



# The influence of bromide-based ionic liquids on solubility of {LiBr (1) + water (2)} system. Experimental (solid + liquid) phase equilibrium data. Part 2

Marta Królikowska<sup>a,b,\*</sup>, Maciej Zawadzki<sup>a</sup>, Michał Skonieczny<sup>a</sup>

<sup>a</sup> Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

<sup>b</sup> Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa

## ARTICLE INFO

### Article history:

Received 19 March 2018

Received in revised form 9 May 2018

Accepted 2 June 2018

Available online 04 June 2018

### Keywords:

Ionic liquids

Additives

LiBr (1) + water (2)

Solubility

Crystallization temperature

## ABSTRACT

The main aim of the work is to investigate ionic liquids (ILs) or zwitterionic compound (ZI) as anti-crystallization additives for {LiBr (1) + water (2)} system, conventionally used as a working pair in absorption refrigeration technology. In this study, solubility of lithium bromide in water has been determined at wide temperature and composition range and compared to the literature data. The transition temperature and enthalpy between lithium dihydrate and lithium monohydrate forms were calculated using the van't Hoff plot. The main purpose of this work is to determine and discuss the solubility of lithium bromide in water in presence of IL, or ZI as an additive. The solubility measurements have been carried out using dynamic method within temperature range from (230 to 370) K. In this work, new ILs namely: *N*-methyl-*N*-(2-hydroxyethyl)morpholinium bromide, [MOR<sub>1,2OH</sub>][Br], *N*-(2-acetyloxy)ethyl-*N*-methyl-morpholinium bromide, [MOR<sub>1,2(OOC)1</sub>][Br], *N*-methyl-*N*-(2-ethoxy-2-oxoethyl)-morpholinium bromide, [MOR<sub>1,1(COO)2</sub>][Br], 1-methyl-3-(2-hydroxyethyl)imidazolium bromide, [Im<sub>1,2OH</sub>][Br], *N*-methyl-*N*-(2-hydroxyethyl)-pyrrolidinium bromide, [PYR<sub>1,2OH</sub>][Br], 2-hydroxyethylpyridinium bromide, [Py<sub>2OH</sub>][Br], *N*-(2-hydroxy-ethyl)-*N,N,N*-triethyl-ammonium bromide, [N<sub>2,2,2,2OH</sub>][Br], *N*-(cyanomethyl)-*N,N,N*-triethylammonium bromide, [N<sub>2,2,2,1CN</sub>][Br], *N*-(2-hydroxyethyl)-*N,N*-dimethyl-*N*-butyl-ammonium bromide, [N<sub>1,1,2OH,4</sub>][Br], *N,N*-di(2-hydroxyethyl)-*N,N*-dimethylammonium bromide, [N<sub>1,1,2OH,2OH</sub>][Br] and ZI namely: 3-(1-methylmorpholinium)propane-1-sulfonate, [MOR<sub>1,3SO3</sub>] were investigated. All compounds have been synthesized and characterized using NMR analysis. The thermophysical characterization of pure compounds, including: temperature of phase transition ( $T_{tr}$ ), enthalpy of phase transition ( $\Delta_{tr}H$ ), melting temperature ( $T_m$ ) and enthalpy of melting ( $\Delta_mH$ ) have been measured using differential scanning calorimetry technique (DSC) at pressure  $p = 100$  kPa. The experimental phase equilibria measurements for {LiBr (1) + IL, or ZI (2) + water (3)} ternary systems, with fixed IL to LiBr mass fraction  $w = 0.3$  for all ILs and  $w = 0.1$  and  $0.2$  for ammonium-based ILs and [MOR<sub>1,3SO3</sub>] have been performed by dynamic method. For all of the tested systems the transition point between lithium bromide dihydrate and monohydrate form was observed. Significant solubility enhancement of lithium bromide in water was obtained by adding ionic liquid, or zwitterionic compound to the lithium bromide + water solution. The experiment shows, that the greatest increase in solubility of LiBr in water was observed when [MOR<sub>1,3SO3</sub>], or [N<sub>1,1,2OH,2OH</sub>][Br] were added. This work is the first step of the experimental work in this area and further research will be carried out.

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## 1. Introduction

In the past years the absorption heat pump has received growing attention in the refrigeration and air-conditioning industry, especially in terms of energy saving and environment aspects [1, 2]. Increasing energy consumption results in an increase of pollution and wastes generated in its production. It is therefore essential to design environmentally

friendly technologies in which waste heat can be used as the driving energy of the refrigerant circuit to allow for reduction of the energy losses.

