

INFLUENCE OF 1,3-DIMETHYLIMIDAZOLIUM CHLORIDE ON THE SOLUBILITY OF LITHIUM BROMIDE IN WATER FOR ABSORPTION REFRIGERATION AND HEAT PUMPS

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Abstract: The effect of the 1,3-dimethylimidazolium chloride ([Dmim][Cl]) on the solubility of lithium bromide (LiBr) in water is analyzed. The solubility curve of ternary water/(LiBr+[Dmim][Cl]), with 3 % and 6 % of [Dmim][Cl] in the absorbent, has been determined using a visual-polythermal method in the range from (0 to 90) °C. To explain the role of the ionic liquid in the solubility of the LiBr, a multivariate curve resolution method was applied to near-infrared spectra of the ternary solutions and H₂O/LiBr at room temperature within a wide composition range. The solubility results show that, in the range from 0.60 to 0.65 in absorbent mass fraction, corresponding to the typical composition in the absorber inlet, the temperature decrease between 11 °C and 13 °C with 3 % of IL, and between 15 °C and 20 °C with 6 % of IL. Spectral calculation results show that in the ternary mixture, the amount of water that remains as bulk water in the presence of LiBr is higher than in the binary mixture. This suggests interactions between both species.

Keywords: water, lithium bromide, solubility, ionic liquids, NIR spectroscopy

1. INTRODUCTION

Absorption refrigeration and heat pump systems constitute an environmentally friendly and promising technology alternative because of their capacity of being powered with low-quality energy. One of the most used absorption working pairs is the water/lithium bromide mixture (H₂O/LiBr), but its operation range is restricted due to the crystallization of lithium bromide. To overcome this limitation, numerous authors have suggested adding different types of compounds, such as inorganic salts, organic solvents [1] or, more recently, ionic liquids [2]. The benefit of using ionic liquids in absorption refrigeration and heat pumps is their usually negligible vapor pressure and their good affinity with water since some of them are hygroscopic compounds. In this study, we have determined the solubility in water of LiBr with 3 % and 6 % of 1,3-dimethylimidazolium chloride [Dmim][Cl] Ionic Liquid in the absorbent, using a polythermal-visual method, in a range of interest for absorption refrigeration and heat pumps applications. In addition, for a better knowledge of the IL role, a study of the interactions between the species in solution has been performed by a methodology based on infrared spectroscopy and multivariate curve resolution of the spectra recorded in the binary H₂O/LiBr and ternary H₂O/(LiBr+[Dmim][Cl]) mixtures.

2. EXPERIMENTAL DEVICES AND METHODS

2.1. Reagents

Lithium bromide (CAS No: 7550-35-8) was purchased from Honeywell Fluka with mass fraction purity higher than 99 %. 1,3-dimethylimidazolium chloride (CAS No: 79917-88-7) was purchased from Angene with mass fraction purity > 97 %. Purified water with resistivity lower than 18.2 M Ω ·cm was used for the solutions. Before their use, both LiBr and [Dmim][Cl] were dried at 90 °C in an oven to remove water traces.

2.2. Solid-Liquid Equilibrium measurements

Solubility curves were obtained for H₂O/(LiBr+[Dmim][Cl]) mixture with 3 % and 6 % of IL in the absorbent, in a range from 0.57 to 0.69 in absorbent mass fraction. The measurements were performed with a visual- polythermal method in a glass solubility cell [3]. In this method, a well-known composition of solution strongly concentrated in the absorbent is slowly heated until the last crystal disappears, determining the phase-change temperature accurately. Then, the samples are sequentially diluted with distilled water, and the measurement process is repeated until covering the studied ranges. The temperature is controlled by an external bath (Huber, mod. CCK6S), with a 50 % water + ethylenglycol mixture, connected to the glass cell, and the mixtures are constantly stirred to facilitate the dissolution of the crystals.

2.3. NIR measurements and data analysis

For the NIR measurements, the solutions must be completely soluble at the temperature of the analysis (around 20 °C). For this study, 20 binary mixtures of H₂O/LiBr and 20 ternary H₂O/(LiBr+[Dmim][Cl]) mixture with 3 % of IL in the absorbent, and 20 more with 6 %, were prepared from pure water to 0.55 in absorbent mass fraction.

