**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. ~~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~~ 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]. ~~A disadvantage is that a large volume of water is needed and that in spite of insulation, heat will be lost.~~ One drawback is that a substantial amount of water is required, and despite insulation, there will still be heat loss. ~~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].~~ Thermal storage technologies appropriate for building applications are categorized into three methods based on the storage principle: sensible heat (such as water tanks and underground storage) [2-4], latent heat (such as ice and 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~~ The latent heat storage method utilizes a reversible physical or chemical reaction, offering higher energy storage density and nearly eliminating heat loss compared to the other two heat storage methods [9]. ~~One promising possibility to store thermal energy is by means of reversible gas solid reactions~~ One promising option for storing thermal energy is through 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~~ Heat is stored in an endothermic dissociation reaction, which splits the thermochemical material into two components (charging). Later, the energy can be recovered through the reverse exothermic reaction between these two components (discharging), following the reaction process [11]. ~~An interesting storage material should be low cost, non-toxic, non-corrosive and stable with high energy storage density~~ An ideal storage material should be inexpensive, non-toxic, non-corrosive, stable, and have a 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~~ Several salt hydrates meet these criteria. Phase change materials (PCMs) enable heat storage by utilizing a phase transition within the material. PCMs generally have a higher 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~~ One drawback is that phase change materials are costly and still experience heat loss during storage because storage must occur at temperature levels that prevent the phase change. In contrast, thermochemical materials (TCMs) store heat through a chemical reaction. TCMs boast a significant storage capacity, necessitating only a small volume to store a large amount of heat. Since heat is stored through a chemical reaction, there is no loss of heat during storage. The storage volumes needed for the annual thermal energy demand of an average household stored in water, PCM, and TCM are provided 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 prevalent TCMs utilized are salt hydrates, where thermal energy is stored by dehydrating the salt hydrate and storing the dry salt and water separately. ~~The reversible reaction of hydration and dehydration of a salt hydrate is shown in Eq. 1.~~  The below equation 1 illustrates the reversible reaction of hydration and dehydration of a salt hydrate.

(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.~~ As temperature rises, the interaction between salt hydrate and water gradually diminishes because of the decrease in the enthalpy of hydrogen bond. Eventually, beyond the critical temperature, phase separation takes place [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~~. In order to comprehend and enhance the phase behaviour, it's imperative to quantify the thermodynamic properties of aqueous solutions of salt hydrates. 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.

~~Utilizing the Modified Pitzer (MP) model, researchers aim to determine activity coefficients, osmotic coefficients, excess Gibbs energy, and water activity,~~ Researchers employ the Modified Pitzer (MP) model to determine osmotic coefficient, activity coefficients, water activity and excess Gibbs energy, 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~~ 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~~ of water-based mixtures containing multiple 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~~ 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 ~~play a pivotal role in the design and optimization of~~ play an important role in 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 Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA) 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~~ 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 used for sorption and reaction-based TCES~~ 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-based salt hydrate and expanded graphite in a thermal energy storage (TES) module~~ 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 ~~columnar packed-bed reactor for thermochemical heat storage~~ 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 ~~salt hydrate-based gas-solid thermochemical energy storage~~ gas-solid thermochemical energy storage system utilizing salt hydrates.

~~A large number of experimental studies have been reported in the literature on the thermodynamic properties of various salt hydrates~~ Numerous experimental investigations detailed in the literature have explored the thermodynamic characteristics of diverse 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~~ These studies cover a range of aspects such as water activity in the solution, phase separation behaviour, and solubility analysis. ~~The findings from these investigations are thoroughly 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],~~ The findings from these investigations are comprehensively documented by reference [35]. The most commonly utilized methods for activity measurements include laser-light scattering [37], vapor pressure osmometry [36], isopiestic method [38], sedimentation technique [40] and dew point method [39].

~~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].~~  In phase separation investigations, the coexistence curves for salt hydrates are derived from cloud-point data. Cloud point is determined either through thermos-optical analysis method [41] or visual observations. Various models have been employed to predict salt hydrate behavior, including those founded on osmotic virial expansion [42], equations of state [43], and 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.~~ A reliable thermodynamic model should seamlessly connect the activity of salt hydrate at lower temperatures with its phase behaviour at higher temperatures. However, current models utilize two distinct sets of parameters: one to correlate low-temperature activity data and another for phase separation data. 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 small inaccuracies in parameter estimation are magnified. Similarly, model inaccuracies compound the issue. Moreover, each activity measurement technique has a relatively limited temperature range over which it's accurate, necessitating the combination of data obtained from multiple techniques to extend the temperature range. However, this process introduces its own set of errors.

