$F\left(\beta^{(0)},\beta^{(1)},\beta^{(2)},C^{\phi}_{MX}\right)=\sum_{i=1}^{ndata}\left[\begin{array}{c}\left(\dfrac{\left(\ln\gamma^{cal}_{\pm,i}\left(\beta^{(0)},\beta^{(1)},\beta^{(2)},C^{\phi}_{MX}\right)\right)-\left(\ln\gamma^{exp}_{\pm,i}\right)}{\left(\ln\gamma^{exp}_{\pm,i}\right)}\right)^{2}+\\ \left(\dfrac{\phi^{cal}_{MX,i}\left(\beta^{(0)},\beta^{(1)},\beta^{(2)},C^{\phi}_{MX}\right)-\phi^{ex}_{MX,i}}{\phi^{ex}_{MX,i}}\right)^{2}\end{array}\right] \tag{15}$$

where ndata represents total number of data points.

**Table 1:** Hydrated radii of ion involved in modified Debye-Huckel expression, as taken from [34].

| **Ions** | **Parameter $a_i$** |
|---|---|
| $H^+$ | 9 |
| $Li^+$ | 6 |
| $Rb^+$, $CS^+$, $NH_4^+$, $Tl^+$, $Ag^+$ | 2.5 |
| $K^+$, $Cl^-$, $Br^-$, $I^-$, $CN^-$, $NO_2^-$, $NO3^-$ | 3 |
| $OH^-$, $F^-$, $NCO^-$, $NCS^-$, $HS^-$, $ClO_3^-$, $ClO_4^-$, $BrO_3^-$, $IO_4^-$, $MnO_4^-$,HCOO- | 3.5 |
| $Na^+$,$CdCl^+$, $ClO_2^-$, $IO_3^-$, $HCO_3^-$, $H_2PO_4^-$, $HSO_3^-$, $H_2AsO_4^-$,$CH3COO^-$ | 4.5 |
| $SO^{2-}{}_4$, $S2O^{2-}{}_3$, $S2O^{2-}{}_6$, $CrO^{2-}{}_4$,$HPO^{2-}{}_4$, $PO^{3-}{}_4$ | 4 |
| $Pb^{2+}$, $CO^{2-}{}_3$ ,$SO^{2-}{}_3$, $MoO^{2-}{}_4$ | 4.5 |
| $Sr^{2+}$, $Ba^{2+}$, $Cd^{2+}$, $S_2O^{2-}{}_4$ | 5 |
| $Ca^{2+}$,$Cu^{2+}$,$Zn^{2+}$, $Sn^{2+}$, $Mn^{2+}$, $Fe^{2+}$, $Ni^{2+}$, $Co^{2+}$, | 6 |
| $Mg^{2+}$, $Be^{2+}$, | 8 |
| $Al^{3+}$,$Fe^{3+}$, $Cr^{3+}$, $Sc^{3+}$, $Y^{3+}$, $La^{3+}$, $In^{3+}$, $Ce^{3+}$, $Pr^{3+}$, $Nd^{3+}$, $Sm^{3+}$ | 9 |

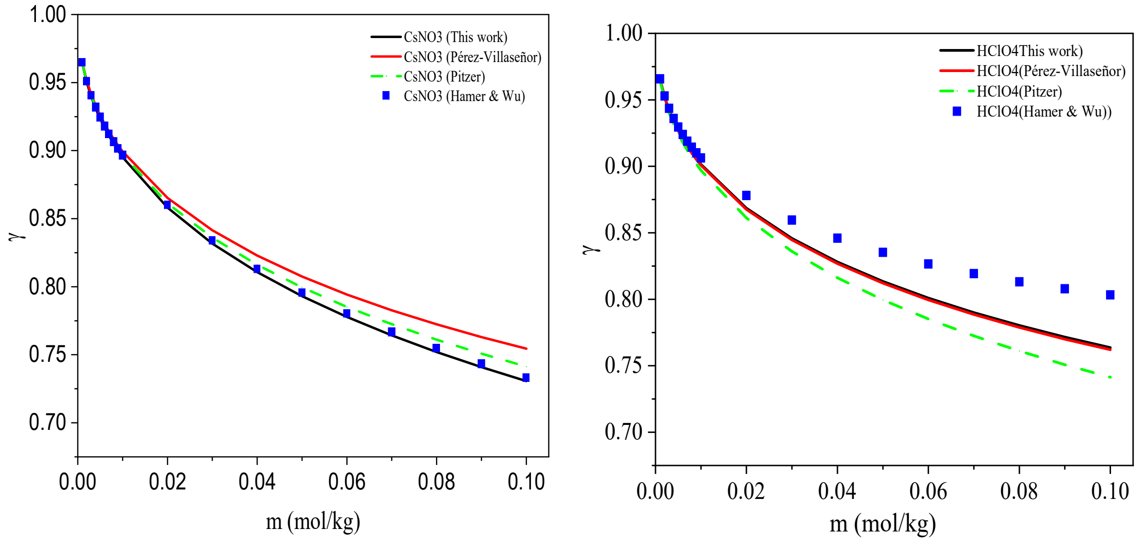
## Results and discussions

### *Estimation of single electrolyte parameters*

Interaction parameters and representation of experimental data for mean ionic activity and osmotic coefficients for 103 single electrolyte systems at 298.15 K are presented in Tables 2-6. These tables include 48 systems of type 1-1 (Table 2), 8 systems of type 1-2 (Table 3), 30 systems of type 2-1 (Table 4), 7 systems of type 2-2 (Table 5), and 10 systems of type 3-1 (Table 6). Experimental data for these systems were obtained from the literature [35-41,47].

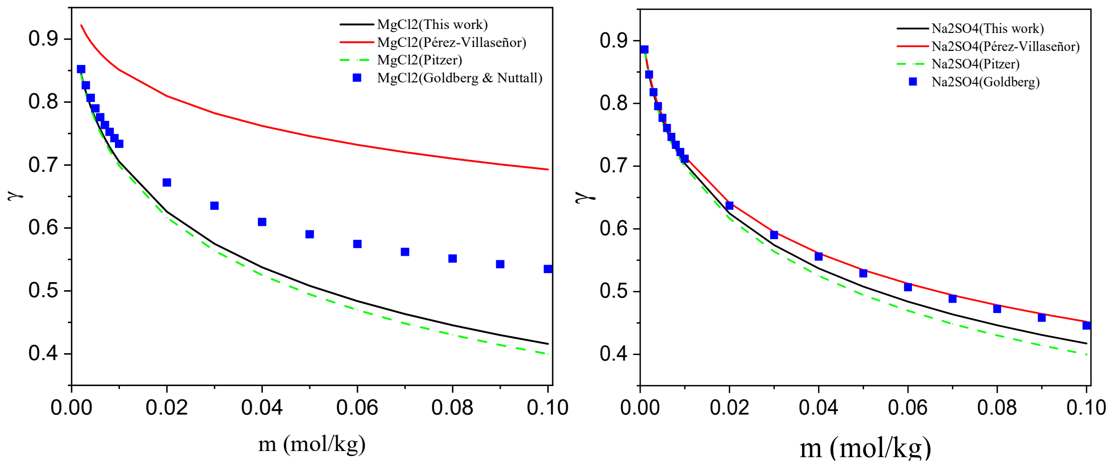
The study compares, at 298.15 K, predictions of mean ionic activity coefficients at infinite dilution obtained with different formulations of Debye–Hückel contribution: the model proposed in this work, those of [24, 25, 35-37], and original Pitzer model with b = 1.2. Unlike Pitzer model, the latter three expressions for DH contribution treat parameter b as an unknown variable, which is optimized jointly with the other parameters of Pitzer model. Figs. 1 and 2 present predicted mean ionic activity coefficient at infinite dilution using different Debye–Hückel contributions. It appears, from these figures, that DH contribution used in the present work, as well as different DH formulations that treat b as unknown, deviate from data obtained in the case of DH with b=1.2, and tend to converge toward data of [35, 36 and 37], for 1-1, $MgCl_2$-$H_2O$ and $Na_2SO_4$ systems, respectively.

Evaluated interaction parameters, and results of representation of mean ionic activity and osmotic coefficients experimental data for 103 single electrolyte systems at 298.15 – 48 systems of type 1-1, 8 systems of type 1-2, 30 systems of type 2-1, 7 systems of type 2-2, and 10 systems of type 3-1, are presented in Tables 2-6, respectively. Experimental data of osmotic and activity coefficients of these systems are collected from literature [36-41,47].



**(a)** **(b)**

**Figure 1:** Mean ionic activity coefficients at infinite dilution of single electrolytes – **(a)** $CsNO_3$ and **(b)** $HClO_4$, at 298.15 K.



**(a)** **(b)**

**Figure 2:** Mean ionic activity coefficients at infinite dilution of single electrolytes- **(a)** $MgCl_2$ and **(b)** $Na_2SO_4$, at 298.15 K.