For each one of the samples, near-infrared spectra were acquired between 900 nm and 1060 nm using an Ocean Optics UV-Vis-NIR (Maya 2000 pro) spectrophotometer. In this spectral region, the characteristic absorption band of the –OH group present in the water can be observed. The spectra were arranged in individual spectra data matrices that were processed using the multivariate curve resolution method based on alternating least square (MCR-ALS) [4] to determine the contribution of the different aqueous chemical species formed in the solutions: water maintaining the typical three-dimensional structure of the bulk water (*BW*), and water being part of different solvates, such as (H₂O)_x(LiBr), (H₂O)_y([Dmim][Cl]) and others. The analysis was done in the MATLAB environment [5].

3. RESULTS

Figure 1 shows the solid-liquid equilibrium of the H₂O/LiBr and H₂O/(LiBr+[Dmim][Cl]) mixtures, with 3 % and 6 % of IL in the absorbent, in the composition range studied. Below each curve, solid salt is present in the solution, and above only, the liquid phase exists. As expected, the higher the temperature, the more salt can dissolve. When the ionic liquid is present in the solution, the quantity of absorbent (LiBr+[Dmim][Cl]) that can be dissolved in the solution is also higher, being greater the more IL is present. This effect is expected, and it agrees with the literature for other ILs [2]. According to the results, when 3 % of IL is added to the absorbent, the average and the maximum temperature drop obtained are 12.8 °C and 23.0 °C, respectively. For 6 % of IL, they are 19.7 °C and 31.7 °C, respectively.

In absorption refrigeration and heat pumps applications, the critical point for the crystallization of the LiBr is the absorbent inlet, where the fluid is more concentrated in salt (between 0.60 and 0.65 in mass fraction), and the temperature is lower. The temperature drop in this range is between 11 °C and 13 °C for the mixtures with 3 % of IL and between 15 °C and 20 °C for the mixtures with 6 % in IL, which implies a considerable decrease in the risk of crystallization.

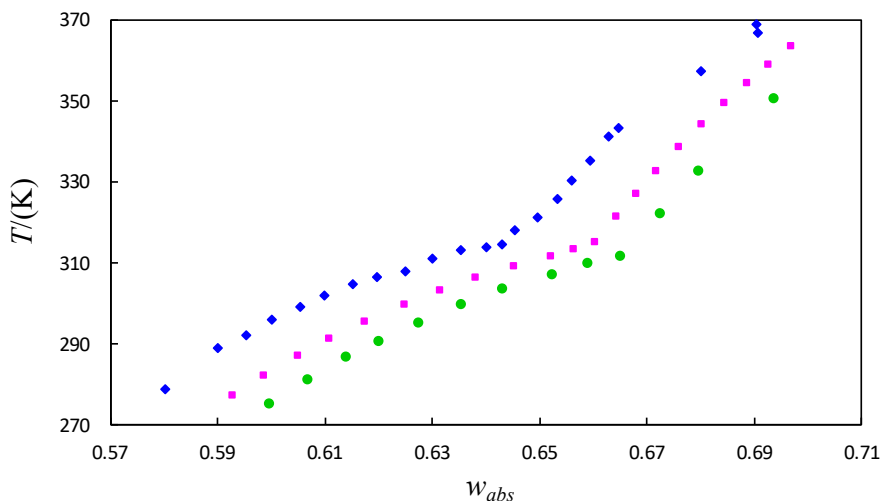


Figure 1. Solid-liquid equilibrium of $\text{H}_2\text{O}/\text{LiBr}$ and $\text{H}_2\text{O}/(\text{LiBr}+[\text{Dmim}][\text{Cl}])$ from 0.57 to 0.70 in absorbent mass fraction ($w_{abs}=w_{\text{LiBr}}+w_{\text{IL}}$). \blacklozenge : $\text{H}_2\text{O}/\text{LiBr}$. \blacksquare : $\text{H}_2\text{O}/(\text{LiBr}+[\text{Dmim}][\text{Cl}])$ with a 3 % of IL in mass the absorbent. \bullet : $\text{H}_2\text{O}/(\text{LiBr}+[\text{Dmim}][\text{Cl}])$ with a 6 % of IL in mass the absorbent.

