Research Paper

Molecular insights into water vapor absorption by aqueous lithium bromide and lithium bromide/sodium formate solutions

Lindong Weng [a,1], Wei Song [b,2], Donald J. Jacobs [b], Gloria D. Elliott [a,*]

[a] Department of Mechanical Engineering and Engineering Sciences, University of North Carolina at Charlotte, Charlotte, NC 28223, United States
[b] Department of Physics and Optical Science, University of North Carolina at Charlotte, Charlotte, NC 28223, United States

HIGHLIGHTS

- Water vapor absorption by LiBr and LiBr + NaCOOH was studied by molecular modeling.
- Ionic clustering and hydrogen-bonding in LiBr + NaCOOH + H_2O were analyzed.
- A higher LiBr concentration increased the vapor absorption rate.
- Strong interactions between Li^+ and $COOH^-$ were found.
- Higher absorption capacity may be due to Li^+–$COOH^-$ clustering.

ARTICLE INFO

ABSTRACT

Aqueous lithium bromide (LiBr) solutions are commonly-employed as liquid desiccants, largely due to their low water vapor pressure at concentrations suitable for applications such as absorption refrigeration. However, LiBr-based desiccants have drawbacks such as corrosivity, crystallization at high concentrations, and high energy inputs to regenerate the absorbent. It was recently shown that adding formate salts (e.g., NaCOOH) into the LiBr + H_2O mixture could mitigate disadvantages while maintaining most advantages, but these experimental findings were unable to elucidate the driving forces at the molecular level. Detailed knowledge of the molecular interactions that underpin absorption phenomenon in both traditional and newly developed ternary working fluids (e.g., LiBr + NaCOOH + H_2O) is still incomplete. The present molecular modeling study of water vapor absorption by LiBr and LiBr + NaCOOH investigated the water vapor absorption kinetics, enabling the analysis of ionic clustering and hydrogen-bonding characteristics. Molecular simulations of LiBr + H_2O compositions demonstrated that increasing the LiBr concentration enhances the absorption rate while decreasing the liquid–vapor interfacial thickness of the LiBr + H_2O layer. The most interesting finding was the strong interaction between Li^+ and $COOH^-$ which may enable the ternary mixture to accommodate more water molecules as a result of Li^+–$COOH^-$ clustering compared to compositions containing only LiBr and H_2O. Despite an increase in water vapor absorption capacity it was found that adding NaCOOH decreased the water vapor absorption rate. Elucidating the molecular origin that affects the performance of liquid desiccants upon addition of formate salts is a first step toward the rational design of new working fluids for liquid desiccant-related applications.

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1. Introduction

Liquid desiccants are used in a range of environmental control systems due to their high affinity for water vapor, which induces or sustains a state of dryness in the solution vicinity. For example, lithium chloride (LiCl) and lithium bromide (LiBr) serve as liquid desiccant materials for use in air-conditioning systems that simultaneously remove moisture and refrigeration load from the air. These systems eliminate the need to overcool the air to control the humidity with far less energy input than a conventional air-conditioning system [1]. Another application of these materials is in absorption refrigeration systems, where liquid desiccants such as LiBr are used to absorb the refrigerant (water vapor), enabling the use of a pump to complete the cycle, instead of a compressor,

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thus reducing the work input compared to a traditional vapor-compression refrigeration cycle. Heat is used to regenerate the refrigerant, which can be provided by combustion of fuels, or more desirably by using waste heat, solar energy, or other available heat sources [2–4].

Absorption refrigeration systems based on the standard single-effect LiBr + H$_2$O absorption cycle were deployed in the late 1960s [5] and have continued to evolve since that time. LiBr has low vapor pressure at concentrations suitable for many applications, and it is a natural and safe chemical [6]. In 1975, Boryta et al. [7] determined the relationships between vapor pressure, temperature and concentration of aqueous lithium bromide of 40–70 wt% solutions via direct static and gas transport methods enabling further engineering performance advances. Patil et al. [8] evaluated the non-ideal behavior of lithium halides including LiCl, LiBr and lithium iodide (LiI) by measuring the vapor pressure, osmotic and activity coefficients at various temperatures (303–343 K), and determined that the ability of ions to associate with water increased in the order of Cl$^-$, Br$^-$ and I$^-$ [8]. Ternary mixtures of these salts have also been explored in order to optimize the range of desired properties of these working fluids [9].