**Table 2:** Modified Pitzer model parameters for electrolyte systems 1-1 at 298.15 K.

| **Electrolyte 1-1** | **Modified Pitzer model** | | | | | | **Pitzer model** | |
|---|---|---|---|---|---|---|---|---|
| | **$m_{max}$** | **$\beta^{(0)}$** | **$\beta^{(1)}$** | **$C^{\phi}_{MX}$** | **$\sigma_\gamma$** | **$\sigma_\phi$** | **$\sigma_\gamma$** | **$\sigma_\phi$** |
| $AgNO_3$ | 6 | -0.072 | 0.1284 | 0.0051 | 0.0012 | 0.006 | 0.007 | 0.005 |
| CsAc | 3.5 | 0.17 | 0.3741 | -0.0065 | 0.0011 | 0.001 | 0.002 | 0.001 |
| CsBr | 5 | 0.037 | 0.1704 | 0 | 0.0014 | 0.001 | 0.011 | 0.002 |
| CsCl | 6 | 0.045 | 0.1587 | -0.0009 | 0.0005 | 0.0005 | 0.002 | 0.002 |
| CsI | 3 | 0.04 | 0.1479 | -0.0053 | 0.0006 | 0.000 | 0.007 | 0.002 |
| $CsNO_3$ | 1.4 | -0.126 | 0.2236 | 0.0358 | 0.0008 | 0.001 | 0.009 | 0.003 |
| HBr | 3 | 0.188 | 0.1789 | 0.0077 | 0.0004 | 0.000 | 0.005 | 0.003 |
| HCl | 6 | 0.1887 | 0.0269 | -0.0030 | 0.0011 | 0.001 | 0.005 | 0.004 |
| $HClO_4$ | 6 | 0.157 | 0.1471 | 0.0097 | 0.0018 | 0.0016 | 0.010 | 0.002 |
| HI | 3 | 0.219 | 0.2941 | 0.0028 | 0.0004 | 0.000 | 0.013 | 0.003 |
| $HNO_3$ | 3 | 0.115 | 0.1546 | -0.0075 | 0.0007 | 0.0005 | 0.012 | 0.010 |
| Kac | 3.5 | 0.158 | 0.3189 | -0.0064 | 0.0011 | 0.001 | 0.001 | 0.001 |
| KBr | 5.5 | 0.066 | 0.3016 | -0.0023 | 0.0004 | 0.000 | 0.001 | 0.001 |
| KCl | 4.5 | 0.057 | 0.2857 | -0.0014 | 0.0006 | 0.0004 | 0.002 | 0.0009 |
| KCNS | 5 | 0.046 | 0.2756 | -0.0026 | 0.0010 | 0.001 | 0.002 | 0.001 |
| KF | 4 | 0.086 | 0.2548 | 0.0005 | 0.0004 | 0.001 | 0.002 | 0.001 |
| $KH_2PO_4$ | 1.8 | -0.111 | 0.0445 | 0.0195 | 0.0005 | 0.000 | 0.011 | 0.003 |
| KI | 4.5 | 0.084 | 0.3317 | -0.0049 | 0.0007 | 0.001 | 0.002 | 0.001 |
| $KNO_3$ | 3.5 | -0.071 | 0.141 | 0.0056 | 0.0007 | 0.001 | 0.009 | 0.003 |
| KOH | 6 | 0.162 | 0.2039 | -0.0011 | 0.0008 | 0.001 | 0.017 | 0.010 |
| LiAc | 4 | 0.092 | 0.1129 | -0.0029 | 0.0019 | 0.002 | 0.006 | 0.001 |
| LiBr | 6 | 0.171 | 0.1965 | 0.0051 | 0.0027 | 0.002 | 0.006 | 0.004 |
| LiCl | 6 | 0.144 | 0.2336 | 0.0039 | 0.0029 | 0.003 | 0.005 | 0.003 |
| $LiClO_4$ | 4 | 0.186 | 0.3259 | 0.002 | 0.0021 | 0.002 | 0.005 | 0.002 |
| LiI | 3 | 0.159 | 0.4957 | 0.0159 | 0.0028 | 0.003 | 0.016 | 0.008 |
| $LiNO_3$ | 6 | 0.137 | 0.2046 | -0.0055 | 0.0010 | 0.0010 | 0.006 | 0.003 |
| LiOH | 4.5 | 0.058 | -0.281 | -0.0074 | 0.0007 | 0.000 | 0.038 | 0.025 |
| NaAc | 3.5 | 0.117 | 0.281 | 0.0000 | 0.0041 | 0.0039 | - | - |
| NaBr | 4 | 0.095 | 0.2784 | 0.0021 | 0.0008 | 0.0007 | 0.002 | 0.002 |
| $NaBrO_3$ | 2.5 | -0.03 | 0.1845 | 0.0082 | 0.0010 | 0.001 | 0.002 | 0.001 |
| NaCl | 6 | 0.076 | 0.2657 | 0.0013 | 0.0007 | 0.0006 | 0.002 | 0.001 |
| $NaClO_3$ | 3.5 | 0.014 | 0.2551 | 0.0025 | 0.0004 | 0.000 | 0.005 | 0.001 |
| NaClO4 | 6 | 0.05 | 0.2516 | -0.0006 | 0.0008 | 0.001 | 0.001 | 0.001 |
| NaCNS | 4 | 0.097 | 0.3075 | -0.0008 | 0.0006 | 0.001 | 0.011 | 0.009 |
| NaF | 1 | 0.022 | 0.1759 | -0.0047 | 0.0003 | 0.000 | 0.001 | 0.001 |
| Na formate | 3.5 | 0.068 | 0.2834 | -0.002 | 0.0006 | 0.001 | 0.004 | 0.003 |
| $NaH_2PO_4$ | 6 | -0.064 | -0.013 | 0.0087 | 0.0053 | 0.005 | 0.010 | 0.005 |
| NaI | 3.5 | 0.127 | 0.2909 | -0.0002 | 0.0005 | 0.000 | 0.006 | 0.002 |
| $NaNO_3$ | 6 | 0.004 | 0.1909 | 0 | 0.0012 | 0.001 | 0.003 | 0.002 |
| NaOH | 6 | 0.089 | 0.2127 | 0.0032 | 0.0028 | 0.0026 | 0.007 | 0.006 |
| $NH_4H_2PO_4$ | 3.5 | -0.0707 | -0.2763 | 0.0072 | 0.0145 | 0.0048 | 0.0901 | 0.021 |
| $NH_4Cl$ | 7.4 | 0.0649 | 0.3095 | -0.0037 | 0.0008 | 0.001 | 0.0015 | 0.001 |
| $NH_4NO_3$ | 6 | 0.003 | 0.1617 | -0.0016 | 0.0015 | 0.001 | 0.012 | 0.002 |
| RbAc | 3.5 | 0.1681 | 0.3497 | -0.0061 | 0.0005 | 0.0007 | 0.003 | 0.001 |
| RbBr | 5 | 0.056 | 0.2461 | -0.0028 | 0.0008 | 0.001 | 0.001 | 0.001 |
| RbCl | 5 | 0.061 | 0.2447 | -0.0025 | 0.0005 | 0.000 | 0.001 | 0.001 |
| RbI | 5 | 0.055 | 0.2336 | -0.0024 | 0.0007 | 0.001 | 0.001 | 0.001 |
| $RbNO_3$ | 4.5 | -0.07 | 0.1203 | 0.0059 | 0.0022 | 0.002 | 0.007 | 0.003 |
| | | **Overall deviation** | | | 0.001 | 0.001 | 0.006 | 0.003 |

**Table 3:** Modified Pitzer model parameters for electrolyte systems 1-2 at 298.15 K.

| **Electrolyte 1-2** | **Modified Pitzer model** | | | | | | **Pitzer model** | |
|---|---|---|---|---|---|---|---|---|
| | **M** | **$(4/3)\beta^{(0)}$** | **$(4/3)\beta^{(1)}$** | **$(2^{2.5})/3\ C^{\phi}_{MX}$** | **$\sigma_\gamma$** | **$\sigma_\phi$** | **$\sigma_\gamma$** | **$\sigma_\phi$** |
| $(NH_4)_2SO_4$ | 4 | 0.108 | 1.325 | -0.0094 | 0.0047 | 0.007 | 0.020 | 0.004 |
| $K_2SO_4$ | 0.7 | 0.207 | 0.5081 | -0.1033 | 0.0016 | 0.001 | 0.022 | 0.007 |
| $Li_2SO_4$ | 3 | 0.121 | 0.5538 | -0.001 | 0.005 | 0.004 | 0.010 | 0.005 |
| $Na_2SO_4$ | 4 | -0.009 | 0.9316 | 0.0150 | 0.0047 | 0.005 | 0.008 | 0.009 |
| $Cs_2SO_4$ | 1.63 | 0.277 | 1.2279 | -0.0773 | 0.002 | 0.002 | 0.029 | 0.008 |
| Na2CrO4 | 4 | 0.067 | 1.3957 | 0.0166 | 0.0287 | 0.005 | 0.031 | 0.002 |
| $Na_2$S2O3 | 3.5 | 0.052 | 1.1586 | 0.0125 | 0.002 | 0.002 | 0.010 | 0.003 |
| $Rb_2SO_4$ | 1.8 | 0.202 | 1.3796 | -0.0445 | 0.0023 | 0.0020 | 0.029 | 0.007 |
| | | | | **Overall deviation** | 0.0062 | 0.0036 | 0.0215 | 0.0056 |

**Table 4:** Modified Pitzer model parameters for electrolyte systems 2-1 at 298.15 K.

| **Electrolyte 2-1** | **Modified Pitzer model** | | | | | | **Pitzer model** | |
|---|---|---|---|---|---|---|---|---|
| | **m** | **$(4/3)\beta^{(0)}$** | **$(4/3)\beta^{(1)}$** | **$(2^{2.5})/3\ C^{\phi}_{MX}$** | **$\sigma_{\gamma}$** | **$\sigma_{\phi}$** | **$\sigma_{\gamma}$** | **$\sigma_{\phi}$** |
| $BaBr_2$ | 2 | 0.447 | 1.9768 | -0.0416 | 0.0022 | 0.002 | 0.009 | 0.003 |
| $BaCl_2$ | 5.1 | 0.3529 | 1.9225 | -0.0289 | 0.009 | 0.005 | 0.022 | 0.005 |
| $BaI_2$ | 2 | 0.544 | 2.6241 | -0.0182 | 0.002 | 0.002 | 0.023 | 0.005 |
| $CaCl_2$ | 5 | 0.424 | 1.9595 | -0.00128 | 0.011 | 0.010 | 0.012 | 0.0071 |
| $CaCl_2$ | 6 | 0.424 | 1.9595 | -0.00128 | 0.0153 | 0.0152 | 0.028 | 0.0202 |
| $CaI_2$ | 2 | 0.422 | 1.9413 | -0.0037 | 0.0014 | 0.0014 | 0.255 | 0.117 |
| $Cd(ClO_4)_2$ | 1.928 | 0.504 | 2.5889 | 0.0418 | 0.0053 | 0.0018 | 0.021 | 0.005 |
| $Cd(NO_2)_2$ | 6 | -0.0097 | -2.3777 | 0.0101 | 0.0413 | 0.0132 | 0.0312 | 0.0133 |
| $Cd(NO_3)_2$ | 2.638 | 0.3928 | 2.391 | -00496 | 0.0049 | 0.0038 | 0.0055 | 0.0037 |
| $Co(ClO_4)_2$ | 3.5 | 0.6273 | 2.5231 | 0.0651 | 0.0096 | 0.0067 | 0.0453 | 0.0175 |
| $Co(NO_3)_2$ | 5.5 | 0.4103 | 2.1044 | -0.0128 | 0.0089 | 0.0057 | 0.0150 | 0.0077 |
| $CoBr_2$ | 5 | 0.5840 | 2.0905 | -0.0197 | 0.0258 | 0.0187 | 0.1585 | 0.1241 |
| $CoCl_2$ | 4 | 0.4847 | 1.8541 | -0.0298 | 0.0135 | 0.0079 | 0.0136 | 0.0109 |
| $CoI_2$ | 6 | 0.7537 | 1.6772 | -0.0297 | 0.0764 | 0.0754 | 0.2851 | 0.2322 |
| $CuBr_2$ | 3.5 | 0.5488 | 2.1369 | -0.0804 | 0.0077 | 0.0045 | 0.0173 | 0.0056 |
| $CuCl_2$ | 6 | 0.315 | 2.0801 | -0.0328 | 0.0248 | 0.023 | 0.246 | 0.203 |
| $Cu(ClO_4)_2$ | 3.5 | 06291 | 2.0435 | 0.0120 | 0.0205 | 0.0103 | 0.0317 | 0.0183 |
| $Cu(NO_3)_2$ | 6 | 0.373 | 2.0904 | -0.0155 | 0.0037 | 0.003 | 0.255 | 0.192 |
| $FeCl_2$ | 2 | 0.4670 | 1.6504 | -0.0261 | 0.0037 | 0.006 | 0.014 | 0.007 |
| $MgBr_2$ | 5 | 0.56 | 1.9122 | 0.0086 | 0.005 | 0.004 | 0.0071 | 0.004 |
| $MgCl_2$ | 5.925 | 0.458 | 1.8144 | 0.0112 | 0.0133 | 0.0071 | 0.014 | 0.006 |
| $MgI_2$ | 5 | 0.641 | 1.9746 | 0.0165 | 0.005 | 0.004 | 0.004 | 0.004 |
| $NiCl_2$ | 5 | 0.508 | 1.7399 | -0.0267 | 0.014 | 0.013 | 0.091 | 0.076 |
| $Pb(ClO_4)_2$ | 6 | 0.435 | 2.0453 | -0.0153 | 0.002 | 0.002 | 0.018 | 0.005 |
| $Pb(NO_3)_2$ | 2 | 0.078 | -0.599 | -0.0545 | 0.006 | 0.005 | 0.061 | 0.014 |
| $SrBr_2$ | 2 | 0.438 | 2.5 | 0.0072 | 0.0019 | 0.0015 | 0.011 | 0.002 |
| $SrCl_2$ | 4 | 0.39 | 2.0347 | -0.0044 | 0.005 | 0.005 | 0.034 | 0.008 |
| $SrI_2$ | 2 | 0.526 | 2.7673 | 0.0124 | 0.003 | 0.002 | 0.032 | 0.013 |
| $ZnCl_2$ | 6 | 0.121 | 2.8134 | 0.0005 | 0.026 | 0.019 | 1.966 | 1.447 |
| $Zn(ClO_4)_2$ | 4 | 0.653 | 1.997 | 0.0246 | 0.00922 | 0.0082 | 0.012 | 0.009 |
| | | **Overall deviation** | | | 0.0116 | 0.0105 | 0.1281 | 0.0888 |

