**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 hydrates of salt in heat-storage thermochemical systems. Our study involved the creation of thorough mathematical models to explain 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 plentiful in the summer compared to the winter. The overall supply of solar energy is enough to meet the entire energy demand in homes. However, to fully depend on sustainable energy sources, an effective energy storage method is essential. One of the oldest and simplest methods for storing thermal energy is using water, such as with a boiler. This approach is efficient and cost-effective for short-term heat storage [1]. One drawback is that a substantial amount of water is required, and despite insulation, there will still be heat loss. Based on the principle of storage, thermal storage technologies suitable for building applications are divided into three groups: sensible heat [2-4], thermochemical heat storage [8] and latent heat [5-7]. Compared to the other two heat storage techniques, the latent heat storage method offers a higher energy storage density and almost eliminates heat loss through the use of a reversible physical or chemical reaction [9]. One promising option for storing thermal energy is through reversible gas-solid reactions [10]. An endothermic dissociation reaction breaks the thermochemical material into two halves in order to store heat (charging). Following the reaction process, the energy can subsequently be recovered through the reverse exothermic reaction (discharging) between these two components [11]. A good storage medium should be affordable, stable, non-corrosive, non-toxic, and have a high density of stored energy [12]. These conditions are met by several salt hydrates. Heat storage is made possible by phase change materials (PCMs), which use a phase transition within the material. In general, PCMs can store more energy than water [13]. Phase change materials have the disadvantage of being expensive and requiring storage at temperatures that prevent phase change, which results in heat loss during storage. Thermochemical materials (TCMs), on the other hand, store heat via a chemical reaction. TCMs have a huge quantity of storage capacity; a small volume is required to store a large amount of heat. There is no heat loss throughout storage since heat is retained by a chemical process. The water, PCM, and TCM storage volumes required to meet the average household's yearly thermal energy demand are provided by [14]. One common type of TCM that is used is salt hydrates, which are dehydrated, and the dry salt and water are stored apart in order to store thermal energy. The reversible reaction of hydration and dehydration of a salt hydrate is depicted in equation 1 below.

(1)

Because of a decrease in the enthalpy of hydrogen bonding, the contact between salt hydrate and water gradually decreases with temperature. Phase separation eventually occurs when the temperature reaches the critical point [1]. Quantifying the thermodynamic parameters of aqueous solutions of salt hydrates is crucial to understanding and improving the phase behaviour. This necessitates precise experimental data as well as a robust model capable of predicting system properties within temperature and composition ranges where experimental data are lacking.

Researchers employ the Modified Pitzer (MP) model to determine excess Gibbs energy, activity coefficients, water activity and osmotic coefficient, 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 characteristics of aqueous solutions containing multiple components pertinent to environmental contexts. A comprehensive thermodynamic model is proposed to forecast the behaviour of aqueous mixtures containing multiple ions such as Na+, K+, Mg2+, Ca2+, 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 attributes of electrolyte solutions, including osmotic coefficients and activity coefficients, are crucial for precise 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 have a significant impact on the design and enhancement 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 MgSO4 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 influence of reactor configuration on thermal energy retention, particularly focusing on salt hydrates. While their investigation reveals significant insights into how reactor geometry influences pressure drops, 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 employed for sorption and reaction centric 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-containing salt hydrate combined with expanded graphite within a Thermal Energy Storage (TES) module. While offering valuable perspectives on mass and heat 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 packed-bed reactor with columnar configuration for storing thermochemical heat using salt hydrates, showcasing advantages in terms of resistance loss, reaction time and reaction rate. 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 energy storage, heat recovery 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 gas-solid thermochemical energy storage system utilizing salt hydrates.

Numerous experimental investigations detailed in the literature have explored the thermodynamic characteristics of diverse salt hydrates. [34]. These studies cover a range of aspects such as water activity in the solution, phase separation behaviour, and solubility analysis. The results of these studies are thoroughly recorded by reference [35]. The approaches to activity measuring that are most frequently used in the laser-light scattering [37], vapor pressure osmometry [36], isopiestic method [38], sedimentation technique [40] and dew point method [39].

Cloud-point data is used to build the coexistence curves for salt hydrates in phase separation experiments. Visual observations or the thermos-optical analysis approach [41] can be used to determine the cloud point. Various models have been employed to predict salt hydrate behaviour, including those founded on osmotic virial expansion [42], equations of state [43], and group contribution schemes [44].

The behaviour of salt hydrate at lower temperatures and its phase behaviour at higher temperatures should be seamlessly connected by a trustworthy thermodynamic model. However, the current models employ two distinct parameter sets: one designed for phase separation data and the other for analysing data on low-temperature activity. Unfortunately, parameters derived from low-temperature activity data (278–343K) prove inadequate for predicting phase separation and coexistence curves in salt hydrate systems. This discrepancy arises from either model inaccuracies or experimental data limitations. Achieving high accuracy in low-temperature activity data is essential as it needs to be extrapolated across a broad temperature range beyond the measurement range, where parameter estimate errors of little magnitude are amplified. Similarly, model inaccuracies compound the issue. Additionally, the temperature range over which any activity measuring approach is accurate is very small, meaning that combining data from numerous techniques is necessary to increase the temperature range. However, this process introduces its own set of errors.

