**Thermodynamic Modelling and Phase Equilibria Analysis of Binary Salt Hydrate Systems**

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**Abstract-** This paper explores the efficient storage of thermal energy, crucial for sustainable energy solutions, particularly focusing on the utilization of salt hydrates in thermochemical heat storage systems. Our study involved the development of comprehensive mathematical models to describe the behaviour of different salt hydrates under varying conditions. These models were designed to capture the intricate interplay between factors such as temperature, osmotic coefficient, and composition, providing a robust framework for understanding the thermodynamic properties of these materials. Utilizing computational techniques, we solved the formulated mathematical models for a range of salt hydrates. This involved intricate calculations and simulations to simulate the behaviour of these materials under different environmental conditions, allowing us to obtain valuable insights into their thermodynamic behaviour and phase transitions. Upon solving the models, we meticulously analysed the results to determine the percent deviation between our predictions and experimental data for each salt hydrate. Notably, our findings revealed significant variations in deviation among different hydrates, with a particularly interesting trend observed. The ultimate validation of our study came from comparing our model predictions with experimental data. Encouragingly, our results were found to closely match experimental observations, thereby confirming the accuracy and efficacy of our developed mathematical models. This validation underscores the reliability of our approach and highlights its potential utility in predicting the thermodynamic behaviour of salt hydrates with high precision.

*Keywords:* Thermal energy storage; Salt hydrates; Computational techniques; Phase transitions; Thermochemical heat storage systems.

1. **Introduction:**

Solar energy is more abundant during summer than in winter. The total solar energy supply is sufficient to answer the total demand of energy in dwellings. However, in order to be able to rely completely on sustainable energy sources an efficient method to store energy is required. One of the oldest and simplest way to store thermal energy is in water, for example by using a boiler. For short timeslots this is an efficient and cheap way to store heat [1]. A disadvantage is that a large volume of water is needed and that in spite of insulation, heat will be lost. Thermal storage technologies suitable for building applications are classified in three methods based on the storage principle used: sensible heat (e.g., water tanks, underground storage) [2-4], latent heat (e.g., ice, phase change materials) [5-7] and thermochemical heat storage [8]. The latent heat storage method makes use of a reversible physical or chemical reaction and has higher energy storage density and almost no heat loss, compared to the two other heat storage methods [9]. One promising possibility to store thermal energy is by means of reversible gas solid reactions [10]. Heat is stored into an endothermal dissociation reaction, splitting the thermochemical material into two components (charging), and, at a later time, the energy can be retrieved from the reverse exothermal reaction between the two components (discharging) according to the reaction [11]. An interesting storage material should be low cost, non-toxic, non-corrosive and stable with high energy storage density [12]. These requirements are fulfilled by a number of salt hydrates. In phase change materials (PCMs) heat can be stored by using a phase transition in the material. PCMs have a larger storage capacity than water [13]. A disadvantage is that phase change materials are expensive and still suffer from heat loss during storage, as storage needs to take place at temperature levels that prevent the phase change. In thermochemical materials (TCMs) heat is stored by performing a chemical reaction. TCMs have a large storage capacity and therefore they only require a small volume to store a large amount of heat. As the heat is stored by performing a chemical reaction, there is no loss of heat during storage. The storage volumes required for the annual thermal energy demand of an average household stored in water, PCM and TCM are given by [14]. The most commonly used TCMs are salt hydrates in which thermal energy is stored by drying the salt hydrate and storing the dry salt and the water separately. The reversible reaction of hydration and dehydration of a salt hydrate is shown in Eq. 1.

(1)

The interaction between salt hydrate and water progressively weakens with increasing temperature due to the reduction in the enthalpy of hydrogen bond and finally, above the critical temperature, phase separation occurs [1]. To understand and optimize the phase behaviour, thermodynamic properties of aqueous solutions of Salt hydrates need to be quantified. This requires both the accurate experimental data and a good model which allows prediction of properties of the system in the range of temperature and composition in which experimental data are not available.

Utilizing the Modified Pitzer (MP) model, researchers aim to determine activity coefficients, osmotic coefficients, excess Gibbs energy, and water activity, thereby offering a comprehensive understanding of interactions within ternary systems involving electrolytes, amino acids, and water across a broad concentration and temperature range [15,16]. The interactions discussed primarily entail ion-ion, ion-solute, solute-solute, and solute-solvent interactions, crucial for predicting thermodynamic properties and phase behaviour. This research trajectory extends to investigating the thermodynamic properties of multicomponent aqueous solutions pertinent to environmental contexts. A comprehensive thermodynamic model is proposed to forecast the behaviour of aqueous mixtures containing ions such as Na+, K+, Ca2+, Mg2+, Cl−, and NO3- [17].

Pitzer's seminal work on the ion interaction model, along with its evolved forms like Pitzer–Simonson–Clegg (PSC), serves as the cornerstone for comprehending electrolyte solutions [18,19]. These models offer critical insights into electrolyte behaviour, particularly in techniques like ion-selective electrodes and pH measurements. They meticulously describe the thermodynamic properties of electrolyte solutions, encompassing activity coefficients and osmotic coefficients, pivotal for accurate data interpretation. Moreover, these models furnish a theoretical framework to predict electrolyte behaviours under diverse conditions, thus facilitating the optimization of processes such as chemical reactions, separations, and electrochemical systems. However, their work focuses on symmetrical systems and does not address asymmetrical systems containing ions of different charge types

Khoshkbarchi, Vera, Pazuki, and Sadowski have significantly enriched our comprehension of ternary systems, exemplified by the (NaCl + I- + proline + water) system, through diverse models and theories [20-22]. Their research elucidates thermodynamic properties across varying concentrations and temperatures, laying the groundwork for further exploration in this domain. Key properties discussed include activity coefficients, solubility, phase equilibria, and excess properties such as enthalpy and Gibbs energy. These insights play a pivotal role in the design and optimization of processes involving ternary systems, encompassing crystallization, extraction, and separation processes.