**Table 5:** Modified Pitzer model parameters for electrolyte systems 2-2 at 298.15 K.

| **Electrolyte 2-2** | **Modified Pitzer model** | | | | | | **Pitzer model** | |
|---|---|---|---|---|---|---|---|---|
| | **m** | **$\beta^{(0)}$** | **$\beta^{(1)}$** | **$C^{\phi}_{MX}$** | **$\beta^{(2)}$** | **$\sigma_{\gamma}$** | **$\sigma_{\phi}$** | **$\sigma_{\gamma}$** | **$\sigma_{\phi}$** |
| $BeSO_4$ | 4 | 0.19 | 0.8707 | 0.021 | -12.5048 | 0.0024 | 0.0026 | 0.003 | 0.001 |
| $MgSO_4$ | 3 | 0.091 | 1.2462 | 0.0417 | -82.4804 | 0.004 | 0.001 | 0.121 | 0.004 |
| $MnSO_4$ | 4 | 0.11 | 1.4996 | 0.0277 | -57.6076 | 0.019 | 0.004 | 0.208 | 0.005 |
| $NiSO_4$ | 2.5 | 0.053 | 1.6331 | 0.0561 | -61.8366 | 0.004 | 0.002 | 0.049 | 0.004 |
| $CuSO_4$ | 1.4 | 0.105 | 1.2429 | 0.0285 | -50.3131 | 0.012 | 0.0015 | 0.009 | 0.003 |
| $ZnSO_4$ | 3.5 | 0.086 | 1.5074 | 0.0455 | -78.9224 | 0.060 | 0.006 | 0.101 | 0.008 |
| $CdSO_4$ | 3.5 | 0.135 | 1.5862 | 0.0195 | -46.1812 | 0.020 | 0.003 | 0.014 | 0.003 |
| | | | | **Overall deviation** | | 0.017 | 0.003 | 0.072 | 0.004 |

**Table 6:** Modified Pitzer model parameters for electrolyte systems 3-1 at 298.15 K.

| **Electrolyte 3-1** | **Modified Pitzer model** | | | | | | **Pitzer model** | |
|---|---|---|---|---|---|---|---|---|
| | **m** | **$(3/2)\beta^{(0)}$** | **$(3/2)\beta^{(1)}$** | **$(3^{2.5}/2)C^{\phi}_{MX}$** | **$\sigma_{\gamma}$** | **$\sigma_{\phi}$** | **$\sigma_{\gamma}$** | **$\sigma_{\phi}$** |
| $AlCl_3$ | 1.8 | 1.039 | 7.1101 | 0.0117 | 0.0100 | 0.0140 | 0.074 | 0.009 |
| $CeC_3$ | 2 | 0.901 | 6.4469 | -0.0714 | 0.0155 | 0.0183 | 0.091 | 0.013 |
| $CrCl_3$ | 1.2 | 1.131 | 6.2978 | -0.1462 | 0.0029 | 0.0078 | 0.047 | 0.005 |
| $Cr(NO_3)_3$ | 1.4 | 1.065 | 6.1218 | -0.1632 | 0.0065 | 0.0100 | 0.060 | 0.004 |
| $LaCl_3$ | 2 | 0.905 | 6.5037 | -0.0779 | 0.0106 | 0.0144 | 0.006 | 0.009 |
| $NdCl_3$ | 2 | 0.907 | 6.3547 | -0.0688 | 0.0110 | 0.0145 | 0.082 | 0.009 |
| $PrCl_3$ | 2 | 0.898 | 6.3966 | -0.0715 | 0.0093 | 0.0134 | 0.080 | 0.007 |
| $ScCl_3$ | 1.8 | 1.049 | 6.2873 | -0.0853 | 0.0074 | 0.0116 | 0.070 | 0.005 |
| $SmCl_3$ | 2 | 0.924 | 6.5152 | -0.0689 | 0.0110 | 0.0145 | 0.082 | 0.008 |
| $YCl_3$ | 2 | 0.946 | 6.4441 | -0.0522 | 0.0124 | 0.0155 | 0.082 | 0.010 |
| | | | **Overall deviation** | | 0.010 | 0.013 | 0.067 | 0.008 |

The performance of this model was compared to that of other models in literature by examining their standard deviations, defined as follows:

$$\sigma_\gamma = \left( \frac{\sum_{i}^{\text{Ndata}} \left( \ln \gamma_{MX}^{cal} - \ln \gamma_{MX}^{exp} \right)^2}{\text{Ndata}} \right)^{1/2} \quad \text{and} \quad \sigma_\phi = \left( \frac{\sum_{i}^{\text{Ndata}} \left( \phi_{MX}^{cal} - \phi_{MX}^{exp} \right)^2}{\text{Ndata}} \right)^{1/2} \qquad (16)$$

For comparison, interaction parameters of Pitzer model were collected from various sources [8-11, 27-33]. In most cases, despite Pitzer model and modified model sharing the same number of parameters, the model developed in this study demonstrates strong alignment with experimental data concerning mean ionic activity and osmotic coefficients in aqueous solutions. Indeed, for single 1:1 electrolyte system, the model achieves a standard deviation of around 0.001 for both activity and osmotic coefficients (Table 2). This represents a higher precision compared to original Pitzer model [8-11], which reports standard deviations of approximately 0.006 and 0.003 for activity and osmotic coefficients, respectively. As shown in Figs. 3a and 3b, both Pitzer three-parameter model and modified model are applied to fit 1:1 electrolyte, with modified model providing an increasingly improved fit over original.

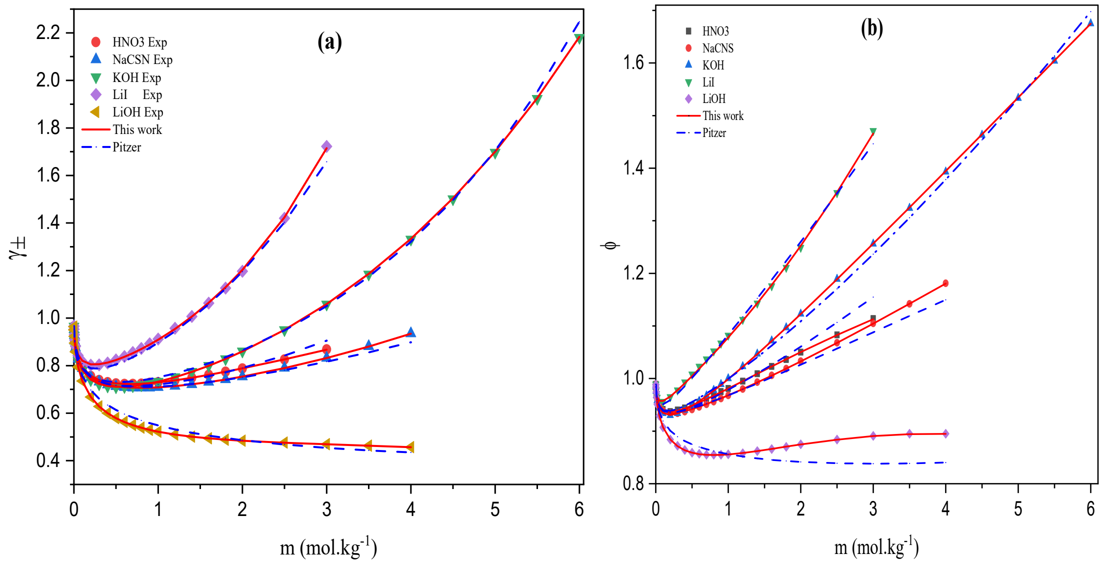


**Figure 3**: Utilization of **(a)** Pitzer three parameter model and **(b)** currently modified model in fitting 1:1 electrolyte for activity coefficients.

Standard deviations, denoted as $\sigma_\gamma$ and $\sigma_\phi$, are calculated to be 0.006 and 0.007, respectively, for systems 1-2 (Table 3). In contrast, original Pitzer model [8-11] yields values of 0.0215 and 0.0056 for same thermodynamic properties. Calculated data for activity and osmotic coefficients in $K_2SO_4$, $Rb_2SO_4$, and $Cs_2SO_4$ single systems using original Pitzer and modified models in the present work (with b = 1.2) are compared in Figs. 4a and 4b. It is clear that modified model consistently exhibits an improved fit.