It is well known that the performances of an absorption heat pump largely depend on the thermophysical properties of working fluids. In absorption refrigeration technology a fluid with high volatility is used as refrigerant, while as an absorbent, the compound with smaller volatility and strong affinity to the refrigerant is usually used. So far, the commercial working fluids in absorption cycles are mainly (water-lithium bromide), or (ammonia-water) [3]. However, there are a number of constraints for each of these mixtures. Aqueous solution of lithium bromide has strong corrosive properties against steel equipment and can

\* Corresponding author at: Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland.  
E-mail address: [mlaskowska@ch.pw.edu.pl](mailto:mlaskowska@ch.pw.edu.pl) (M. Królikowska).

easily crystallize when the concentration of LiBr is high, with a minimum operating temperature of 279 K. Hence, refrigeration systems with better properties such as: good thermal stability, less corrosive and without risk of crystallization are sought for [3–8]. Due to the crystallization of the salt inside the storage tank, it is essential to prevent this from occurring this process. In the literature a variety of information regarding the solubility of lithium bromide in water are available. Linke and Seidell [9] pointed out that there is a poor agreement between published data, especially in the range of interest from the point of view of the refrigeration device. Boryta [10] attempted to define the solubility curve and correlate the experimental value with literature data. He presented the solubility of LiBr in water in the temperature range from (–50 to 100 °C) which encompasses a concentration of 45 and 75 wt % lithium bromide. In 1999 Knoxville and Dean [11] also reported the solubility data of LiBr in water. More recently, the fitting equations relating the solubility of lithium bromide monohydrate, dihydrate and trihydrate were proposed by Duvall et al. [12]. In 2015 Lefebvre et al. [13] reported the solubility of LiBr in water and metastable zone limit curves were assessed using an agitated and thermostated batch crystallizer. The solubility was determined within the temperature range from (5 to 90 °C). A video sensor was employed for assessment of the crystals morphology. The transition temperature between lithium bromide monohydrate and dihydrate as well as between lithium dihydrate and trihydrate were found and the crystallization enthalpy were calculated. Despite the fact that the solubility of LiBr in water has been widely investigated in a wide range of temperature and concentration, the available data show a wide discrepancy. The authors suggested that the differences between the results of many investigators are due to the different techniques used to overcome the tendency of saturated lithium bromide solution to form different solid forms: dihydrate and trihydrate. One of the aims of this study is to determine the solubility of lithium bromide in water and compare the results obtained with the literature data.

Adding a small amount of additive having nonvolatile and hygroscopic properties is one of the common methods to reduce the crystallization temperature of working fluids. In the available literature, many organic compounds are proposed as anti-crystallization additives.

Boryta [10] presents the solubility curve and show the effects of a small excess of lithium hydroxide and hydrogen bromide on the solubility. Biermann and Rehnann [14] performed extensive research on the characteristics of lithium bromide + ethylene glycol + water system, where ethylene glycol was added as an anti-crystallization agent. Ten years later, some work on lithium bromide + lithium chloride + ethylene glycol + water and lithium bromide + lithium iodide + ethylene glycol + water systems in which ethylene glycol was used as an anti-crystallization additive were presented [15, 16]. Kim et al. [17–20] and Park et al. [21] presented several physical and thermal properties of two ternary systems in which ethanolamine and 1,3-propanediol were added to suppress crystallization of the lithium bromide + water solution. Donate et al. [22] proposed mixing salts formulations of potassium formate and other salts of similar chemical and physical properties (sodium formate, potassium acetate and sodium lactate), in combination with lithium bromide to reduce the crystallization temperature of conventional (LiBr + water) system. The physicochemical and thermodynamic properties of: water + lithium bromide + sodium formate, and water + lithium bromide + potassium formate systems including, vapor pressure, densities and viscosities have been presented by Lucas et al. [23]. The main advantage of these working fluids is the reduction of the vapor pressure of the solution with respect to the traditional LiBr–H<sub>2</sub>O, which is very desirable in view of the application in the area being undertaken.