Trausel et al. (2014) [14] present compelling evidence that magnesium chloride (MgCl2), sodium sulphide (Na2S), calcium chloride (CaCl2), and magnesium sulphate (MgSO4) exhibit remarkable potential for thermochemical storage due to their impressive volumetric energy densities. However, further investigation into the properties of salt hydrates is imperative to ensure informed material selection, tailored to diverse operating conditions and requirements. Crucial insights into operational parameters are provided by Clausius-Clapeyron diagrams, while thermogravimetric analysis (TGA) under controlled humidity offers valuable insights into phase diagrams, with equilibrium reached more rapidly under vacuum conditions. Encapsulation using water-permeable polymers may address challenges related to the chemical and physical stability of salt hydrates. Linnow et al. (2014) [23] contribute significantly to understanding hydration kinetics, demonstrating the high theoretical energy densities of MgSO4∙7H2O and Na2SO4∙10H2O. Piperopoulos (2020) [24] further underscores the potential of magnesium sulphate as a storage material, especially for seasonal solar heat storage, given its exothermic hydration reaction. This research collectively propels advancements in thermochemical storage, facilitating efficient and sustainable energy utilization across diverse applications.

In the pursuit of advancing thermochemical energy storage (TCES) systems, multiple research endeavours have emerged to explore various aspects of materials, reactor design, and operational parameters. Gaeini et al. (2019) [25] focus on potassium carbonate as a thermochemical material for heat storage, meticulously investigating its de/re-hydration reactions through kinetic modelling using Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) methods. However, the exclusive concentration on potassium carbonate overlooks the potential of other materials, narrowing the scope of exploration within the field. Furthermore, the study primarily examines the behaviour of potassium carbonate with water vapor, omitting crucial factors like thermal conductivity and system design, which are pivotal for real-world applicability. Similarly, Hawwash et al. (2020) [26] delve into the impact of reactor design on thermal energy storage, particularly focusing on salt hydrates. While their investigation reveals significant insights into how reactor geometry influences pressure drop, charging time, and thermochemical heat storage, the study's confinement to cylindrical and truncated cone shapes may overlook potential variations in reactor design, urging further exploration into alternative geometries for a comprehensive understanding. Desai et al. (2021) [27] contribute a comprehensive review of TCES systems, emphasizing materials used for sorption and reaction-based TCES, along with discussions on challenges and experimental investigations. However, gaps exist, particularly regarding detailed information on certain TCES materials' safety, stability, and solubility, warranting further exploration and analysis. Conversely, Li et al. (2022) [28] provide numerical insights into the hydration process of a sorbent comprising lithium-based salt hydrate and expanded graphite in a thermal energy storage (TES) module. While offering valuable perspectives on heat and mass migration behaviours, the focus solely on numerical investigation and specific operating conditions may limit the study's ability to fully capture real-world complexities and variations. Hao et al. (2024) [29] propose a multimodule columnar packed-bed reactor for thermochemical heat storage using salt hydrates, showcasing advantages in terms of reaction rate, reaction time, and resistance loss. However, reliance on numerical simulations without experimental validation, coupled with the study's narrow focus on specific reactor design parameters, underscores the need for broader applicability considerations and validation through experimental studies.

Aforementioned salt hydrate models, focus on their application in thermochemical heat transformers (THT) for industrial waste heat recovery, energy storage, and space heating. Studies highlight salt hydrates' high energy storage density, safety, and potential for long-duration storage [30, 31]. Research emphasizes optimizing factors like thermal conductivity, porosity, and system type for efficient heat storage [32]. Kinetic studies explore dehydration/hydration rates, emphasizing the impact of temperature, pressure, particle size, and additives on reaction kinetics [33]. Composite salt hydrates show faster desorption/sorption kinetics, with diffusion being a key limiting factor. The review also discusses the classification of salt hydrate-based systems, reactor design, theoretical models, challenges, and future prospects for salt hydrate-based gas-solid thermochemical energy storage.

A large number of experimental studies have been reported in the literature on the thermodynamic properties of various salt hydrates [34] These include activity of water in the solution, phase separation behaviour and solubility analysis. The data obtained from these studies are well documented by [35]. The most widely used methods for activity measurements are vapor pressure osmometry [36], laser-light scattering [37], isopiestic method [38], dew point method [39], and sedimentation technique [40],

Regarding the phase separation studies, the coexistence curves for salt hydrates are obtained from the cloud-point data. The cloud point is measured by using either thermos-optical analysis method [41] or through visual observations. Several models have been used for predicting the behaviour of salt hydrates viz. those based on the osmotic virial expansion [42] those based on equations of state [43], and the group contribution schemes [44].

A good thermodynamic model should be able to relate the activity of salt hydrate at low temperatures with its phase behaviour at high temperatures. Unfortunately, models described above use two separate sets of parameters, one to correlate the low-temperature activity data for salt hydrate and the other to correlate the phase separation data. The parameters obtained from the activity data in the low-temperature range (278–343K) are not suitable to predict phase separation and the coexistence curve of salt hydrate systems. This failure stems from inaccuracies in either the model or the experimental data. A very high accuracy of the low-temperature activity data is needed since the data need to be extrapolated over a wide interval of the temperature beyond the range of the measurement and small inaccuracies in the parameter estimates are magnified. Same can be said about the inaccuracies in the model. The task is made difficult by the fact that each activity measurement technique has a relatively narrow range of temperature over which it is accurate. The data obtained using two or more technique needs to be combined in order to extend the range of temperature. This procedure is also a source of error.

Utilizing correlations based on the models, namely the generalized Flory-Huggins theory [45] and the Extended Debye Hückel theory [46], and incorporating activity data obtained from various techniques, an attempt has been made to predict the coexistence curve for the salt hydrate systems in the phase separation region. The work is presented as follows: Firstly, we describe the models governing the thermodynamics of salt hydrate systems. Then, we present the methodology used to estimate the coefficients of these models from the data on the activity of water in the salt hydrate systems. This is followed by the analysis of the results to obtain the model parameters. Finally, the selected model is utilized to grade the quality of the reported solution activity data.

1. **Development of the basis for Model**

The osmotic coefficient (φ) of an aqueous electrolyte is related to the chemical potential of water, (µw), as follow:

(1)

where, µ0w is the chemical potential of water in its standard state. Mw is the molecular mass of water. is the number of ions produced on dissociation of one molecule of the electrolyte. is the molality of the electrolyte solution, *R* is the gas constant, and *T* is the absolute temperature. These variables collectively determine the extent of deviation from ideal behaviour in solutions, providing insights into the behaviour of solutes and solvents in solution dynamics.

In this work, total Gibbs free energy of the system is given by summation of long range (Lr) and short-range interactions (Sr), i.e.,

(2)

Long range interaction, is also termed as electrostatic interaction is given by Pitzer`s form of the Debye- Huckle (PDH) function,

(3)

where, , are the number of moles of water, salt respectively. , are the partial molar volume (m3/mole) of salt, solvent respectively. is the closest approach parameter. Total no. of ions per salt is defined by . is the ionic strength.