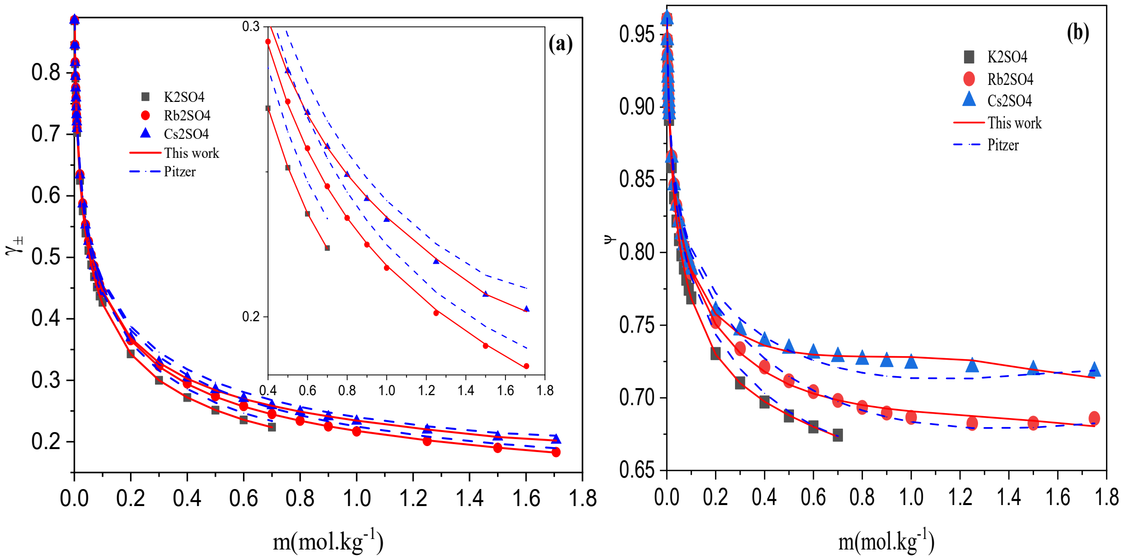


**Figure 4:** Comparison of both Pitzer three parameter and currently modified models in fitting 1:2 electrolytes for - **(a)** activity and **(b)** cosmotic coefficients.

Similarly, for systems 2-1, Table 4 indicates that the present work results in deviation standards of around 0.006 and 0.007 for osmotic and activity coefficients, respectively. In contrast, original Pitzer model [8-11] yields significantly higher values of 0.124 and 0.180 for these coefficients. Fig. 5a and 5b present results of Pitzer three-parameter and modified models in fitting 2:1 electrolyte for activity and osmotic coefficients, focusing on $CaI_2$, $CuCl_2$, $Cu(NO_3)_2$ and $SrI_2$ electrolytes. It is evident from these figures that variation of osmotic and activity coefficients is less pronounced for $CaI_2$, $CuCl_2$, $Cu(NO_3)_2$ and $SrI_2$. The use of Pitzer model parameters for simple electrolyte systems like $CaI_2$, $CuCl_2$ and $Cu(NO_3)_2$, leads to inaccuracy. However, modified model is notably more successful in correlating osmotic and activity coefficients behavior of these systems, highlighting a progressively improved fit.

As shown in Table 5, which presents standard deviation of activity coefficient and osmotic coefficient for electrolyte systems 2-2, the modified model in the present work presents deviation standards $\sigma_\gamma$ and $\sigma_\phi$ less than 0.017 and 0.003, respectively. In comparison, original Pitzer model [8-11] produces a significantly higher value of 0.072 for the activity coefficient. Figs. 6a and 6b illustrate the application of both Pitzer four-parameter model and the presently modified model in fitting 2:2 electrolytes for activity and osmotic coefficients. Both models prove to be suitable, and the modified model exhibits a progressively enhanced fit.

Table 6 shows the standard deviation for the estimation of the activity coefficient ($\gamma_{MX}$) and osmotic coefficient ($\phi_{MX}$) for systems 3-1. The values obtained in the present work are 0.01 for $\gamma_{MX}$ and 0.012 for $\phi_{MX}$. In contrast, original Pitzer model [8-11] yields values of 0.068 for $\gamma_{MX}$ and 0.008 for $\phi_{MX}$.

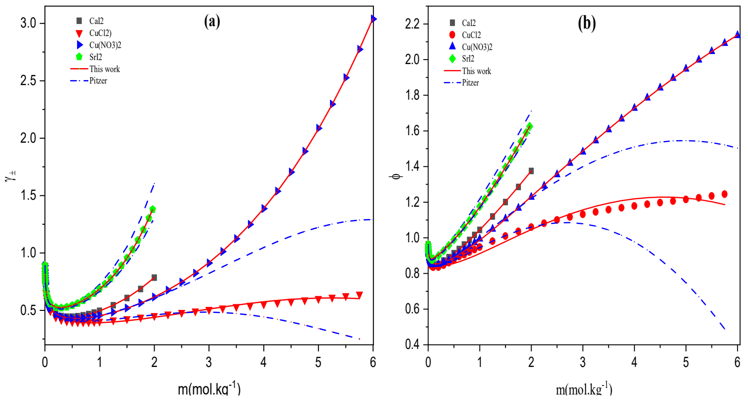


**Figure 5:** Comparison of Pitzer three parameter and currently modified models in fitting 2:1 electrolyte for - **(a)** activity and **(b)** osmotic coefficients.

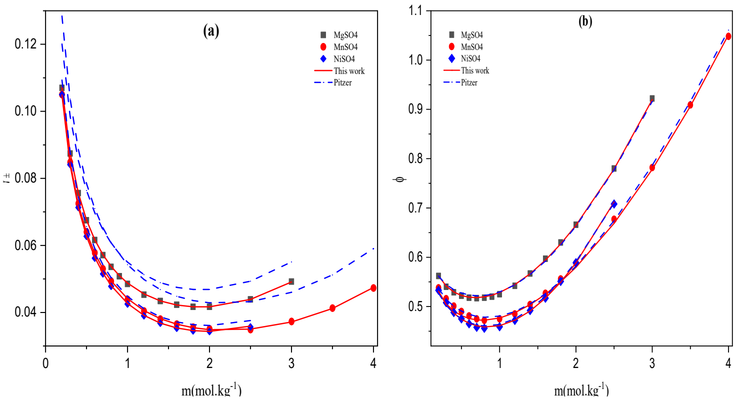


**Figure 6:** Comparison of Pitzer three parameter and currently modified models in fitting 2:2 electrolytes for - **(a)** activity and **(b)** osmotic coefficients.

Figs. 7a and 7b provide a presentation of the application of both Pitzer three-parameter and the present modified models for fitting process of 3:1 electrolyte system, specifically focusing on activity and osmotic coefficients.

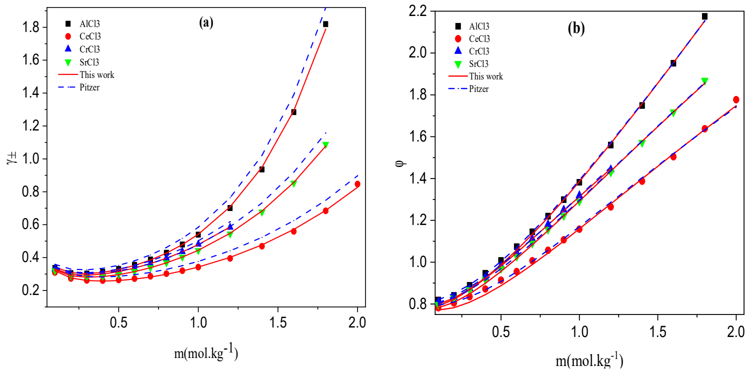


**Figure 7:** Utilization of Pitzer three parameter and currently modified models in fitting 3:1 electrolyte for - **(a)** activity and **(b)** osmotic coefficients.

The analysis indicates that both models are well-suited for the task, and modified model, in particular, exhibits a continually improved fit over observed data.
To assess the performance of modified Pitzer model developed in this study and compare it to other models in literature [5-20], standard error of correlation generated by various thermodynamic models was herein examined. This evaluation involves comparing standard deviation of several models, including original Pitzer [8], electrolyte-NRTL [12, 13], NRTL-NRF [19], Wilson [20], and modified Wilson models [21]. Parameters used in all tested thermodynamic models have been previously reported in literature [9, 12, 20, 21, 27]. Comparison results are presented in Fig. 8 for different electrolyte systems.

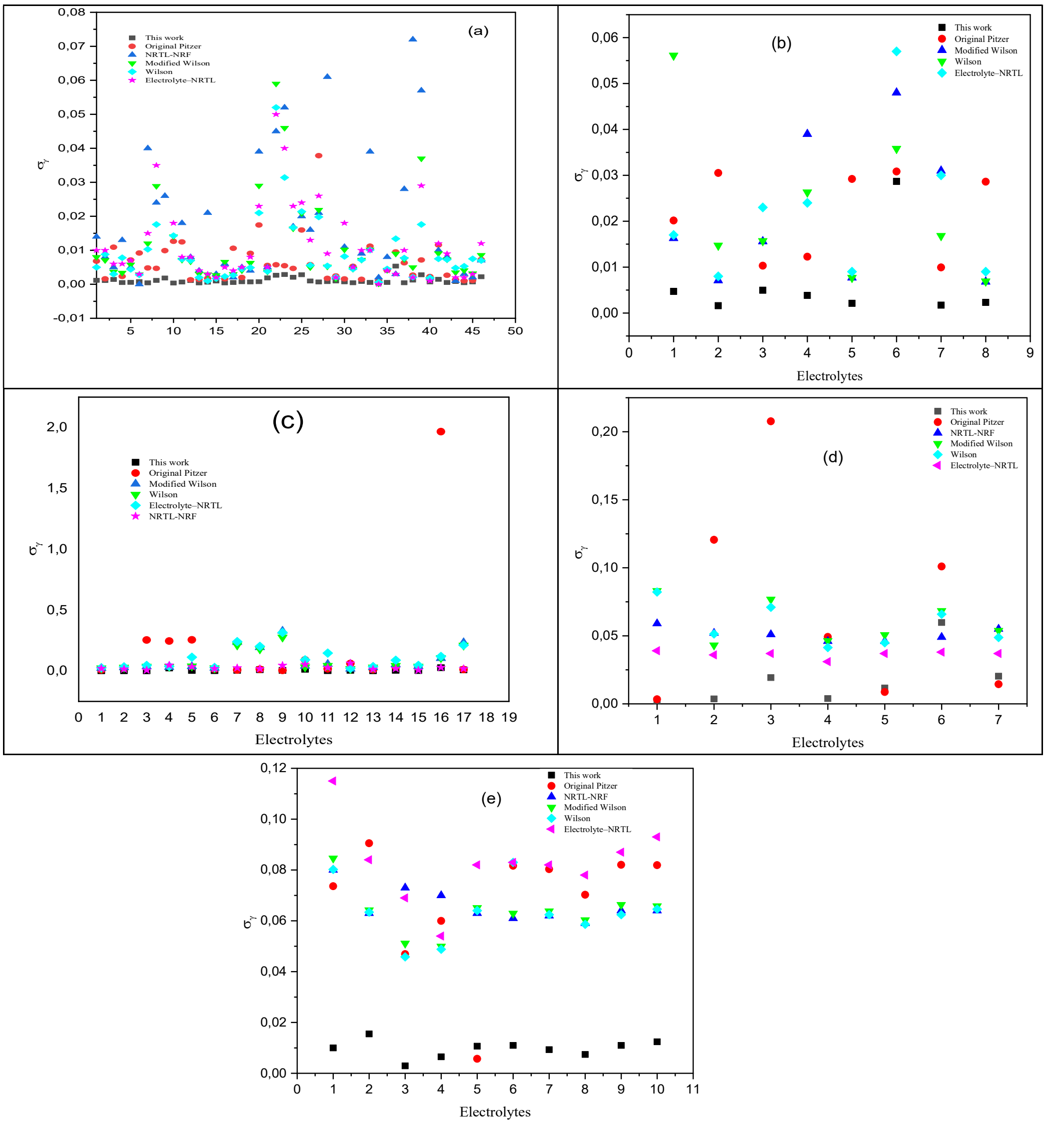


**Figure 8:** Comparison of standard deviation of fit obtained from modified with original Pitzer, NRTL, NRTL-NRF, Wilson and modified Wilson models to ionic activity coefficient data at 298.15 K for electrolyte systems - **(a)** 1-1, **(b)** 1-2, **(c)** 2-1, **(d)** 2-2 and **(e)** 3-1.