~~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.~~ By leveraging correlations derived from models such as the generalized Flory-Huggins theory [45] and the Extended Debye Hückel theory [46], and integrating activity data from various techniques, an endeavour has been made to forecast the coexistence curve for salt hydrate systems within the phase separation region. The approach unfolds as follows: Initially, we delineate the models governing the thermodynamics of salt hydrate systems. Subsequently, we outline the methodology employed to estimate the coefficients of these models’ using data on the activity of water in salt hydrate systems. This is succeeded by the analysis of results to derive the model parameters. Ultimately, the chosen model is applied to assess the reliability of the reported solution activity data.

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

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

(1)

where, µ0w is the standard state chemical potential of water. ~~M~~~~w~~ ~~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.~~ Mw represents the molecular mass of water, denotes the number of ions produced upon dissociation of one molecule of the electrolyte, stands for the molality of the electrolyte solution, *R* represents the gas constant, and *T* signifies 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 expressed as 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, , stands for 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* represents Avogadro number, *K* stands for Boltzmann constant, *ε* is permittivity of vacuum, *e* for electronic charge, *DS* is dielectric constant of water, *VS* signifies 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 which represents 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 are 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 particular temperature *T* are acquired by solving Equations (13) and (14) simultaneously. The critical point is identified by the following condition:

(15)

and (16)

Substituting the second and third derivatives of the free energy of the salt hydrate system (Eqn (8)) into the above equations yields two equations. (These equations derivations are mention separately in supplementary file). The critical temperature, *Tc*, and critical salt hydrate volume fraction, , are established by solving these two equations simultaneously.

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 are determined 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.~~ 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 H2O in salt hydrate systems across a range of temperatures and compositions for the regression of all the constants.

Two different values of n, namely n = 3 and 4 are employed to evaluate the influence of n (the degree of polynomial in in Equation (18)) on the accuracy 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 = 1,2…., 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.~~ Initially, we analyse the results of the regression analysis conducted on the data using 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 l~~~~2~~~~-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 presents the l2-norm of the residuals, ||R||, for the optimal fit values of the constants. It's observed that the value of ||R||, for n = 1 is notably larger than those for n = 2, 3 and 4. Consequently, the linear form n=1 is disregarded in further analysis. The values of ||R||,for n = 3 and 4 exhibit no significant difference from each other, thus both are deemed acceptable.

**Table-1 - l2-norm of the data. Duals, ||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 and 3 lists the regression estimates of the constants *, and*  ***,*** (i = 0, 1, . . ., n), for n = 3 and 4 respectively.

***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 (or eutectic points), 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 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. The accuracy of the correlation is illustrated through parity plots.

**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 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.~~ Given the substantial density changes expected near the upper critical temperature, it is likely that the ratio becomes considerably more sensitive to both pressure and temperature in this region. Unfortunately, density data for this system near the upper critical temperature are currently unavailable, making it impossible to verify this hypothesis.

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**

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| Fig 1. Phase diagram of the NaCl + H2O system Symbols: experimental data reported in reference data [1-2]. Lines: the present model results. | | |
| 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 + H~~~~2~~~~O 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 NaCl + H2O system's phase diagram is shown in Figure 4, with sections representing different NaCl and water combinations at different temperatures. The lowest temperature at which a liquid phase remains stable at a particular pressure is known as the eutectic point, 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**

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| --- | --- | --- |
| Fig 5. Phase diagram of the LiCl + H2O system.  Symbols: experimental data reported in reference data [3-6]. Lines: the present model results. | | |
| 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 + H~~~~2~~~~O 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·H~~~~2~~~~O is approximately 20 mol/kg of H~~~~2~~~~O 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·5H~~~~2~~~~O. 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 + H~~~~2~~~~O system shows good agreement with the available experimental data.~~ 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**

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| Fig 9. Phase diagram of the CaCl2 + H2O system Symbols: experimental data reported in reference data [7-12]. 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 CaCl~~~~2~~ ~~+ H~~~~2~~~~O system~~, The phase diagram for the CaCl2 + H2O system is shown in Figure 9 describing the 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**

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| Fig 13. Phase diagram of the Li2SO4+H2O system.  Symbols: experimental data reported in reference data [13-16, 18]. Lines: the present model results. | | |
| 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. Phase diagram of the MgSO4 + H2O system Symbols: experimental data reported in reference data [14, 16-18]. 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.

**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 modeling, we can unlock the full potential of salt hydrates and pave the way towards a more sustainable future.

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