In eqn. 3, Debye Hückel type constant is defined as function of the dielectric constant of water as follows,

(4)

where *Mw* is molecular weight of solvent i.e., water in gram/mol, *NA* is Avogadro number, *K* is Boltzmann constant, *ε* is permittivity of vacuum, *e* is electronic charge, *DS* is dielectric constant of water, *VS* is the molar volume of water.

In eqn. 3, the ionic strength, is defined as function of the molarity as follows,

or (5)

The expression for the short-range interaction contribution of aqueous salt solution is obtained from Generalized Flory- Huggins theory as given below,

(6)

In eqn. (6), volume fraction of the salt hydrate is define as

(7)

In eqn. (6), The term is the generalized Flory-Huggins parameter and should be regarded as a function of the volume fraction of the salt hydrate , and temperature, of the system. By combining Eqn. 2, 3, & 6, total Gibbs free energy of the system is given as,

(8)

where, and represent the moles of salt hydrate and water in salt hydrate solution, respectively.

Derivative of Equation (8) w. r. t. moles of water and salt gives us chemical potential of water and salt hydrate respectively.

(9)

(10)

The criteria governing phase equilibrium between two distinct phases (referred to as the phase and phase) are specified by

(11)

(12)

By substituting Equations (9) and (10) into Equations (11) and (12), we derive the following equations that govern the phase equilibria.

(13)

(14)

The values of and at a specific temperature *T* are obtained by solving Equations (13) and (14) simultaneously. The critical point is determined by the following condition:

(15)

Substituting the second and third derivatives of the free energy of the salt hydrate system (Eqn (8)) into the above equations yields...

………………………………(16)

…………………………………..(17)

The critical temperature, *Tc* , and critical salt hydrate volume fraction, , are determined by solving the above two equations simultaneously.

**\*THE STEPS OF MODEL IS GIVEN BRIEFLY IN SEPARATE DOCUMENT\***

1. **Procedure for regression of the model parameters**

The parameter in the Flory-Huggins theory governs the interaction between salt and water, thus determining the thermodynamic characteristics of Salt hydrate systems. Various correlation forms for this parameter have been documented in the literature [47-50]. In this analysis, we explore the empirical form of as follows:

(18)

is temperature dependent coefficient and as expressed as:

(19)

where, and are constants.

This form necessitates determining 3(n+1) empirical constants using the experimental data. For this representation of , we have

(20)

And

(21)

We observe from the above equations that coefficients are eliminated during the partial differentiation of with respect to temperature. To estimate the constants, we solely rely on the data concerning the osmotic coefficient of water in salt hydrate systems across a range of temperatures and compositions for the regression of all the constants.

Three different values of n, namely n = 3 and 4 are utilized to assess the impact of n (the degree of polynomial in in Equation (18)) on the quality of the estimates. The nonlinear least-square method of Levenberg-Marquardt is employed for regression in all cases. The -norm of the residual (∣∣R∣∣) is employed to evaluate the quality of the regression. It is defined as:

(22)

where and (j = 1,….., n data) respectively denote the experimental value and the corresponding model prediction of the quantity to be fitted (osmotic coefficient data), and σ j is the standard deviation.

1. **Results and Discussion: -**

We initially examine the outcomes of the regression analysis conducted on the data utilizing the proposed method. This methodology relies solely on the osmotic coefficient data. Within the existing literature, there are limited studies that quantify the activity of water (osmotic coefficient) in salt hydrates across a broad spectrum of temperatures and concentrations.

The table-1 list the l2-norm of the residuals, ||R||, for the best fit values of the constants. It is seen that the value of ||R|| for n = 1 is significantly larger than those for n = 2, 3 and 4. Hence the linear form (n = 1) is not used in the further analysis. The values of ||R|| for n = 3 and 4 are not significantly different from each other and hence both are accepted.

**Table-1 - l2-norm of the residuals, ||R||, for the best fit values of the constants for our work to the experimental data**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Salt Hydrates** | **n = 1** | **n = 2** | **n = 3** | **n = 4** |
| **NaCl** | 38.2962 | 1.70324 | 1.402143 | 1.00947 |
| **LiCl** | 67.1905 | 10.85738 | 6.976521 | 1.479885 |
| **CaCl2** | 49.3203 | 6.616037 | 1.918884 | 0.615101 |
| **Li2SO4** | 81.5631 | 6.766015 | 3.255115 | 1.160013 |
| **MgSO4** | 84.14794 | 9.856403 | 4.550855 | 2.99597 |

Table 2 lists the regression estimates of the constants *, and*  ***,*** (i = 0, 1, . . ., n), for n = 3. Table 3 lists the regression estimates of the constants *, , and* (i = 0, 1, . . ., n), for n = 4.

***Table-2 The least square estimates of constants , and , obtained from osmotic coefficient data for n = 3***

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Parameters** | **NaCl** | **LiCl** | **Li2SO4** | **MgSO4** | **CaCl2** |
|  | 79.25810001 | -13416.83325 | 1805.607702 | 41812.72232 | 6917.205725 |
|  | 0.392577746 | -13655.82569 | -1.52985731 | -1710403.759 | -2045.137046 |
|  | 406.7499327 | 1438.11892 | -162.818885 | -124710.7606 | -40191.75976 |
|  | 79.25813745 | -17830.20198 | 1804.459355 | 25437.18659 | 8303.19844 |
|  | 0.393322704 | 1813.197152 | -1.53831223 | -1693135.758 | -6.0165132628 |
|  | 406.7499327 | 1840.796406 | -314.8768451 | 114649.0606 | 38116.51935 |
|  | -461.7558628 | 216895.324 | -16834.84598 | -49205.42678 | -55686.377 |
|  | -1.299947942 | 15369.79572 | -5.859168109 | 3900142.407 | 1578.732542 |
|  | -2712.455354 | -25218.75124 | -5264.96013 | 5674.916688 | 7106.784597 |
|  | -286.6609284 | -200587.7443 | -73341.05538 | -57730.37146 | 109013.936 |
|  | -0.825744651 | -92.36609842 | -3.144404132 | 75602.14676 | -3999.432868 |
|  | -1677.795905 | 6619.358175 | 4942.140603 | 4823.346649 | -22960.88857 |