This figure compares activity coefficient for all studied systems using different thermodynamic models, including current modified Pitzer model. It is evident that modified Pitzer model is notably more effective in correlating the behavior of the activity coefficient in the studied systems compared to other thermodynamic models.

*Application for ternary electrolyte systems*

Experimental data for both osmotic and ionic mean activity coefficients, as well as solubility of salts in aqueous solution, are often found in literature for many mixed aqueous solutions. Consequently, these thermodynamic properties are commonly utilized to evaluate the effectiveness of modified Pitzer model.

Computation of activity coefficient for mixed electrolyte

The current model was used to calculate activity and osmotic coefficients for multiple components in aqueous solutions. Experimental data on mean activity and osmotic coefficients for mixed electrolyte systems were collected from literature sources [50-71]. Table 7 illustrates standard deviation between calculated and experimental data. In this comparison, standard deviation of both Pitzer model [8-11] and modified version proposed by [24, 25] was herein considered. Current model was applied with and without mixing ternary parameters, $\theta$ and $\psi$, along with the parameter previously determined from binary data. Perez-Villasenor model utilized parameters optimized from binary data. Pitzer model was employed with parameters estimated for single electrolyte systems, as well as with mixing ternary parameters, $\theta$ and $\psi$. It can be seen that current model and Perez-Villasenor one, without mixing ternary parameters, $\theta$ and $\psi$, allow to predict mean activity and osmotic coefficients of ternary electrolyte systems with an accuracy around standard deviations of Pitzer model [8-11] with mixing ternary parameters, $\theta$ and $\psi$. Optimization parameters, $\theta$ and $\psi$, in current model permit to improve precision of estimation of activity and osmotic coefficients for multiple components in aqueous solutions.

Prediction of solubility for mixed electrolyte

When a solid phase $M_{vc}X_{va}(H_2O)_h$ is in equilibrium with its saturated aqueous solution and undergoes dissociation into its anionic and cationic components, concentrations of these ionic species in the liquid phase are controlled by its solubility product:

$$\ln K_{sp} = \nu_a \ln(m_a \gamma_a) + \nu_c \ln(m_c \gamma_c) + n \ln\left(a_w\right) \qquad (17)$$

The set of interaction parameters estimated in this work for single and mixed electrolyte systems was used to predict solubility of salts in aqueous solutions at 25°C. Studied ternary systems include $NaCl–KCl–H_2O$, $NH_4Cl–NH_4H_2PO_4–H_2O$, $NaCl–NaOH–H_2O$, $NaCl–HCl–H_2O$, $KCl–HCl–H_2O$, $NaCl–CaCl_2–H_2O$, $NaCl–MgCl_2–H_2O$, $CaCl_2–HCl–H_2O$ and $MgCl_2–HCl–H_2O$, at 298.15 K. Solubility data measured and presented in literature [42, 43, 61, 62, 73-81] for these systems are used for comparison. Solubility product values of salts used in this calculation are taken from literature [42, 61, 62, 80, 81].

**Table 7:** Comparison of ternary system results from modified Pitzer model with those from other models.

| System | Data | This work | This work | | | P-V* | Pitzer | Data source |
|---|---|---|---|---|---|---|---|---|
| | | $\Theta_{MN} = \psi_{MNX} = 0$ | $\Theta_{MN}$ | $\psi_{MNX}$ | $\sigma$ | $\Sigma$ | $\sigma$ | |
| $CsCl-BaCl_2$ | $\phi$ | 0.0209 | -0.0891 | -0.0184 | 0.0023 | 0.01865 | 0.05652 | [50] |
| $HCl-CaCl_2$ | $\gamma_A$ | 0.0226 | 0.0439 | 0.0177 | 0.0031 | 0.02243 | 0.02633 | [51] |
| $HCl-MgCl_2$ | $\gamma_A$ | 0.0166 | -0.1239 | 0.0279 | 0.0436 | 0.01112 | 0.0142 | [52] |
| $HCl-MgCl_2$ | $\gamma_B$ | 0.0747 | -0.1239 | 0.0279 | 0.0255 | 0.0256 | 0.07461 | [52] |
| $KCl-MgCl_2$ | $\phi$ | 0.0467 | 0.0031 | -0.0259 | 0.0121 | 0.05431 | 0.03364 | [53] |
| $LiCl-BaCl_2$ | $\phi$ | 0.0061 | -0.0778 | 0.0227 | 0.0017 | 0.02796 | 0.04769 | [50] |
| Naacetate-Liacetate | $\phi$ | 0.0214 | 0.039 | -0.0128 | 0.0027 | 0.04247 | 0.02094 | [54] |
| $NaBr-(Me)_4NBr$ | $\phi$ | 0.0173 | 0.026 | -0.0521 | 0.0019 | 0.0232 | 0.02124 | [55] |
| $NaBr-(Me)_4NBr$ | $\gamma_A$ | 0.0213 | 0.026 | -0.0521 | 0.0034 | 0.02139 | 0.02185 | [55] |
| $NaBr-(Me)_4NBr$ | $\gamma_B$ | 0.016 | 0.026 | -0.0521 | 0.0012 | 0.04071 | 0.01511 | [55] |
| $NaBr-CaBr_2$ | $\gamma_A$ | 0.0763 | 0.0883 | -0.0285 | 0.0575 | 0.04459 | 0.06321 | [57] |
| $NaBr-CaBr_2$ | $\gamma_B$ | 0.0869 | 0.0883 | -0.0285 | 0.0447 | 0.15519 | 0.1027 | [57] |
| $NaBr-LiBr$ | $\gamma_A$ | 0.0236 | 0.1489 | -0.0932 | 0.0155 | 0.06429 | 0.02971 | [56] |
| $NaBr-LiBr$ | $\gamma_B$ | 0.0465 | 0.1489 | -0.0932 | 0.0141 | 0.04743 | 0.07766 | [56] |
| $NaCl-LiCl$ | $\phi$ | 0.0025 | 0.0099 | -0.002 | 0.0019 | 0.03995 | 0.02855 | [54,58] |
| $NaNO_3-LiNO_3$ | $\phi$ | 0.0212 | -0.0018 | -0.0034 | 0.0065 | 0.0582 | 0.03913 | [54] |
| $NaCl-LiCl$ | $\phi$ | 0.02539 | -0.0468 | 0.0059 | 0.01983 | | 0.02809 | [54] |
| $NaCl-LiCl$ | $\gamma_A$ | 0.14783 | -0.0468 | 0.0059 | 0.14917 | | 0.1495 | [54,58] |
| $NaCl-LiCl$ | $\gamma_B$ | 0.04354 | -0.0468 | 0.0059 | 0.01211 | | 0.01333 | [54,58] |
| $NH_4Cl-KCl$ | $\phi$ | 0.00514 | 0.0116 | -0.0021 | 0.00457 | | 0.01345 | [59] |
| $NH_4Cl-KCl$ | $\gamma_A$ | 0.01397 | 0.0116 | -0.0021 | 0.01175 | | 0.01826 | [59] |
| $NH_4Cl-KCl$ | $\gamma_B$ | 0.04875 | 0.0116 | -0.0021 | 0.04451 | | 0.01662 | [59] |
| $NH_4Cl-CsCl$ | $\phi$ | 0.02017 | -0.0167 | 0.0029 | 0.01095 | | 0.0136 | [60] |
| $NH_4Cl-CsCl$ | $\gamma_A$ | 0.01775 | -0.0167 | 0.0029 | 0.0177 | | 0.01555 | [60] |
| $NH_4Cl-CsCl$ | $\gamma_B$ | 0.02 | -0.0167 | 0.0029 | 0.02084 | | 0.02021 | [60] |
| $NH_4Cl -NH_4H_2PO_4$ | $\phi$ | 0.0317 | 0.0562 | 0.0088 | 0.0085 | | | [62] |
| $NH_4H_2PO_4-NH_4NO_3$ | $\phi$ | 0.0359 | 0.0216 | 0.0206 | 0.00586 | | | [62] |
| $CsCl-LiCl$ | $\phi$ | 0.04698 | 0.0537 | -0.0115 | 0.03 | | 0.03695 | [63] |
| $CsCl-LiCl$ | $\gamma_A$ | 0.09772 | 0.0537 | -0.0115 | 0.09028 | | 0.00486 | [63] |
| $CsCl-LiCl$ | $\gamma_B$ | 0.0653 | 0.0537 | -0.0115 | 0.05226 | | 0.11554 | [63] |
| $LiCl-KCl$ | $\phi$ | 0.0522 | -0.0338 | -0.0067 | 0.0152 | | 0.01693 | [64] |
| $NH_4NO_3-KNO_3$ | $\phi$ | 0.00849 | 0.014 | -0.0011 | 0.00938 | | 0.00938 | [65] |
| $NH_4NO_3-KNO_3$ | $\gamma_A$ | 0.01249 | 0.014 | -0.0011 | 0.00775 | | 0.00872 | [65] |
| $NH_4NO_3-KNO_3$ | $\gamma_B$ | 0.05075 | 0.014 | -0.0011 | 0.04737 | | 0.04583 | [65] |
| $CsCl-NaCl$ | $\phi$ | 0.02202 | 0.0529 | -0.0089 | 0.01541 | | 0.02104 | [63] |
| $CsCl-NaCl$ | $\gamma_A$ | 0.05458 | 0.0529 | -0.0089 | 0.05495 | | 0.05653 | [63] |
| $CsCl-NaCl$ | $\gamma_B$ | 0.13391 | 0.0529 | -0.0089 | 0.12575 | | 0.14633 | [63] |
| $NH_4Cl-LiCl$ | $\phi$ | 0.02976 | 0.068 | -0.0137 | 0.02664 | | 0.03338 | [66] |
| $NH_4Cl-LiCl$ | $\gamma_A$ | 0.31731 | 0.068 | -0.0137 | 0.34324 | | 0.24361 | [66] |
| $NH_4Cl-LiCl$ | $\gamma_B$ | 0.21631 | 0.068 | -0.0137 | 0.20991 | | 0.22464 | [66] |
| $NaCl-BaCl_2$ | $\phi$ | 0.09583 | -0.01 | 0.0252 | 0.08385 | | 0.08727 | [67] |
| $NaCl-BaCl_2$ | $\gamma_A$ | 0.03367 | -0.01 | 0.0252 | 0.00348 | | 0.00119 | [67] |
| $NaCl-BaCl_2$ | $\gamma_B$ | 0.13582 | -0.01 | 0.0252 | 0.09661 | | 0.09688 | [67] |
| $NaCl-MgCl_2$ | $\phi$ | 0.0167 | 0.0392 | -0.0011 | 0.01076 | | 0.0117 | [68] |
| $(NH_4)_2SO_4–K_2SO_4$ | $\phi$ | 0.05295 | -0.5873 | 0.7027 | 0.01732 | | 0.05849 | [69] |
| $NH_4NO_3-(NH_4)_2SO_4$ | $\phi$ | 0.0599 | -0.143 | 0.0062 | 0.02068 | | 0.0412 | [70] |
| $(NH_4)_2SO_4–Li_2SO_4$ | $\phi$ | 0.07588 | 0.0052 | 0.0545 | 0.03464 | | 0.07547 | [71] |
| $(NH_4)_2SO_4– Li_2SO_4$ | $\gamma_A$ | 0.01629 | 0.0052 | 0.0545 | 0.02282 | | 0.03006 | [71] |
| $(NH_4)_2SO_4– Li_2SO_4$ | $\gamma_B$ | 0.10072 | 0.0052 | 0.0545 | 0.0851 | | 0.08497 | [71] |
| $(NH_4)_2SO_4–Na_2SO_4$ | $\phi$ | 0.03333 | -0.0863 | 0.0672 | 0.0233 | | 0.03322 | [71] |