To discard the effect of the IL amount in the total composition, the phase equilibrium diagram is represented to the $\text{LiBr}/\text{H}_2\text{O}$ ratio (Figure 2). As it can be seen, the trend of the curves is similar to Figure 1, and in both ternary mixtures, the quantity of LiBr that can be dissolved is greater than in the $\text{H}_2\text{O}/\text{LiBr}$ mixture at the same temperature.

Figure 2 shows that there is not a significant difference between the addition of 3 % or 6 % of IL in the absorbent, almost overlapping both curves in the figure. For the composition of 0.60 and 0.65, corresponding to the typical absorbent mass fraction in the absorber inlet, the temperature drop is between 7.0 °C and 9.1 °C with 3 % in IL, and between 9.3 °C and 11.1 °C with 6 % in IL. From the point of view of the application, this is an important aspect, because due to the high viscosity of the ionic liquids is better to add as little as possible.

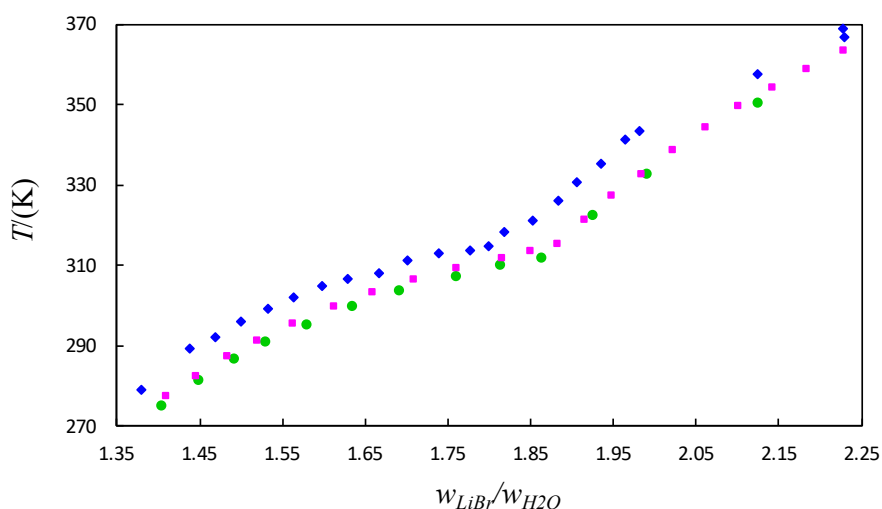


Figure 2. Solid-liquid equilibrium of $\text{H}_2\text{O}/\text{LiBr}$ and $\text{H}_2\text{O}/(\text{LiBr}+[\text{Dmim}][\text{Cl}])$ from 0.57 to 0.70 in absorbent mass fraction, represented in function of $\text{LiBr}/\text{H}_2\text{O}$ ratio. \blacklozenge : $\text{H}_2\text{O}/\text{LiBr}$. \blacksquare : $\text{H}_2\text{O}/(\text{LiBr}+[\text{Dmim}][\text{Cl}])$ with a 3 % of IL in mass the absorbent. \bullet : $\text{H}_2\text{O}/(\text{LiBr}+[\text{Dmim}][\text{Cl}])$ with a 6 % of IL in mass the absorbent.

To understand better the role of the IL in the solution, a quantitative analysis of the bulk water in the solutions was obtained from MCR-ALS of NIR spectra data at room temperature.

The bulk water present in the solution is directly related to the solubility of the salt: the bulk water indicates the water that is not solvating the ions or molecules of the solutions, which gives information about the interactions between the species.

Figure 3 shows the percentage of bulk water of the studied mixtures in function of the LiBr/H₂O ratio. The quantity of bulk water decreases for the three mixtures when the absorbent composition increases, as expected. Comparing the ternary mixtures with the binary one, the quantity of bulk water is greater when IL is present than the existing in the H₂O/LiBr mixture. A possible explanation is that the ions that belong from the LiBr interact with the IL molecules, as was reported by Varela et al. [6].