***Table-3 The least square estimates of constants , , and obtained from osmotic coefficient data for n = 4***

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Parameters** | **NaCl** | **LiCl** | **Li2SO4** | **MgSO4** | **CaCl2** |
|  | -0.212294839 | -8475.14118 | 1583.531513 | 735.2502247 | 8261.720861 |
|  | -335.4371663 | 1.951984408 | -1.523361753 | -0.791706136 | 0.574569962 |
|  | 10342.4994 | 11063.71503 | 335.0484774 | -175.5402835 | -2205.145069 |
|  | -0.207433846 | -8762.679933 | 1586.790475 | 735.2499917 | 8514.638057 |
|  | -323.2401916 | 1.945589229 | -1.521177232 | -0791302324 | 0.57414814 |
|  | -35421.30669 | -5249.227446 | 309.9047436 | -175.5427682 | 637.5750879 |
|  | -4.150170132 | 139528.488 | -21459.34288 | 6263.204201 | -64139.42738 |
|  | 357.187306 | -2.140533011 | -5.649620842 | -1.789600289 | -1.661789026 |
|  | 3024.992372 | -42267.20539 | -16192.5649 | -3417.892075 | 1822.071307 |
|  | -1.176700102 | -28829.39158 | -51230.10337 | -10121.37875 | 119035.627 |
|  | 9279.052789 | -3.087335404 | -3.048952414 | -1.185368643 | -1.257998805 |
|  | 0 | 49056.73421 | 52595.85194 | 2229.518494 | -1687.598625 |
|  | 102073.3323 | -139583.3918 | -4265.223202 | -1750.261638 | 5734.631344 |
|  | -0.353976317 | -2.475147526 | -1.159889792 | -0.569492703 | -0.617783764 |
|  | -33101.67039 | -35949.50214 | -78519.87037 | -6399.459638 | -28747.96172 |

A single temperature (considered the base temperature) serves as the data point. Given that activity data are derived from various measurement techniques, a selection must be made. Three criteria guide the choice of the most suitable data. Firstly, the quality of regression is assessed based on the l2-norm. Secondly, the accuracy of predicting critical constants, namely Tc and (the critical volume fraction of salt hydrate), utilizing the estimated parameters is evaluated. These critical constants are determined by solving Eqs. (16) and (17) concurrently. Thirdly, the precision of predicting the binodal curve is considered. The binodal curve is approximated by simultaneously solving Eqs. (13) and (14).

We use sets of parameters from Table-2 and Table-3 to predict the Phase diagram of salt hydrates. In Figure 1, the predicted binodal curves for n = 3, 4 are juxtaposed with experimental data for salt hydrates. Notably, the predicted Phase diagram aligns remarkably well with the experimental observations, particularly when utilizing the parameter set derived from activity data. This congruence underscores the reliability of the predictive model in accurately capturing the phase behaviour of the salt hydrates. The accuracy of the correlation is illustrated through parity plots.

An attempt was made to expand the current correlation to forecast the closed-loop phase diagraph for various Salt hydrates (NaCl, LiCl, CaCl2, Li2SO4, and MgSO4), as illustrated in Figure 1,5,9,13, and 17. However, it is evident that the phase diagraph predicted by the model does not enclose the upper critical temperature. One potential explanation for this deviation lies in the failure of our assumption regarding the independence of (volume of salt/volume of water) concerning temperature, pressure, and salt composition. The assumption of constant is likely to hold true for temperatures up to and around the lower critical temperature as previous studies have demonstrated its independence from pressure across a broad range [51]. Nonetheless, this assumption may not remain valid beyond this range. Indications suggest that (volume of salt/volume of water) is independent of pressure, particularly around the lower critical temperature, as evidenced by its stability across a broad pressure range. However, the upper critical temperature aligns closely with the critical point of water (647.1K), which is anticipated to decrease further with the addition of salt hydrate, potentially converging with the upper critical temperature. Given the significant density changes anticipated near the upper critical temperature, it is likely that the ratio becomes markedly more sensitive to both pressure and temperature in this vicinity. Unfortunately, density data for this system near the upper critical temperature are currently unavailable, preventing verification of this hypothesis.

In following section, we have described the phase diagram of 1-1 salt hydrate such as NaCl and LiCl, 2-1 salt hydrate such as CaCl2, 1-2 salt hydrate such as Li2SO4, 2-2 salt hydrate such as MgSO4.

**a. NaCl**

|  |  |  |
| --- | --- | --- |
| Fig 1. Phase diagram of the NaCl + H2O system Symbols: experimental data reported in reference data [1-2]. Lines: the present model results. (Regions are NOT well defined. Please replace graph) | | |
| A graph of a line  Description automatically generated with medium confidence  Fig 2. Parity plot of NaCl for n = 2 | Fig 3. Parity plot of NaCl for n = 3 | Fig 4. Parity plot of NaCl for n = 4 |

Figure 4 illustrates the phase diagram of the NaCl + H2O system, depicting regions that represent specific mixtures of NaCl and water at various temperatures. The eutectic point, at 253K, is the lowest temperature at which a liquid phase is stable under a given pressure. At this point, a solid solute, a solid solvent, and a liquid mixture coexist in equilibrium. The eutectic point, also known as the eutectic temperature, represents the lowest possible melting point across all mixing ratios of the components. The solid-liquid equilibrium data closely match with available experimental values. Figures 2, 3, and 4 are parity plots for n = 2, n = 3, and n = 4, respectively. These plots demonstrate that the model calculations for n = 3 and n = 4 are more reliable than those for n = 2.

**b. LiCl**

|  |  |  |
| --- | --- | --- |
| Fig 5. Phase diagram of the LiCl + H2O system.  Symbols: experimental data reported in reference data [1-3]. Lines: the present model results. (please add 4 H2O also as curly bracket) | | |
| A graph of a function  Description automatically generated with medium confidence  Fig 6. Parity plot of LiCl for n = 2 | Fig 7. Parity plot of LiCl for n = 3 | Fig 8. Parity plot of LiCl for n = 4 |

Figure 5 depicts the phase diagram for the LiCl + H2O system. In addition to anhydrous LiCl, there are four solid lithium chloride hydrates, each containing 1, 2, 3, 4, or 5 water molecules. These hydrates are highly soluble in water. For instance, the solubility of the monohydrate LiCl·H2O is approximately 20 mol/kg of H2O in pure water at 273 K. At the eutectic temperature of 199 K, which is one of the lowest among alkali + water or alkaline earth + water systems, the stable solid is LiCl·5H2O. Despite this very low temperature, the saturated solution has a high concentration, with a 24% volume fraction of salt at the eutectic point. The calculated liquidus line in the LiCl + H2O system shows good agreement with the available experimental data. Figures 6, 7, and 8 are parity plots for n = 2, n = 3, and n = 4, respectively. These plots demonstrate that the model calculations for n = 3 and n = 4 are more reliable than those for n = 2.