***Perez-Villasenor**

Fig. 9(a-d) shows solubility diagrams for symmetrical systems of mixed electrolytes 1-1. For $NaCl–KCl–H_2O$, $NaCl–NaOH–H_2O$, $NaCl–HCl–H_2O$ and $KCl–HCl–H_2O$ systems, NaCl and KCl were formed as solid phases. In

$NH_4Cl$–$NH_4H_2PO_4$–$H_2O$ system, crystallized salts in solubility diagram are $NH_4Cl$ and $NH_4H_2PO_4$. Experimental data were taken from literature [42, 61, 62, 72-81].

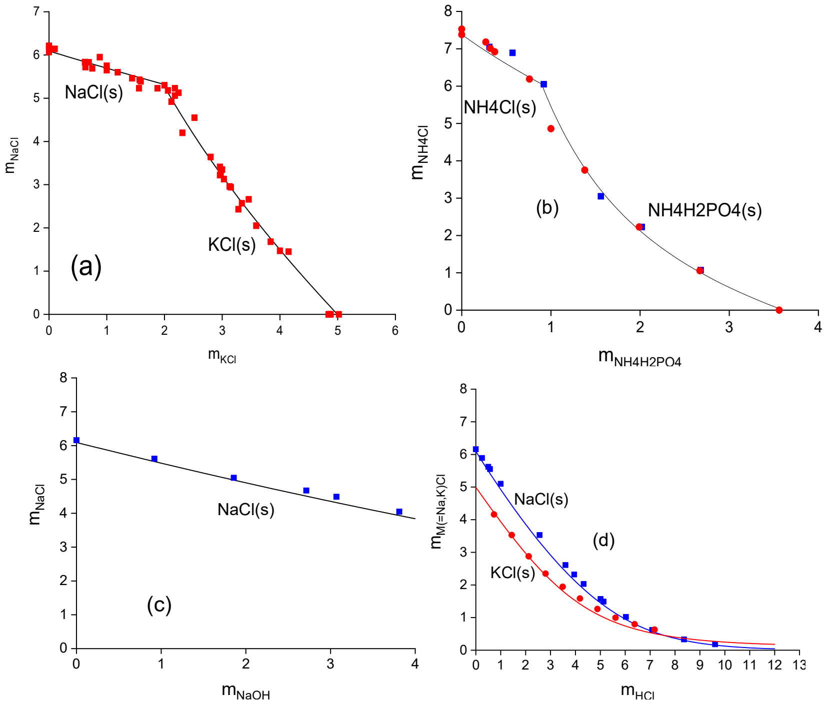


**Figure 9:** Comparison of predicted and measured solubility diagram at 25 °C- **(a)** NaCl-KCl-$H_2O$, **(b)** $NH_4H_2PO_4$-$NH_4Cl$-$H_2O$, **(c)** NaCl-NaOH-$H_2O$ and **(d)** M($Na^+$, $K^+$)-HCl-$H_2O$.

As shown in these figures, current model provides reasonable predictions for solubility diagrams of mixed salts in studied systems, with close agreement between calculated and experimental solubility data. For a system like NaCl–KCl–$H_2O$, predicted solubility curves align well with experimental data, particularly in the region where NaCl and KCl crystallize as solid phases. Similarly, the model successfully predicts solubility salts, NaCl and KCl, in aqueous hydrochloric acid. Small discrepancies between the model and experimental data [42] may be attributed to factors such as experimental uncertainties or interactions not fully accounted for in the model, but overall, it demonstrates strong predictive capability across a concentration range of electrolytes. Also, good agreement between predicted solubility of NaCl in aqueous solution of the system NaCl–NaOH–$H_2O$ was observed in Fig. 9c. Fig. 9d shows that the present model accurately predicts dual crystallization of $NH_4Cl$ and $NH_4H_2PO_4$ in $NH_4Cl$–$NH_4H_2PO_4$–$H_2O$ system. This validates the reliability of interaction parameters used in the model and confirms its applicability for predicting solubility behavior of salts in both single and mixed electrolyte systems 1-1.

Fig. 10(a–d) displays a comparison between predicted and experimental solubility diagrams for four different unsymmetrical mixed electrolyte systems: NaCl–$CaCl_2$–$H_2O$, NaCl–$MgCl_2$–$H_2O$, $CaCl_2$–HCl–$H_2O$ and $MgCl_2$–HCl–$H_2O$, at a constant temperature of 298.15 K.

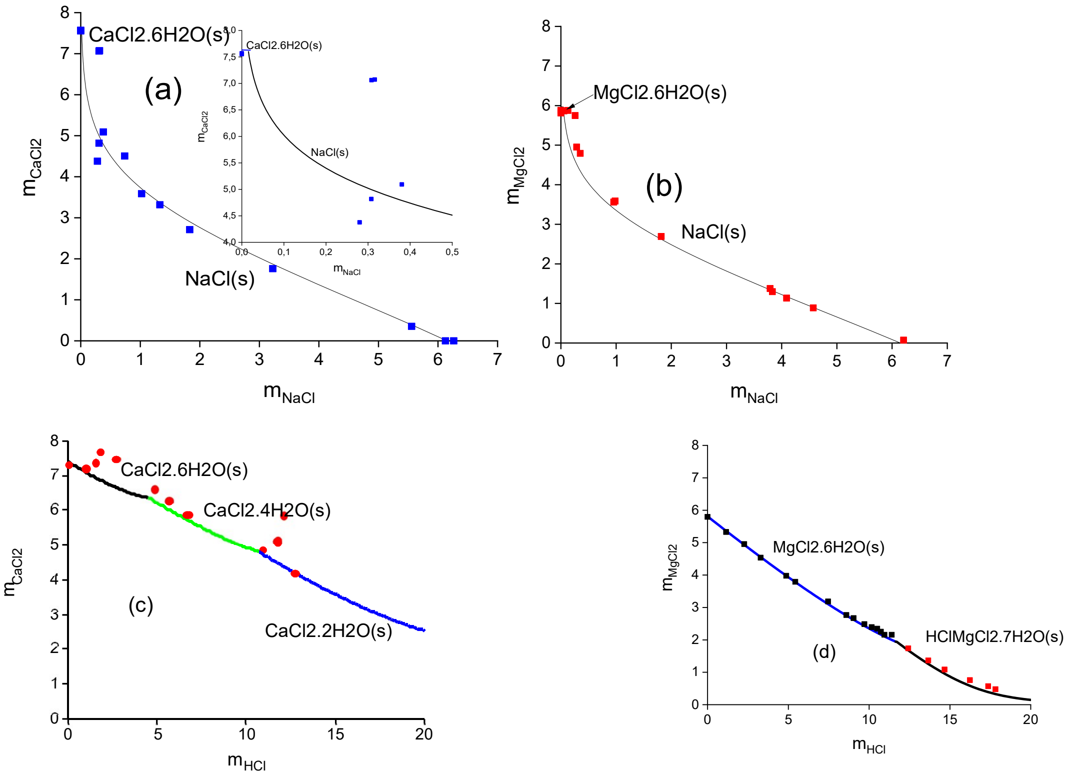


**Figure 10:** Comparison of predicted and measured solubility diagram at 25°C- **(a)** NaCl-CaCl2-H2O, **(b)** NaCl-MgCl2-H2O, **(c)** HCl-CaCl2-H2O and **(d)** HCl-MgCl2-H2O.

As shown in Fig.10a, solid phases that precipitate from NaCl-$CaCl_2$-$H_2O$ solution system are NaCl and $CaCl_2$•$6H_2O$, as reported by [75, 76]. However, the form crystallized in the $CaCl_2$-HCl-$H_2O$ system, as seen in Fig. 10b, in addition of NaCl and $CaCl_2$•$6H_2O$, is $CaCl_2$•$4H_2O$ [80]. Fig. 10c and 10d presents solubility diagrams of NaCl-$MgCl_2$-$H_2O$ and HCl-$MgCl_2$-$H_2O$. Crystallized forms in these systems are NaCl and $MgCl_2$•$6H_2O$ for NaCl-$MgCl_2$-$H_2O$ system, as reported by [75], and $MgCl_2$•$6H_2O$(s) and HCl•$MgCl_2$•$7H_2O$(s) complex salt for HCl– $MgCl_2$–$H_2O$ system. It can be concluded from these figures that the current model accurately predicts the solubility behavior of these mixed electrolyte systems, with good agreement between predicted and measured data. This highlights the effectiveness of the current model in predicting solubility diagrams for unsymmetrical systems of mixed electrolytes.

## Conclusion

Pitzer model is widely used to represent activity and osmotic coefficients in electrolyte systems. Nonlinear parameter b, incorporated into this model as a function of the distance between ions of opposite charge, was initially arbitrarily set at 1.2 without specific justification and assuming identical ionic radii. Some researchers regard b as a parameter requiring optimization with the other model parameters for each electrolyte, while others suggest that it is proportional to ion's hydration radius. In this study, Debye-Huckel equation was modified to account for ion size, expressed as average between contributions of anions and cations.

Values of ion hydration radii reported by Kielland are used in this work. Current modified model was applied to simple electrolyte systems, 1-1, 1-2, 2-1, 2-2 and 3-1 at 298.15 K. Obtained results emphasize notable effectiveness of current model in correlating the behavior of activity coefficient in the studied systems compared to other thermodynamic models.