Due to the unique properties, such as: extremely low volatility, low combustibility, high chemical and thermal stability, wide temperature range for the liquid state, low melting temperature, or total or partial solubility in polar or non-polar compounds, ionic liquids (ILs) are widely tested and used in many fields [24, 25]. Among the additives

proposed in the literature so far, the studies on the effect of using an IL on the properties of the working fluid are scarce. The effects for adding: 1,3-dimethylimidazolium chloride, [DMIM]Cl and 1,3-dimethylimidazolium tetrafluoroborate, [DMIM][BF<sub>4</sub>] to the working pairs of (LiBr + H<sub>2</sub>O) and (LiCl + H<sub>2</sub>O) were investigated by Jing [26]. In 2017 the LiNO<sub>3</sub>–[BMIM]Br/H<sub>2</sub>O and LiNO<sub>3</sub>–[BMIM]Cl/H<sub>2</sub>O ternary systems have been proposed as a new absorption working pair to improve the shortcomings of high crystallization temperature for LiNO<sub>3</sub>/H<sub>2</sub>O and high viscosity for [BMIM]Br/H<sub>2</sub>O working pairs. These mixtures have been presented [27, 28].

In this work ten ionic liquids and one zwitterionic compounds have been investigated as anti-crystallization additives for (LiBr + water) working fluid in absorption refrigeration technology. The data presented in this work give an opportunity to discuss the influence of IL's cation on solubility of lithium bromide in water. From absorption refrigeration point of view, vapor + liquid phase equilibrium (VLE) data are the most important. It is very important to know, that the solid + liquid phase equilibrium (SLE) data are also significant. Based on SLE measurements it is possible to determine the relationship between the composition of the solution and the dissolution temperature. It is well known, that for absorption refrigeration machines, the coefficients of performance (COP) depends on the properties of working fluids, thus the physicochemical and thermodynamic characterization of the solution are required. Extension of the absorption cycle to improve the performance of those machines is often limited by crystallization of the absorbent, which is a function of concentration and pressure in the absorber. The main objective of this work is to present the solubility of lithium bromide in water in presence of different ionic liquids (ILs) or zwitterionic compound (ZI) as anti-crystallization additives. The addition of a small amount of IL, or ZI to (LiBr + water) solution would allow the absorber to operate in a wider composition range compared to a conventional system (LiBr + water) system. The higher concentration of LiBr in solution (in the absorber) gives a significant reduction in the vapor pressure, which has a positive effect on COP.

## 2. Experimental section

### 2.1. Materials

Lithium bromide (CAS No. 7550-35-8) was purchased from Fluka with nominal mass fraction purity > 0.99. The temperature and enthalpy of fusion of pure LiBr were determined using DSC measurements.

The pure water used for the SLE experiment was deionized by a reverse osmosis unit with an ion-exchange system with conductivity < 0.05 μS·cm<sup>-1</sup> (Cobrabid-Aqua, Poland) and next degassed in an ELMA Germany ultrasonic bath at about 320 K before each measurement.

All additives tested in this work were synthesized in our laboratory. Detailed description of synthesis procedures are given below. Compound structures were verified by <sup>1</sup>H NMR and <sup>13</sup>C NMR. Purity of the compounds were estimated from <sup>1</sup>H NMR and are higher than 95%.

#### 2.1.1. Synthesis of *N*-methyl-*N*-(2-hydroxyethyl)morpholinium bromide, [MOR<sub>1,20H</sub>][Br]

To a flask containing 11.183 g of methylmorpholine (0.1106 mol, Sigma-Aldrich 99%, Reagent Plus, used as received), 17.370 g of 2-bromoethanol (0.1390 mol, 25% excess, Sigma-Aldrich 98%, used as received) and 100 cm<sup>3</sup> of acetonitrile (P.O.Ch for HPLC) were added. The mixture was stirred for 24 h in oil bath at temperature *T* = 353.2 K. The product precipitates as white solid. Afterwards the product was filtered and purified by crystallization from acetonitrile/2-propanol (ratio 10/1 vol/vol) and washed with ethyl acetate to give 18.811 g of white crystalline powder. Reaction yield was 75.25%.

<sup>1</sup>H NMR δ<sub>H</sub> (500 MHz; D<sub>2</sub>O) ppm: 3.17–3.24 (3H, m), 3.39–3.49 (2H, m), 3.50–3.62 (4H, m), 3.91–4.04 (6H, m).

<sup>13</sup>C NMR δ<sub>C</sub> (100 MHz; D<sub>2</sub>O) ppm: 48.170, 54.954, 60.462, 60.548, 65.722.

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