**c. CaCl2**

|  |  |  |
| --- | --- | --- |
| Fig 9. Phase diagram of the CaCl2 + H2O system Symbols: experimental data reported in reference data [4-8]. Lines: the present model results. | | |
| A graph of a graph  Description automatically generated  Fig 10. Parity plot of CaCl2 for n = 2 | Fig 11. Parity plot of CaCl2 for n = 3 | Fig 12. Parity plot of CaCl2 for n = 4 |

Figure 9 illustrates the phase diagram for the CaCl2 + H2O system, showing equilibrium phases as a function of the volume fraction of CaCl2 and temperature. There are three solid CaCl2 hydrates: CaCl2·2H2O, CaCl2·4H2O, and CaCl2·6H2O. CaCl2·6H2O and CaCl2·2H2O occur naturally, known as antarctictite and sinjarite, respectively. The eutectic point of this system is around 223.5 K.

Our model shows excellent agreement with the available experimental data. Figures 10, 11, and 12 are parity plots for n = 2, n = 3, and n = 4, respectively. These plots demonstrate that the model calculations for n = 3 and n = 4 are more reliable than those for n = 2.

**d. Li2SO4**

|  |  |  |
| --- | --- | --- |
| Fig 13. Phase diagram of the Li2SO4+H2O system.  Symbols: experimental data reported in reference data [1-3]. Lines: the present model results. (Regions are NOT well defined. Please replace graph) | | |
| A graph of a graph with red dots  Description automatically generated with medium confidence  Fig 14. Parity plot of Li2SO4 for n = 2 | Fig 15. Parity plot of Li2SO4 for n = 3 | Fig 16. Parity plot of Li2SO4 for n = 4 |

Figure 13 illustrates the phase diagram of the Li2SO4 + H2O system, which exhibits a simple curve. The solubility of Li2SO4 shows a slight increase until reaching the eutectic point at around 250K. At this point, only one hydrate form of the salt, Li2SO4·H2O, exists. Our model demonstrates excellent agreement with the available experimental data. Figures 14, 15, and 16 depict parity plots for n = 2, n = 3, and n = 4, respectively, highlighting that the model calculations for n = 3 and n = 4 are more reliable than those for n = 2.

1. **MgSO4**

|  |  |  |
| --- | --- | --- |
| Fig 17. Phase diagram of the MgSO4 + H2O system Symbols: experimental data reported in reference data [9,10,14,15,16]. Lines: the present model results. | | |
| A graph of a graph of data points  Description automatically generated  Fig 18. Parity plot of MgSO4 for n = 2 | Fig 19. Parity plot of MgSO4 for n = 3 | Fig 20. Parity plot of MgSO4 for n = 4 |

Figure 17 depicts the phase diagram of the MgSO4 + H2O system, presenting a more intricate structure due to the presence of multiple phases. Apart from the solid, liquid, and gas phases, there are several hydrate phases with varying numbers of water molecules, ranging from 1 to 11. The complexity of the phase diagram for the MgSO4 + H2O system provides valuable insights into the system's behaviour under different conditions. For instance, it can help determine the conditions under which magnesium sulphate heptahydrate forms or decomposes. Such information finds application in various fields, including magnesium sulphate production and water desalination. Our model exhibits excellent agreement with the available experimental data. Figures 18, 19, and 20 show parity plots for n = 2, n = 3, and n = 4, respectively, underscoring the greater reliability of the model calculations for n = 3 and n = 4 compared to n = 2.

**Table-4 The eutectic point (or critical point) values, estimated using our model ,equation 16 and 17**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | **Our Model Calculation** | | **Reference Data** | | **% Error** | |  |
| *Salt hydrates* | *Critical Molality* | *Critical Temperature* | *Critical Molality* | *Critical Temperature* | *Temperature Deviation* | *Molality Deviation* | *Reference Papers* |
| **CaCl2** | 3.936351 | 229.065 | 4.4195 | 222.978 | 2.729865727 | -10.9322 | [4-8] |
| **Li2SO4** | 3.450383 | 250.217 | 3.519 | 250.15 | 0.02678393 | 1.949909 | [1-3] |
| **LiCl** | 8.682483 | 192.166 | 8.217 | 198.071 | 2.981254197 | 5.664876 | [1-3] |
| **MgSO4** | 1.841605 | 270.406 | 1.75 | 269.45 | 0.354796808 | 5.23456 | [9, 14-16] |
| **NaCl** | 4.958393 | 251.974 | 5.19 | 251.9 | 0.029376737 | 4.462556 | [1-2] |

The table above compares the eutectic points derived from our study with the reference values. The eutectic point denotes the endpoint of a phase equilibrium curve in a phase diagram, signifying the stage where a substance's liquid and solid phases merge. This point holds significance as it defines the conditions under which a substance undergoes a phase transition between solid and liquid states. Our model indicates a slight, yet acceptable, deviation from the reference values, as outlined in the table.

**Conclusion -** The utilization of salt hydrates in thermochemical heat storage systems presents a promising avenue for achieving efficient and sustainable thermal energy storage, crucial for advancing renewable energy integration and addressing seasonal variations in energy generation. The exploration conducted in this paper underscores the significant potential of salt hydrates, such as sodium chloride, calcium chloride, and magnesium sulfate, lithium chloride, in efficiently storing and retrieving thermal energy. Sensible heat storage, latent heat storage using phase change materials (PCMs), and thermochemical heat storage have all been investigated, with thermochemical heat storage standing out due to its high energy storage density and minimal heat loss during storage.Furthermore, various models, including mean field theory and correlations derived from the Flory-Huggins theory and Extended Debye Huckel theory, have been employed to predict their thermodynamic properties, emphasizing the importance of precise experimental data for accurate modeling. Analysis of results revealed slight deviations between predictions and experimental data, with notable trends observed. Validation against experimental data confirmed the accuracy of our models, emphasizing their potential utility in predicting salt hydrate behavior accurately.

In summary, salt hydrates offer significant potential for efficient and sustainable thermal energy storage, promising to address challenges in renewable energy integration and contribute to a greener, more resilient energy infrastructure. By leveraging insights from experimental studies and thermodynamic modeling, we can unlock the full potential of salt hydrates and pave the way towards a more sustainable future.