## Authors' contributions

R**. Chatit, H. Elmaazouzi**: wrote original draft; conceptualization; visualization. **B. Messnaoui, A. Tounsi**: reviewed and edited the manuscript. **R. Chatit, H. Elmaazouzi, B. Messnaoui**: investigation; data curation; reviewed, edited and visualized the manuscript.

## References

1. Debye P, Hückel E. Zur Theorie der Elektrolyte. Physikal Zeitschr. 1923;9:185-206.
2. Davies CW. The Extent of Dissociation of Salts in Water. Part VIII. An Equation for the Mean Ionic Activity Coefficient of an Electrolyte in Water, and a Revision of the Dissociation Constants of Some Sulphate. J Chem Soc. 1938(0):2093-2098. https://doi.org/10.1039/JR9380002093
3. Guggenheim EAL. The specific thermodynamic properties of aqueous solutions of strong electrolytes. Lond Edinb Dub Philos Magaz J Sci. 1935;19(127):588-643. https://doi.org/10.1080/14786443508561403
4. Guggenheim EAL, Turgeon JC. Specific interaction of ions. Trans Farad Soc. 1955;51;747-761. https://doi.org/10.1039/TF9555100747
5. Fowler RH, Guggenheim EAL. Statistical Thermodynamics, Cambridge University Press, 1956.
6. Bromley LA. Approximate individual ion values of β (or B) in extended Debye-Hückel theory for uni-univalent aqueous solutions at 298.15 K. J Chem Thermodyn. 1972;4(5):669-673. https://doi.org/10.1016/0021-9614(72)90038-9
7. Bromley LA. Thermodynamic properties of strong electrolytes in aqueous solutions. AIChE J. 1973;19(2):313-320. https://doi.org/10.1002/aic.690190216
8. Pitzer KS. Thermodynamics of Electrolytes Part 1: Theoretical Basis and General Equations. J Phys Chem. 1973;77(2):268-277. https://doi.org/10.1021/j100621a026
9. Pitzer KS, Mayorga G. Thermodynamics of Electrolytes: II. Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent. J Phys Chem. 1973;77(19):2300-2308. https://doi.org/10.1021/j100638a009
10. Pitzer KS, Mayorga G. Thermodynamics of Electrolytes: III. Activity and Osmotic Coefficients for 2–2 Electrolytes, in: World Scientific Series in 20th Century Chemistry. World Sci. 1993;3(7):405-412. https://doi.org/10.1142/9789812795960_0059

11. Pitzer KS. Theory: Ion interaction approach, in: R.M. Pytkowicz (Ed.), Activity Coefficients in Electrolyte Solutions. CRC Press, Boca Raton, 1979;1:157-208.
12. Chen CC, Britt HI, Boston JF et al. Local composition model for excess Gibbs energy of electrolyte systems. Part I: Single solvent, single completely dissociated electrolyte systems. AIChE J. 1982;28(4):588-596. https://doi.org/10.1002/aic.690280410
13. Chen CC, Evans LB. A local composition model for the excess Gibbs energy of aqueous electrolyte systems. AIChE J. 1986;32(3):353-528 https://doi.org/10.1002/aic.690320311
14. Sander Bo, Fredenslund A, Rasmussen P. Calculation of vapour-liquid equilibria in mixed solvent/salt systems using an extended UNIQUAC equation. Chem Eng Sci. 1986;41(5):1171-118. https://doi.org/10.1016/0009-2509(86)87090-7
15. Thomsen K, Iliuta MC, Rasmussen P. Extended UNIQUAC model for correlation and prediction of vapor–liquid–liquid–solid equilibria in aqueous salt systems containing non-electrolytes. Part B. Alcohol (ethanol, propanols, butanols)–water–salt systems. Chem Eng Sci. 2004;59(17):3631-3647. https://doi.org/10.1016/j.ces.2004.05.024
16. Messnaoui B, Ouiazzane S, Bouhaouss A et al. A modified electrolyte-Uniquac model for computing the activity coefficient and phase diagrams of electrolytes systems. Calphad. 2008;32(35):566-576. https://doi.org/10.1016/j.calphad.2008.04.003
17. Clegg SL, Pitzer KS. Thermodynamics of multicomponent, miscible, ionic solutions: generalized equations for symmetrical electrolytes. J Phys Chem. 1992;96(8):3513-3520. https://doi.org/10.1021/j100187a061
18. Clegg SL, Pitzer KS, Brimblecombe P. Thermodynamics of multicomponent, miscible, ionic solutions. II. Mixtures including unsymmetrical electrolytes. J Phys Chem. 1992;96(23):9470-9479. https://doi.org/10.1021/j100202a074
19. Haghtalab A, Vera JH. Nonrandom factor model for electrolyte solutions. AIChE J. 1991;37(1):147-149. https://doi.org/10.1002/aic.690370114
20. Zhao E, Yu M, Sauvé RE et al. Extension of the Wilson model to electrolyte solutions. Fl Phas Equil. 2000;173(2):161-175. https://doi.org/10.1016/S0378-3812(00)00393-9
21. Xu X, Macedo EA. New Modified Wilson Model for Electrolyte Solutions. Ind Eng Chem Res. 2003;42:5702-5707. https://doi.org/10.1021/ie030514h
22. Simões MC, Hughes KJ, Ingham DB et al. Estimation of Pitzer Parameters for 1–1, 2–1, 3–1, 4–1, and 2–2 Single Electrolytes at 25 °C. J Chem Eng Data. 2016;61(7):2536-2554. https://doi.org/10.1021/acs.jced.6b00236

23. Marshall SL, May PM, Hefter GT. Least-Squares Analysis of Osmotic Coefficient Data at 25 °C According to Pitzer's Equation. 1. 1:l Electrolytes. J Chem Eng Data. 1996;40(5):1041-1052. https://doi.org/10.1021/je00021a003
24. Pérez-Villaseñor F, Iglesias-Silva GA, Hall KR. Osmotic and Activity Coefficients Using a Modified Pitzer Equation for Strong Electrolytes 1:1 and 1:2 at 298.15 K. Ind Eng Chem Res. 2002;41(5):1031-1037. https://doi.org/10.1021/ie0103153.
25. Pérez-Villaseñor F, Iglesias-Silva GA, Hall KR. Prediction of Osmotic and Activity Coefficients Using a Modified Pitzer Equation for Multicomponent Strong Electrolyte Systems at 298 K. Ind Eng Chem Res. 2003;42(5):1087-1092. https://doi.org/10.1021/ie0204787
26. Boukhalfa N, Méniai A-H. Assessment of a thermodynamic model for aqueous electrolyte systems. Intern J Hydrog Ener. 2018;43(10):5358-5364. https://doi.org/10.1016/j.ijhydene.2017.11.126
27. Appelo CAJ. Principles, caveats and improvements in databases for calculating hydrogeochemical reactions in saline waters from 0 to 200 °C and 1 to 1000 atm. Appl Geochem. 2015(55):62-71. https://doi.org/10.1016/j.apgeochem.2014.11.007
28. Harvie, CE, Weare JH. The prediction of mineral solubilities in natural waters: the Na–K–Mg–Ca–Cl–$SO_4$–$H_2O$ system from zero to high concentration at 25 ºC. Geochim Cosmochim Acta. 1980;44(7):981-997. https://doi.org/10.1016/0016-7037(80)90287-2
29. Harvie EH, Møller N, Weare JH. The prediction of mineral solubilities in natural waters: the Na–K–Mg–Ca–H–Cl–$SO_4$–OH–$HCO_3$–$CO_3$–$CO_2$–$H_2O$ system to high ionic strengths at 25 ºC. Geochim Cosmochim Acta. 1984,48(4):723-751. https://doi.org/10.1016/0016-7037(84)90098-X
30. Pabalan RT, Pitzer KS. Thermodynamics of concentrated electrolyte mixtures and the prediction of mineral solubilities to high temperatures for mixtures in the system Na–K–Mg–Cl–$SO_4$–OH–$H_2O$. Geochim Cosmochim Acta 1987;51(9):2429-2443. https://doi.org/10.1016/0016-7037(87)90295-X
31. Greenberg JP, Møller N. The prediction of mineral solubilities in natural waters: a chemical equilibrium model for the Na–K–Ca–Cl–$SO_4$–$H_2O$ system to high concentration from 0 to 250 ºC. Geochim Cosmochim Acta. 1989;53(10):2503-2518. https://doi.org/10.1016/0016-7037(89)90124-5
32. He S, Morse JW. The carbonic acid system and calcite solubility in aqueous Na–K–Ca–Mg–Cl–$SO_4$ solutions from 0 to 90 C. Geochim Cosmochim Acta. 1993;57(15):3533-3554. https://doi.org/10.1016/0016-7037(93)90137-L
33. Marion GM, Farren RE. Mineral solubilities in the Na–K–Mg–Ca–Cl–$SO_4$–$H_2O$ system: a re-evaluation of the sulfate chemistry in the Spencer–Møller–Weare model. Geochim Cosmochim Acta. 1999;63(9):1305-1318. https://doi.org/10.1016/S0016-7037(99)00102-7

34. Kielland J. Individual activity coefficients of ions in aqueous solutions. J Am Chem Soc. 1937;59(9):1675-1678. https://doi.org/10.1021/ja01288a032
35. Hamer WJ, Wu Y-C. Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at 25 °C. J Phys Chem Ref Dat. 1972;1(4):1047-1100. https://doi.org/10.1063/1.3253108
36. Goldberg RN, Nuttall RL, Staples BR. Evaluated activity and osmotic coefficients for aqueous solutions: iron chloride and the bi-univalent compounds of nickel and cobalt. J Phys Chem Ref Dat. 1979;8(4):923-1004. https://doi.org/10.1063/1.555615
37. Goldberg RN, Nuttall RL. Evaluated activity and osmotic coefficients for aqueous solutions: The alkaline earth metal halides. J Phys Chem Ref Dat. 1978;7(1):263-310. https://doi.org/10.1063/1.555569
38. Goldberg RN. Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Thirty-Six Uni-Bivalent Electrolytes. J Phys Chem Ref Dat. 1981;10(3):671-764. https://doi.org/10.1063/1.555646
39. Goldberg RN. Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Bi-univalent Compounds of Lead, Copper, Manganese, and Uranium. J Phys Chem Ref Dat. 1979;8(4):1005-1050. https://doi.org/10.1063/1.555611
40. Robinson RA, Stokes RH. Electrolyte Solutions, Butterworth Scientific Publications, London, 1955.
41. EL Guendouzi M, Mounir A, Dinane A. Water activity, osmotic and activity coefficients of aqueous solutions of $Li_2SO_4$, $Na_2SO_4$, $K_2SO_4$, $(NH_4)_2SO_4$, $MgSO_4$, $MnSO_4$, $NiSO_4$, $CuSO_4$, and $ZnSO_4$ at T = 298:15 K. J Chem Thermodyn. 2003;35(2):209-220. https://doi.org/10.1016/S0021-9614(02)00315-4
42. Zemaitis JF, Clark DM, Rafal M. Handbook of aqueous electrolyte thermodynamics: theory & application, Wiley, Hoboken, 2010.
43. Robinson RA, Stokes RH. Electrolyte Solutions, 2nd ed., Butterworth and Co., London, 1970.
44. Stokes RH, Robinson RA. Ionic Hydration and Activity in Electrolyte Solutions. J Am Chem Soc. 1948;70(5):1870-187. https://doi.org/10.1021/ja01185a065
45. Neff GW. Use of a Modification of Debye-Huckel Equation to Calculate Activity Coefficients from Measured Activities in Electrolyte Solutions. Analyt Chem. 1970;42(13):1579-1582. https://doi.org/10.1021/ac60295a028
46. Linder P, Murray K. Correction of formation constants for ionic strength, from only one or two data points: an examination of the use of the extended Debye-Huckel equation. Talanta. 1982;29(5):371-382 https://doi.org/10.1016/0039-9140(82)80172-0