Despite being a widely-used liquid desiccant, LiBr has drawbacks when used in a binary solution with water. Specifically, LiBr crystallizes at high concentrations and it tends to corrode the very metals that are common materials for constructing industrial systems [6,10]. It also requires a high temperature in the generator to evaporate water and regenerate the absorber solution [6,10]. A great deal of effort has been dedicated to empirically seek out better working fluids for liquid desiccant-related applications. Toward this end, two main approaches were employed: finding new working pairs (e.g., potassium formate + H$_2$O) or adding compounds into the original LiBr + H$_2$O mixture. For example, Riffat et al. [2] evaluated the performance of a new working fluid, potassium formate (KCOOH) + H$_2$O, by comparing its sorption behavior with LiBr + H$_2$O. They found that KCOOH, which is less corrosive and cheaper, had a similar absorption pattern as LiBr but had a higher desorption rate, reducing the energy requirement in the generator [2]. Lucas et al. [11] evaluated the performance of a ternary mixture of LiBr + KCOOH + H$_2$O as a new absorbent, demonstrating an improvement in the Coefficient of Performance (COP) of the absorption cycle. In subsequent studies Donate et al. [12] performed thermodynamic analysis to study the effect of adding sodium and potassium (formate, acetate and lactate) into LiBr + H$_2$O. It was concluded that the optimal mass ratio of LiBr:salt was 2:1, which generated a much lower dilution heat and a dramatic decrease in the phase change temperature in the generator compared with conventional working pairs [12]. In 2009, Chen et al. [13] examined the suitability of adding glycols into LiCl or LiBr + H$_2$O by measuring their vapor pressure and density and determined that these candidates yielded smaller vapor pressures than conventional compositions [13]. De Lucas et al. [6] reported, specifically, LiBr + NaCOOH + H$_2$O (30 wt% solute, mass ratio of LiBr:NaCOOH = 2:1) and LiBr + KCOOH + H$_2$O (30 wt% solute, mass ratio of LiBr:KCOOH = 2:1) had relative absorption capacities of 30 g and 33.7 g, respectively, compared with 11.85 g for LiBr + H$_2$O (30 wt% LiBr). A further study showed that an absorption refrigeration cycle using LiBr + NaCOOH + H$_2$O solution of the above composition produced a higher COP of 0.94, compared to that of LiBr + H$_2$O (i.e., 0.75) [12].

Macroscopic experimental approaches to composition design, while yielding advances in solution performance, do not probe the molecular driving forces that affect the performance of liquid desiccants under evaluation, and thus do not provide a rational basis for future design efforts. Ultimately, the net effect of molecular interactions manifested through clustering among ions and molecules determine properties such as vapor pressure and

absorption rate. The exploration into the interactions among solute molecules (e.g., LiBr and NaCOOH) or between solute and water molecules would yield insights into why macroscopic properties change as molecular composition and molecular interactions change. This is especially important given that the best liquid desiccants do not exhibit ideal solution behavior. To this end, molecular dynamics (MD) simulations have been increasingly applied to advance the development of new working fluids. For example, molecular dynamics simulations of the liquid–vapor interface of aqueous LiBr solutions have been carried out to better understand the evolution of density profiles and the effect of local surface tension on absorption [14]. The results of these simulations indicated that LiBr ions existed in the liquid apart from the surface and this tendency was strengthened as the solute concentration decreased. On the other hand, the number of water molecules in the bulk vapor decreased with an increase of the solute concentration [14]. Lithium chloride ionic associations in dilute aqueous solutions have also been studied with molecular simulation, in which the microscopic association structures demonstrated the existence of a strong hydration effect associated with the lithium ion and the bridging role of its hydrating complex [15].

Despite the insight that molecular dynamics simulation can provide about solution behavior, simulation studies devoted to determining the microscale kinetics of traditional and novel liquid desiccants, including newly-developed ternary working fluids, have been sparse. Inspired by recent experimental findings [6,10–12], the current work reports on a series of molecular dynamics simulations of the absorption of water vapor into LiBr + H$_2$O and LiBr + NaCOOH + H$_2$O mixtures in the temperature range from 303 to 443 K. Non-equilibrium canonical (isothermal–isovolumetric) simulations were performed in a sandwiched spatial arrangement as solution/vapor/water/vapor/solution. Water vapor absorption rates, ionic clustering and other structural preferences of the molecular interactions were analyzed to elucidate the molecular basis for the practical benefits of adding formate salts into LiBr + H$_2$O. This work represents a step forward toward a rational molecular design approach in order to optimize the advantages of lithium bromide, while at the same time, improve the crystallization tendency of the mixture, and reduce the thermal energy needed in the generator, which can be achieved by including specific compounds such as organic salts in liquid desiccant compositions.

2. Simulation methods

For simulations involving binary LiBr + H$_2$O mixtures, Li$^+$, Br$^-$ ions and water molecules were randomly mixed in a cubic box (larger than 50 Å × 50 Å × 50 Å) to achieve a concentration of 0, 15, 30, 45 or 60 wt% LiBr. The simulation box was equilibrated with NVT (for 20 ps) and NPT (for 5 ns) ensembles successively with the temperature T fixed at 303, 338, 373, 408, or 443 K, respectively. The equilibrated simulation box was then cut to a uniform size of 50 Å × 50 Å × 50 Å for each concentration and temperature. Two identical equilibrated LiBr + H$_2$O boxes were then placed on each end of a pure water box (50 Å × 50 Å × 50 Å) centered at (0, 0, 0), with a distance of 105 Å between these boxes, resulting in a distance of 310 Å between the center of each of the LiBr + H$_2$O layers, as shown in Fig. 1. The initial vapor phase between the LiBr + H$_2$O and pure water layers is void of water molecules [16]. This setup produced a sandwiched solution/vapor/water/vapor/solution spatial arrangement. The two-phase complex, the composition of which was defined in Table 1, was simulated with an NVT ensemble for 20 ns for data analysis.

In the case of LiBr + NaCOOH + H$_2$O mixtures, Li$^+$, Br$^-$, Na$^+$, COOH$^-$ ions and water molecules were randomly mixed in various