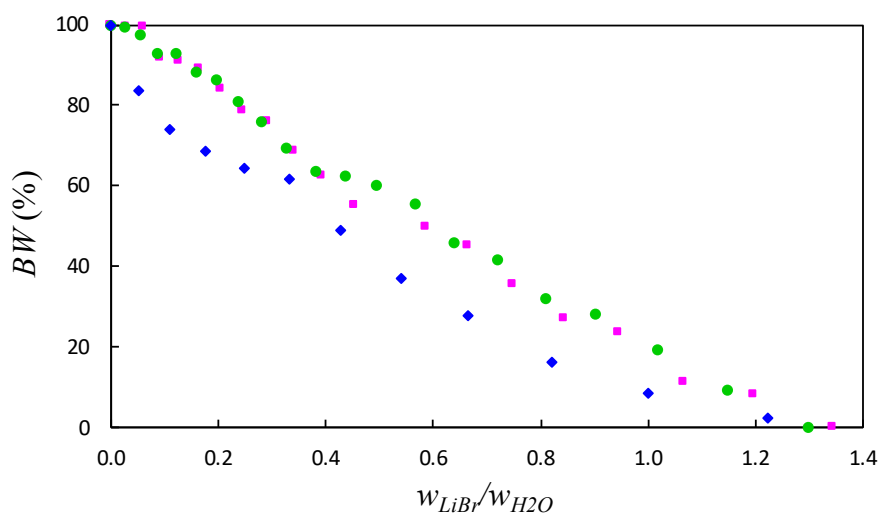


Figure 3. Bulk water percentage of H₂O/LiBr and H₂O/(LiBr+[Dmim][Cl]) as a function of the mass fraction relation between LiBr and H₂O. ♦: H₂O/LiBr; ■: H₂O/(LiBr+[Dmim][Cl]) with a 3 % of IL in mass the absorbent; ●: H₂O/(LiBr+[Dmim][Cl]) with a 6 % of IL in mass the absorbent.

The NIR technique can be also used to estimate the maximum amount of absorbent that can be solved in water, determining when the bulk water disappear: if there is no bulk water in the solution, the ions of the salt cannot

be solvated, and they finally precipitate. Table 1 collects the solubility of the absorbent in water at 20 °C, experimentally obtained by the solid-liquid equilibrium and estimated from the bulk water analysis. In the case of the binary mixture H₂O/LiBr, the difference between the solubility obtained by both methods was around 3 %, while for the ternary mixtures was 5 % and 6 %, which we consider a good estimation from the NIR technique in order to explain the role of the IL in the solubility.

Table 1. Calculation of the solubility concentration at 20 °C.

Measurement	H ₂ O/LiBr	H ₂ O/(LiBr+[Dmim][Cl]) 3 %	H ₂ O/(LiBr+[Dmim][Cl]) 6 %
SLE	0.597	0.614	0.623
NIR	0.57	0.58	0.58

4. CONCLUSIONS

The solubility of lithium bromide in water is affected by the presence of 1,3-dimethylimidazolium chloride, decreasing the phase-change temperature with respect to H₂O/LiBr mixtures up to 23.0 °C and 31.7 °C, for ternary mixtures with 3 % and 6 % of IL in the absorbent. This temperature drop is of interest in absorption refrigeration and heat pumps because it

reduces the risk of crystallization of lithium bromide, and allows increasing the quantity of absorbent, which can suppose an increase in the absorption process and therefore in the cycle performance. However, for a complete study, the solubility of the water in the new absorbent is required.

The higher bulk water percentages in ternary mixtures than in the binary H₂O/LiBr suggests the existence of interactions between LiBr and [Dmim][Cl]. The results from the bulk water analysis agree with those from the solid-liquid equilibrium measurements: the higher the bulk water content, which happens in the presence of [Dmim][Cl], the more salt can dissolve in the solution. From both methods can be concluded that no significant differences are observed between 3 % and 6 % of IL in absorbent.

Finally, the NIR technique could be used to make a fast screening of the additives in the selection process because the quantitative analysis of the bulk water allows estimating if the additive enhances the solubility of the salt in water and also allows estimating the maximum concentration of salt that dissolves at a determined temperature.

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