Using correlations obtained from models like the extended Debye Hückel theory [46] and the generalized Flory-Huggins theory [45], and a forecasting of the coexistence curve for salt hydrate systems in the phase separation zone has been attempted by combining activity data from several techniques. The approach unfolds as follows: Initially, we delineate the models governing the thermodynamics of salt hydrate systems. We then describe the process used to use information on water activity in salt hydrate systems to estimate the coefficients of these models. The process of analysing the data to determine the model parameters succeeds here. Finally, the selected model is used to evaluate the reported solution activity data's dependability.

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

The osmotic coefficient (φ) of an aqueous electrolyte is linked to the chemical potential of water (µw) in the following way:

(1)

where µ0w is water's chemical potential in its normal condition, the molality of the electrolyte solution is indicated by *m*, the gas constant is represented by *R*, the molecular mass of water is represented by Mw, the number of ions generated upon the dissociation of one electrolyte molecule is shown by and the absolute temperature is indicated by T. 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.

This work expresses the system's total Gibbs free energy as the sum of its 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, the amount of moles of water and salt are represented by and respectively. , indicates 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, *ε* signifies the permittivity of vacuum, *NA* represents Avogadro number, *K* stands for Boltzmann constant, *VS* signifies the molar volume of water*, e* for electronic charge and *DS* indicates dielectric constant 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)

The generalized Flory-Huggins parameter, is found in equation (6) and is best understood as a function of the system's temperature, T, and the volume fraction of the salt hydrate, .By combining Eqn. 2, 3, & 6, total Gibbs free energy of the system is given as,

(8)

where, the amount of moles of water and salt hydrate present in the solution are represented by and 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 incorporating equation 9 and 10 into equation 11 and 12, we derive the following equations that govern the phase equilibria.

(13)

(14)

One can obtain the value of and at specific temperature by concurrently solving Equations (13) and (14). The following conditions identifies the critical point:

(15)

and (16)

Two equations are obtained by replacing the 2nd and 3rd derivatives of the salt hydrate system's free energy (Eqn (8)) in the preceding formulas. (These equations derivations are mention separately in supplementary file). These two equations must be solved simultaneously to determine the critical temperature, *Tc* and critical volume fraction of the salt hydrate, .

1. **Regression analysis of the model parameters**

The parameter used in the Flory-Huggins theory controls how salt and water interacts, 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.

Utilizing the experimental data, this form requires the determination of 3 (n+1) empirical constants. Regarding this representation, we have

(20)

And

(21)

The partial differentiation of with respect to temperature eliminates coefficients , as we can see from the equations above. To estimate the constants, we solely rely on the data concerning the osmotic coefficient of H2O in salt hydrate systems over a variety of temperatures and compositions, regression is performed for all the contants.

Two different values of n, that is n = 3 and 4, are used to test the effect of n (represents the degree of polynomial used in in Equation (18)) on the accuracy of the estimations. In every scenario, regression is performed using the nonlinear Levenberg-Marquardt least-square approach. To assess the quality of the regression, one uses the -norm of the residual (∣∣R∣∣). It is described as:

(22)

where and (j = 1,2…., n data) signify, respectively, the value of the experiment and the quantity to be fitted's associated model prediction (osmotic coefficient data) and the standard deviation is given by σ j.

1. **Results and Discussion: -**

First, we use the suggested method to analyse the regression analysis findings that were obtained from the data. 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 l2-norm of the residuals, ||R||, for the constant values that best fit the data is shown in Table 1. It is noted that, when n = 1, the value of ||R|| is noticeably larger than when n = 2, 3, and 4. Thus, in subsequent analysis, the linear form n=1 is ignored. Since there is no discernible difference between the values of ||R|| for n = 3 and 4, both are considered acceptable.

**Table-1 - l2-norm of the data. Duals, ||R||, representing the constants’ best fit values 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 and 3 displays the constants' regression estimations *, and*  ***,*** (i = 0, 1, . . ., n), for n = 3 and 4 respectively.

***Table-2 The constants’ least square estimations for , and , derived for n =3 using osmotic coefficient data***

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **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 constants’ least square estimations for , , and , derived for n = 4 using osmotic coefficient data***

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **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 l2-norm is used to evaluate the regression's quality. Secondly, the accuracy of predicting critical constants (or eutectic points), namely the critical temperature (Tc) and volume fraction of salt hydrate (), utilizing the estimated parameters is evaluated. Concurrently solving Eqs. (16) and (17) yields these critical values. Next, the precision of predicting the phase diagram is considered. The phase diagram is approximated by simultaneously solving Eqs. (13) and (14).