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**References: -**

1. Tatsidjodoung, P.; Le Pierrès, N.; Luo, L. Renewable and Sustainable Energy Reviews 2013, 18, 327.
2. Kalaiselvam S, Parameshwaran R. Seasonal thermal energy storage. Therm energystorageTechnolSustain-SystDesAssessAppl.ElsevierInc;2014.p. 145–62.http://dx.doi.org/10.1016/B978-0-12-417291-3.00007-4.
3. GaoL,Zhao J, Tang Z. A review on bore hole seasonal solar thermal energy storage. Energy procedia,vol.70.ElsevierB.V;2015.p.209–18.http://dx.doi. org/10.1016/j.egypro.2015.02.117.
4. Pinel P, Cruickshank Ca, Beausoleil-MorrisonI, Wills A. A review of available methods for seasonal storage of solar thermal energy in residential applications. Renew Sustain Energy Rev 2011;15:3341–59. http://dx.doi. org/10.1016/j.rser.2011.04.013.
5. Pielichowska K, Pielichowski K. Phase change materials for thermal energy storage. Prog Mater Sci 2014;65:67–123. [http://dx.doi.org/10.1016/j. pmatsci.2014.03.005](http://dx.doi.org/10.1016/j.%20pmatsci.2014.03.005).
6. Nkwetta DN, Haghighat F. Thermal energy storage with phase change material- a state-of-the art review. Sustain Cities Soc 2014;10:87–100. http://dx.doi.org/10.1016/j.scs.2013.05.007.
7. Sharif MKA, Al-abidi AA, Mat S, Sopian K, Ruslan M H. Review of the application of phase change material for heating and domestic hot water systems. Renew Sustain Energy Rev 2015;42:557–68. http://dx.doi.org/ 10.1016/j.rser.2014.09.034.
8. P. Tatsidjodoung, N.L. Pierrs, L. Luo, A review of potential materials for thermal energy storage in building applications, Renew. Sustain. Energy Rev., 18 (2013), pp. 327-349
9. D. Aydin, S.P. Casey, S. Riffat, The latest advancements on thermochemical heat storage systems, Renew. Sustain. Energy Rev., 41 (2015), pp. 356-367
10. Blarke M B, Lund H. The effectiveness of storage and relocation options in renewable energy systems. Renew Energy 2008;33:1499–507. http://dx.doi. org/10.1016/j.renene.2007.09.001.
11. M. Gaeini, H.A. Zondag, C.C.M. Rindt, Effect of kinetics on the thermal performance of a sorption heat storage reactor, Applied Thermal Engineering, 102, (2016), 520-531
12. H. Zondag, A. Kalbasenka, M. van Essen, L. Bleijendaal, R. Schuitema, W. van Helden, L. Krosse, First studies in reactor concepts for thermochemical storage, Proc. Eurosun (2008)
13. Pinel, P.; Cruickshank, C. A.; Beausoleil-Morrison, I.; Wills, A. Renewable and Sustainable Energy Reviews 2011, 15, 3341.
14. Trausel, F et al., “A review on the properties of salt hydrates for thermochemical storage”, SHC 2013, International Conference on Solar Heating and Cooling for Buildings and Industry September 23-25, 2013, Freiburg, Germany, Energy Procedia; 2014
15. Ali, H., Sarkisian, E.: Thermodynamics of vapor–liquid equilibrium in mixed solvent electrolyte sys tems. Sci. Iran **5**, 67–81 (1998)
16. Haghtalab, A., Vera, J.: A nonrandom factor model for the excess Gibbs energy of electrolyte solu tions. AIChE J. **34**, 803–813 (1988)
17. Holmes, H.F., Baes Jr., C.F., Mesmer, R.E.: Isopiestic studies of aqueous solutions at elevated temperatures I. KCl, CaCl2, and MgCl2. J. Chem. Thermodyn. **10**, 983–996 (1978)
18. Clegg, S.L., Pitzer, K.S., Brimblecombe, P.: Thermodynamics of multicomponent, miscible, ionic  solutions. Mixtures including unsymmetrical electrolytes. J. Phys. Chem. **96**, 9470–9479 (1992)
19. Clegg, S.L., Pitzer, K.S.: Thermodynamics of multicomponent, miscible, ionic solutions: generalized equations for symmetrical electrolytes. J. Phys. Chem. **96**, 3513–3520 (1992)
20. Ghalami-Choobar, B., Mossayyebzadeh-Shalkoohi, P.: Activity coeffcient measurements and ther modynamic modeling of (CaCl2+ l-alanine + water) system based on potentiometric determination  at *T* = (298.2, 303.2, and 308.2) K. J. Chem. Eng. Data **60**, 2879–2894 (2015)
21. Ghalami-Choobar, B., Sayyadi-Nodehi, F.: Thermodynamic study of the (NaCl + serine + water)  mixtures using potentiometric measurements at *T* = (298.2 and 303.2) K. Fluid Phase Equilib. **380**,  48–57 (2014)
22. Ghalami-Choobar, B., Mirzaie, S.: Thermodynamic study of (KCl + proline + water) system based  on potentiometric measurements at *T* = (298.2 and 303.2) K. J. Mol. Liq. **169**, 124–129 (2012)
23. K. Linnow, M. Niermann, D. Bonatz, K. Posern, M. Steiger, Experimental studies of the mechanism and kinetics of hydration reactions, Energy Procedia, 48 (2014), pp. 394-404, 10.1016/j.egypro.2014.02.046
24. Piperopoulos, E.; Calabrese, L.; Bruzzaniti, P.; Brancato, V.; Palomba, V.; Caprì, A.; Frazzica, A.; Cabeza, L.F.; Proverbio, E.; Milone, C. Morphological and Structural Evaluation of Hydration/Dehydration Stages of MgSO4 Filled Composite Silicone Foam for Thermal Energy Storage Applications. Appl. Sci. 2020, 10, 453. <https://doi.org/10.3390/app10020453>
25. M. Gaeini, S.A. Shaik, C.C.M. Rindt, Characterization of potassium carbonate salt hydrate for thermochemical energy storage in buildings, Energy and Buildings, 196, (2019), 178-193
26. A.A. Hawwash, Hamdy Hassan, Khalid El feky, Impact of reactor design on the thermal energy storage of thermochemical Materials, Applied Thermal Engineering, 168, (2020), 114776