47. Pitzer KS. Thermodynamic Properties of Aqueous Solutions of Bivalent Sulphates. J Chem Soc Farad Trans. 1972;68(0):101-113. https://doi.org/10.1039/F29726800101
48. Eberhart R, Kennedy J. A new optimizer using particle swarm theory,"MHS'95. Proceedings of the Sixth International Symposium on Micro Machine and Human Science, Nagoya, Japan, 04-06 October 1995: 39-43. https://doi.org/10.1109/MHS.1995.494215.
49. Khan SU, Yang S, Wang L et al. A modified particle swarm optimization algorithm for global optimizations of inverse problems. IEEE Transact Magn. 2016;52(3):1-4. https://doi.org/10.1109/TMAG.2015.2487678
50. Lindenbaum S, Rush RM, Robinson RA. Osmotic and activity coefficients for mixtures of lithium chloride with barium chloride and cesium chloride with barium chloride in water at 298.15 K. J Chem Thermodyn. 1972;4(3):381-389. https://doi.org/10.1016/0021-9614(72)90021-3
51. Khoo KH, Chan CY, Lim TK. Thermodynamics of electrolyte solutions. The system HCl + $CaCl_2$+ $H_2O$ at 298.15 K. J Sol Chem. 1977;6(10):651-662. https://doi.org/10.1007/BF00645882
52. Roy RN, Gibbons JJ, Bliss DP et al. Activity coefficients for ternary systems: VI. The system HCl + $MgCl_2$+ $H_2O$ at different temperatures; application of Pitzer's equations. J Sol Chem. 1980;9(12):911-930. https://doi.org/10.1007/BF00646403
53. Kuschel F, Seidel J. Osmotic and activity coefficients of aqueous potassium sulfate-magnesium sulfate and potassium chloride-magnesium chloride at 25 ºC. J Chem Eng Dat. 1985;30(4):440-445. https://doi.org/10.1021/je00042a021
54. Robinson RA, Wood RH, Reilly PJ. Calculation of excess Gibbs energies and activity coefficients from isopiestic measurements on mixtures of lithium and sodium salts. J Chem Thermodyn. 1971;3(4):461-471. https://doi.org/10.1016/S0021-9614(71)80028-9
55. Yan W, Han S. Activity and osmotic coefficients for the ternary system (sodium bromide -tetramethylammonium bromide - water) at T = 298.15 K. J Chem Thermodyn. 1998;30(6):743-749. https://doi.org/10.1006/jcht.1997.0340
56. Yan W. Measurement and correlation of activity coefficients for (sodium bromide + lithium bromide + water) at T = 298.15 K. J Chem Thermodyn. 2000;32(5):631-637. https://doi.org/10.1006/jcht.1999.0626
57. Usha A, Raju K, Atkinson G. Thermodynamics of concentrated electrolyte mixtures. Activity coefficients in aqueous sodium bromide-calcium bromide mixtures at 25 ºC. J Phys Chem. 1987;91(18):4796-4799. https://doi.org/10.1021/j100302a029
58. El Guendouzi M, Benbiyi A, Dinane A et al. Thermodynamic properties of multicomponent NaCl–LiCl–$H_2O$ aqueous solutions at temperature = 298.15 K. Calphad. 2004;28(1):97-103. https://doi.org/10.1016/j.calphad.2004.05.004

59. Dinane A, Mounir A. Hygrometric Determination of Water Activities and Osmotic and Activity Coefficients of $NH_4Cl$–$KCl$–$H_2O$ at 25 °C. J Sol Chem. 2003;32(5):395-404. https://doi.org/10.1023/A:1024516726950
60. El Guendouzi M, Azougen R, Benbiyi A et al. Thermodynamic properties of the system $\{yNH_4Cl+(1-y)CsCl\}(aq)$ at temperature 298.15 K. Calphad. 2004;28(3):329-336. https://doi.org/10.1016/j.calphad.2004.11.001
61. El Fadel W, El Hantati S, Nour Z et al. Thermodynamic properties data of ternary system $NH_4Cl$-$NH_4H_2PO_4$-$H_2O$ at 298.15 K including the solubility data. J Mol Liq. 2022;359:11938. https://doi.org/10.1016/j.molliq.2022.119381
62. El Fadel W, El Hantati S, Nour Z et al. Experimental Determination of Osmotic Coefficient and Salt Solubility of System $NH_4NO_3$–$NH_4H_2PO_4$–$H_2O$ and Their Correlation and Prediction with Pitzer–Simonson–Clegg Model. Industr Eng Chem Res. 2023;62(43):17986-17996. https://doi.org/10.1021/acs.iecr.3c01356
63. El Guendouzi M, Benbiyi A, Azougen R et al. Thermodynamic properties of two ternary systems $\{yCsCl+(1-y)LiCl\}(aq)$ and $\{yCsCl+(1-y)NaCl\}(aq)$ at temperature = 298.15 K. Calphad. 2004;28(4):435-244. https://doi.org/10.1016/j.calphad.2004.12.001
64. El Guendouzi M, Benbiyi A, Dinane A et al. The thermodynamic study of the system $LiCl$–$KCl$–$H_2O$ at the temperature = 298.15 K. Calphad. 2003;27(2):213-219. https://doi.org/10.1016/j.calphad.2003.08.001
65. El Guendouzi M, Marouani M. Thermodynamic properties of the system $NH_4NO_3$–$KNO_3$–$H_2O$ at 298.15 K. Fl Phas Equil. 2004;216(2):229-233. https://doi.org/10.1016/j.fluid.2003.10.009
66. El Guendouzi M, Dinane A, Mounir A. Hygrometric Determination of Water Activities and Osmotic and Activity Coefficients of $NH_4Cl$–$LiCl$–$H_2O$ at 25 °C. J Sol Chem. 2002;31(2):119-129. https://doi.org/10.1023/A:1015296919047
67. El Guendouzi M, Benbiyi A, Dinane A et al. Determination of water activities and osmotic and activity coefficients of the system $NaCl$–$BaCl_2$–$H_2O$ at 298.15 K. Calphad. 2003;27(4):375-381. https://doi.org/10.1016/j.calphad.2004.01.006
68. Dinane A, Mounir A. Water activities, osmotic and activity coefficients in aqueous mixtures of sodium and magnesium chlorides at 298.15 K by the hygrometric method. Fl Phas Equil. 2003;206(1-2):13-25. https://doi.org/10.1016/S0378-3812(02)00300-X
69. El Guendouzi M, Azougen R, Mounir A et al. Water activities, osmotic and activity coefficients of the system $(NH_4)_2SO_4$–$K_2SO_4$–$H_2O$ at the temperature 298.15 K. Calphad. 2003;27(4):409-414. https://doi.org/10.1016/j.calphad.2004.02.002

70. El Guendouzi M, Errougui A. Thermodynamic properties of the system $NH_4NO_3 + (NH_4)_2SO_4 + H_2O$ at 298.15 K. Fl Phas Equil. 2005;230(1-2):29-35. https://doi.org/10.1016/j.fluid.2004.11.017
71. Mounir A, El Guendouzi M, Dinane A. Thermodynamic properties of $\{(NH_4)_2SO_4\ (aq) + Li_2SO_4\ (aq)\}$ and $\{(NH_4)_2SO_4\ (aq) + Na_2SO_4\ (aq)\}$ at a temperature of 298.15 K. J Chem Thermodyn. 2002;34(8):1329-1339. https://doi.org/10.1006/jcht.2002.0984
72. Linke WF, Seidell A. Solubilities of Inorganic and Metal-Organic Compounds. Am Chem Soc. Washington, D.C. 1965;II:1050-1055.
73. Völz-Fladrich, H. Physikalisch-chemische Untersuchungen an den Systemen $MgCl_2$–HCl–$H_2O$, NaCl–HCl–$H_2O$ und KCl–HCl–$H_2O$; Akademie-Verlag: Berlin, 1962. (Cited in Zdanovskii A, Solov'eva E, Liahovskaia E, Shestakov et al. Experimental Data on the Solubility of Multicomponent Aqueous Salt Systems; Khimiizdat: St. Petersburg, 1973;(1-2):912-913.
74. Cameron FK, Bell JM, Robinson WO. The Solubility of Certain Salts Present in Alkali Soils. J Phys Chem. 1907;11(5):396-420. https://doi.org/10.1021/j150086a007
75. Zdanovskii AB, Solov'eva, Lyakhovskaya EI. Handbook of Experimental Data on Solubility of Multicomponent Water-Salt Systems. Vol. 1: Three-Component Systems, 2nd ed. (Khimia, Leningrad, 1973), Book 2: 297.
76. Silcock HL. Solubilities of Inorganic and Organic Compounds. Ternary and Multicomponent Systems of Inorganic Substances 3 Pergamon Press, Oxford, 1979.
77. Gerlach KH. The systems KCl–$MgCl_2$–$H_2O$ and NaCl–$MgCl_2$–$H_2O$. Kali. 1923;17:261-265.
78. Takegami S. Reciprocal salt pairs: $Na_2Cl_2 + MgSO_4 \rightarrow Na_2SO_4 + MgCl_2$ at 25 ° C. Memo Coll Sci Kyot Imp Univ. 1921;4(7):317-342.
79. Milikan J. Die Oxyhaloide der alkalischen Erden Gleichgewichte in ternären Systemen II. Zeitschr Phys Chem. 1918;92U(1):496-510. https://doi.org/10.1515/zpch-1918-9228
80. Lassin A, André L, Lach A et al. Solution properties and salt-solution equilibria in the H-L–Na–K–Ca–Mg–Cl–$H_2O$ system at 25 °C: a new thermodynamic model based on Pitzer's equations. Calphad. 2018;61:126-139. https://doi.org/10.1016/j.calphad.2018.03.005
81. Meng L, Li D. Pitzer thermodynamic modeling study on solid–liquid equilibria of the quinary system LiCl–NaCl–$CaCl_2$–$SrCl_2$–$H_2O$ at 298.15 K. RSC Adv. 2017;7(86):54313-54317. https://doi.org/10.1039/C7RA11544J