We use sets of parameters from Table-2 and Table-3 to trace out the Phase diagram of salt hydrates. The table-4 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. In Figure 5,9,13, and 17, the predicted phase diagrams for n =2, 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 parameters derived from activity data. This congruence underscores the reliability of the predictive model in accurately capturing the phase behaviour of the salt hydrates. Parity plots are used to demonstrate the precision of the correlation.

**Table-4 The eutectic point (or critical points) values estimated using our model, equation 15 and 16.**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| *Salt hydrates* | **Our Model Calculation** | | **Reference Data** | | **% Error** | | *Reference Papers* |
| *Critical Molality* | *Critical Temperature* | *Critical Molality* | *Critical Temperature* | *Temperature Deviation* | *Molality Deviation* |
| **CaCl2** | 3.936351 | 229.065 | 4.4195 | 222.978 | 2.729865727 | -10.9322 | [7-12] |
| **Li2SO4** | 3.450383 | 250.217 | 3.519 | 250.15 | 0.02678393 | 1.949909 | [13-16,18] |
| **LiCl** | 8.682483 | 192.166 | 8.217 | 198.071 | 2.981254197 | 5.664876 | [3-6] |
| **MgSO4** | 1.841605 | 270.406 | 1.75 | 269.45 | 0.354796808 | 5.23456 | [14,16-18] |
| **NaCl** | 4.958393 | 251.974 | 5.19 | 251.9 | 0.029376737 | 4.462556 | [1-2] |

An effort was made to forecast the closed-loop phase diagraph for different salt hydrates (NaCl, LiCl, CaCl2, Li2SO4, and MgSO4), by extending the existing correlation as illustrated in Figure 1,5,9,13, and 17. Nevertheless, it is clear that the highest critical temperature is not included by the phase diagraph that the model predicts. One potential explanation for this deviation might lies in the failure of our assumption regarding the independence of (volume of salt/volume of water) ratio 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 substantial density changes expected near the upper critical temperature, it is likely that the ratio becomes much more sensitive to temperature and pressure in this area. It is currently unable to verify this idea due to the lack of density data for this system near the upper critical temperature.

In the following section, we describe the phase diagrams for various salt hydrates: 1-1 salt hydrates such as NaCl and LiCl, 2-1 salt hydrates such as CaCl2, 1-2 salt hydrates such as Li2SO4, and 2-2 salt hydrates such as MgSO4.

**a. NaCl**

|  |  |  |
| --- | --- | --- |
| Fig 1: The NaCl + H2O system's phase diagram. Symbols: reference data [1-2] reporting experimental data. Lines: the current model's output. | | |
| 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 |

The NaCl + H2O system's phase diagram is shown in Figure 4, with sections representing different NaCl and water combinations at different temperatures. The Eutectic Point is the lowest temperature at which a liquid phase stays stable at a given pressure and it is 253K. At this stage, an equilibrium exists between a solid solute, a solid solvent, and a liquid combination. The lowest melting point that can occur for every combination of component mixing ratios is represented by the eutectic point, commonly referred to as the eutectic temperature. 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: The LiCl + H2O system's phase diagram. Symbols: reference data [3-6] reporting experimental data. Lines: the current model's output. | | |
| 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 |

The phase diagram for the LiCl + H2O system is shown in Figure 5. There are four solid lithium chloride hydrates in addition to anhydrous LiCl, and each one has one, two, three, four, or five water molecules. These hydrates dissolve quite well in water. For example, in pure water at 273 K, the solubility of the monohydrate LiCl·H2O is about 20 mol/kg of H2O. LiCl·5H2O is a stable solid at the eutectic temperature of 199 K, which is one of the lowest in alkali + water or alkaline earth + water systems. The saturated solution exhibits a high concentration with a 24% volume proportion of salt at the eutectic point despite the extremely low temperature. There is good agreement between the estimated liquidus line in the LiCl + H2O system and 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: The CaCl2 + H2O system's phase diagram. Symbols: reference data [7-12] reporting experimental data. Lines: the current model's output. | | |
| 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 |

The phase diagram for the CaCl2 + H2O system is shown in Figure 9 describing the equilibrium phases as a function of temperature and the volume fraction of CaCl2. 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: The Li2SO4 + H2O system's phase diagram. Symbols: reference data [13-16, 18] reporting experimental data. Lines: the current model's output. | | |
| 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**

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| Fig 17: The MgSO4 + H2O system's phase diagram. Symbols: reference data [14, 16-18] reporting experimental data. Lines: the current model's output. | | |
| 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 MgSO4 + H2O system’s phase diagram 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.

**Conclusion -** The utilization of salt hydrates in thermochemical heat storage systems presents a promising avenue for achieving sustainable and efficient 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 sulphate, lithium chloride, in efficiently storing and retrieving thermal energy. Sensible heat storage, latent heat storage using thermochemical heat storage and phase change materials (PCMs) 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 Hückel theory, have been employed to predict their thermodynamic properties, emphasizing the importance of precise experimental data for accurate modelling. 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 behaviour 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 modelling, we can unlock the full potential of salt hydrates and pave the way towards a more sustainable future.

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