27. Wei Li, Qiuwang Wang, Min Zeng, Heat transformation performance of salt hydrate-based thermochemical energy storage sorbent during hydration, Cleaner Chemical Engineering, 1, (2022), 100006
28. Fenil Desai, Sunku Prasad Jenne, P. Muthukumar, Muhammad Mustafizur Rahman, Thermochemical energy storage system for cooling and process heating applications: A review, Energy Conversion and Management, 229, (2021), 113617
29. Changsheng Hao, Guosheng Feng, Changjie Ma, Camila Barreneche, Xiaohui She, Performance analysis of a novel multi-module columnar packed bed reactor with salt hydrates for thermochemical heat storage, Journal of Energy Storage, 86 (Part A), (2024), 111170
30. Hayatina I, Auckaili A, Farid M. Review on Salt Hydrate Thermochemical Heat Transformer. Energies. 2023; 16(12):4668. <https://doi.org/10.3390/en16124668>
31. Weisan Hua, Hongfei Yan, Xuelai Zhang, Xidong Xu, Liyu Zhang, Yao Shi, Review of salt hydrates-based thermochemical adsorption thermal storage technologies. Journal of Energy Storage, 56 (C), 106158 (2022)
32. Zhendong Ye, Hongzhi Liu, Wantong Wang, Han‐Wen Liu, Jing Lv, Fan Yang, Reaction/sorption kinetics of salt hydrates for thermal energy storage, Journal of Energy Storage, 56(B), 106122 (2022)
33. Hui Yan Yang, Chengcheng Wang, Lige Tong, Shaowu Yin, Li Wang, Yulong Ding, Salt Hydrate Adsorption Material-Based Thermochemical Energy Storage for Space Heating Application: A Review, Energies 2023, 16(6), 2875; https://doi.org/10.3390/en16062875
34. Kenisarin, M., & Mahkamov, K. (2016). Salt hydrates as latent heat storage materials: Thermophysical properties and costs. Solar Energy Materials and Solar Cells, 145, 255-286.
35. Guillen, G. R., Pan, Y., Li, M., & Hoek, E. M. (2011). Preparation and characterization of membranes formed by nonsolvent induced phase separation: a review. Industrial & Engineering Chemistry Research, 50(7), 3798-3817.
36. S. K. Sharma, C. K. Jotshi, Amrao Singh, Density of molten salt hydrates—experimental data and an empirical correlation, The Canadian Journal of Chemical Engineering 65 (1987) 171-174
37. A. Minevich, Y. Marcus, and L. Ben-Dor, Densities of Solid and Molten Salt Hydrates and Their Mixtures and Viscosities of the Molten Salts, J. Chem. Eng. Data 49 (2004) 1451–1455
38. Joseph A. Rard, The Isopiestic Method: 100 Years Later and Still in Use, Journal of Solution Chemistry 48 (2019) 271–282
39. IngeRörig-Dalgaard, Direct Measurements of the Deliquescence Relative Humidity in Salt Mixtures Including the Contribution from Metastable Phases, ACS Omega 6 (2021) 16297−16306
40. Elena N. Tsurko, Roland Neueder and Werner Kun, Activity of Water, Osmotic and Activity Coefficients of Sodium Glutamate and Sodium Aspartate in Aqueous Solutions at 310.15 K, Acta Chim. Slov. 56 (2009) 58–64
41. Magin RL, Mangum BW, Statler JA, Thornton DD. Transition Temperatures of the Hydrates of Na2SO4, Na2HPO4, and KF as Fixed Points in Biomedical Thermometry. J Res Natl Bur Stand (1977). 1981 Mar-Apr;86(2):181-192. doi: 10.6028/jres.086.007. PMID: 34566042; PMCID: PMC6756278.
42. Archer, D. G., & Rard, J. A., Isopiestic Investigation of the Osmotic and Activity Coefficients of Aqueous MgSO4 and the Solubility of MgSO4. 7H2O (cr) at 298.15 K: Thermodynamic Properties of the MgSO4+ H2O System to 440 K. Journal of Chemical & Engineering Data, 43(5), (1998) 791-806.
43. Pitzer, K. S., & Shi, Y., Thermodynamics of calcium chloride in highly concentrated aqueous solution and in hydrated crystals. Journal of solution chemistry, 22, (1993) 99-105.
44. Monnin, C., Dubois, M., Papaiconomou, N., & Simonin, J. P., Thermodynamics of the LiCl+ H2O system. Journal of Chemical & Engineering Data, 47(6), (2002) 1331-1336.
45. Kenneth S. Pitzer, Thermodynamics of electrolytes. I. Theoretical basis and general equations, J. Phys. Chem. 77 (2) (1973), 268–277
46. Pitzer, K.S. (1991). Activity Coefficients in Electrolyte Solutions (2nd ed.). CRC Press. <https://doi.org/10.1201/9781351069472>
47. Maojie Chai, Min Yang, Rundong Qi, Zhangxin Chen, Jing Li, (2022) Vapor-liquid equilibrium (VLE) prediction for dimethyl ether (DME) and water system in DME injection process with Peng-Robinson equation of state and composition dependent binary interaction coefficient, Journal of Petroleum Science and Engineering, 211, 110172
48. Irong Nie, Ziwei Zheng, Mingxia Lu, Shun Yao, Dong Guo. (2022) Phase Behavior of Ionic Liquid-Based Aqueous Two-Phase Systems. International Journal of Molecular Sciences, 23 (20), 12706. <https://doi.org/10.3390/ijms232012706>
49. Lalaso V. Mohite, Vinay A. Juvekar, Jyoti Sahu. (2019) Quantification of Polymer–Surface Interaction Using Microcalorimetry. Industrial & Engineering Chemistry Research, 58 (18), 7495-7510. <https://doi.org/10.1021/acs.iecr.8b04792>
50. Edgar J. Acosta, Arti S. Bhakta. (2009) The HLD‐NAC Model for Mixtures of Ionic and Nonionic Surfactants. Journal of Surfactants and Detergents,12 (1), 7-19. <https://doi.org/10.1007/s11743-008-1092-4>
51. P.A.J. Donkers, L.C. Sögütoglu, H.P. Huinink, H.R. Fischer, O.C.G. Adan, (2017) A review of salt hydrates for seasonal heat storage in domestic applications, Applied Energy, **199**, 45-68. <https://doi.org/10.1016/j.apenergy.2017.04.080>

**REFERENCES FOR CONCLUSION AND RESULTS**

1. Pielichowska, K.; Pielichowski, K. Phase change nanomaterials for thermal energy storage. In *Nanotechnology for Energy Sustainability*; Wiley: Hoboken, NJ, USA, 2017; pp. 459–484.
2. H. Lahmidi, S. Mauran, V. Goetz, Definition, test and simulation of a thermochemical storage process adapted to solar thermal systems, Sol. Energy 80 (7) (2006) 883–893
3. Li, D., Zeng, D., Yin, X., Han, H., Guo, L., & Yao, Y. (2016). Phase diagrams and thermochemical modelling of salt lake brine systems. II. NaCl+ H2O, KCl+ H2O, MgCl2+ H2O and CaCl2+ H2O systems. *Calphad*, *53*, 78-89.
4. Guendouzi, M. E., Mounir, A., & Dinane, A. (2003). Water activity, osmotic and activity coefficients of aqueous solutions of Li2SO4, Na2SO4, K2SO4,(NH4) 2SO4, MgSO4, MnSO4, NiSO4, CuSO4, and ZnSO4 at T= 298.15 K. *The Journal of Chemical Thermodynamics*, *35*(2), 209-220.
5. Pillay, V., Gärtner, R. S., Himawan, C., Seckler, M. M., Lewis, A. E., & Witkamp, G. J. (2005). MgSO4+ H2O System at Eutectic Conditions and Thermodynamic Solubility Products of MgSO4⊙ 12H2O (s) and MgSO4⊙ 7H2O (s). *Journal of Chemical & Engineering Data*, *50*(2), 551-555.
6. Li, D., Zeng, D., Yin, X., & Gao, D. (2018). Phase diagrams and thermochemical modeling of salt lake brine systems. III. Li2SO4+ H2O, Na2SO4+ H2O, K2SO4+ H2O, MgSO4+ H2O and CaSO4+ H2O systems. *Calphad*, *60*, 163-176.
7. Archer, D. G., & Rard, J. A. (1998). Isopiestic Investigation of the Osmotic and Activity Coefficients of Aqueous MgSO4 and the Solubility of MgSO4⊙ 7H2O (cr) at 298.15 K: Thermodynamic Properties of the MgSO4+ H2O System to 440 K. *Journal of Chemical & Engineering Data*, *43*(5), 791-806.
8. Yang, H., Zeng, D., Wang, Q., Chen, Y., & Voigt, W. (2016). Isopiestic measurements of water activity for the Li2SO4–MgSO4–H2O system at 323.15 and 373.15 K. *Journal of Chemical & Engineering Data*, *61*(9), 3157-3162.
9. Guendouzi, M. E., Mounir, A., & Dinane, A. (2003). Water activity, osmotic and activity coefficients of aqueous solutions of Li2SO4, Na2SO4, K2SO4,(NH4) 2SO4, MgSO4, MnSO4, NiSO4, CuSO4, and ZnSO4 at T= 298.15 K. *The Journal of Chemical Thermodynamics*, *35*(2), 209-220.
10. Monnin, C., Dubois, M., Papaiconomou, N., & Simonin, J. P. (2002). Thermodynamics of the LiCl+ H2O system. *Journal of Chemical & Engineering Data*, *47*(6), 1331-1336.
11. Pátek, J., & Klomfar, J. (2006). Solid–liquid phase equilibrium in the systems of LiBr–H2O and LiCl–H2O. *Fluid Phase Equilibria*, *250*(1-2), 138-149.
12. Li, D., Zeng, D., Han, H., Guo, L., Yin, X., & Yao, Y. (2015). Phase diagrams and thermochemical modeling of salt lake brine systems. I. LiCl+ H2O system. *Calphad*, *51*, 1-12.
13. Rard, J. A., Clegg, S. L., & Palmer, D. A. (2007). Isopiestic determination of the osmotic and activity coefficients of Li 2 SO 4 (aq) at T= 298.15 and 323.15 K, and representation with an extended ion-interaction (Pitzer) model. *Journal of solution chemistry*, *36*, 1347-1371.
14. Hamer, W. J., & Wu, Y. C. (1972). Osmotic coefficients and mean activity coefficients of uni‐univalent electrolytes in water at 25° C. *Journal of Physical and Chemical Reference Data*, *1*(4), 1047-1100.
15. Rudakov, A. M., Sergievskii, V. V., & Nagovitsyna, O. A. (2017). Dependences of the osmotic coefficients of aqueous calcium chloride solutions on concentration at different temperatures. *Russian Journal of Physical Chemistry A*, *91*, 2361-2365.
16. Czerwienski, G. J. (1986). Osmotic and mean activity coefficients of CaCl2, NaI, LiBr and LiCl in ethanol at 50 degrees C.
17. Partanen, J. I. (2012). Traceable mean activity coefficients and osmotic coefficients in aqueous calcium chloride solutions at 25 C up to a molality of 3.0 mol· kg–1. *Journal of Chemical & Engineering Data*, *57*(11), 3247-3257.
18. DUCKETT, L., HOLLIFIELD, J., & PATTERSON, C. (1986). Osmotic coefficients of aqueous CaCl2 solutions from 3 to 12 m at 50 oC. *Journal of chemical and engineering data*, *31*(2), 213-214.
19. Ananthaswamy, J., & Atkinson, G. (1985). Thermodynamics of concentrated electrolyte mixtures. 5. A review of the thermodynamic properties of aqueous calcium chloride in the temperature range 273.15-373.15 K. *Journal of Chemical and Engineering Data*, *30*(1), 120-128.
20. Gruszkiewicz, M. S., & Simonson, J. M. (2005). Vapor pressures and isopiestic molalities of concentrated CaCl2 (aq), CaBr2 (aq), and NaCl (aq) to T= 523 K. *The Journal of Chemical Thermodynamics*, *37*(9), 906-930.
21. Goldberg, R. N., & Nuttall, R. L. (1978). Evaluated activity and osmotic coefficients for aqueous solutions: The alkaline earth metal halides. *Journal of Physical and Chemical Reference Data*, *7*(1), 263-310.
22. Staples, B. R., & Nuttall, R. L. (1977). The activity and osmotic coefficients of aqueous calcium chloride at 298.15 K. *Journal of Physical and Chemical Reference Data*, *6*(2), 385-408.
23. Pitzer, K. S., & Shi, Y. (1993). Thermodynamics of calcium chloride in highly concentrated aqueous solution and in hydrated crystals. *Journal of solution chemistry*, *22*, 99-105.