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

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# ABSTRACT

The main aim of the work is to investigate ionic liquids (ILs) or zwitterionic compound (ZI) as anti-crystallization additives for  $\{\text{LiBr}(1) + \text{water}(2)\}$  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 20H</sub>][Br], N-(2-acetyloxy)ethyl-N-methyl-morpholinium bromide, [MOR1.2(00C)1][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>1,20H</sub>][Br], Nmethyl-N-(2-hydroxyethyl)-pyrrolidinium bromide, [PYR<sub>120H</sub>][Br], 2-hydroxyethypyridinium bromide, [Py<sub>20H</sub>] Br], N-(2-hydroxy-ethyl)-N,N,N-triethyl-ammonium bromide, [N<sub>2.2.2.0H</sub>][Br], N-(cyanomethyl)-N,N, Ntriethylammonium bromide, [N2,2,2,1CN][Br], N-(2-hydroxyethyl)-N,N-dimethyl-N-butyl-ammonium bromide, [N<sub>1.1.20H4</sub>][Br], N,N-di(2-hydroxyethyl)-N,N-dimethylammonium bromide, [N<sub>1.1.20H20H</sub>][Br] and ZI namely: 3-(1methylmorpholinium)propane-1-sulfonate, [MOR1,3SO3] 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  $(\Delta_m H)$  have been measured using differential scanning calorimetry technique (DSC) at pressure p = 100 kPa. The experimental phase equilibria measurements for  $\{\text{LiBr}(1) + \text{IL, or ZI}(2) + \text{water}(3)\}$  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>1.3</sub>SO<sub>3</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>1.3</sub>SO<sub>3</sub>], or [N1.1.20H20H][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

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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  $(-50 \text{ to } 100 \degree \text{C})$  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 Relnann [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 + ethyllene glycol + water and lithium bromide + lithium iodide + ethylene glycol + water systems in which ethylene glycol was used as an anticrystallization 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  $< 0.05 \ \mu\text{S}\cdot\text{cm}^{-1}$  (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 2bromoethanol (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%.

 $^{1}\text{H}$  NMR  $\delta_{\text{H}}(500$  MHz; D\_2O) 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).

 $^{13}\text{C}$  NMR  $\delta_{\text{C}}(100$  MHz; D\_2O) ppm: 48.170, 54.954, 60.462, 60.548, 65.722.

2.1.2. Synthesis of N-(2-acetyloxy)ethyl-N-methylmorpholinium bromide, [MOR<sub>1,2(00C)1</sub>][Br]

To a flask containing 11.380 g of methylmorpholine (0.1125 mol, Sigma-Aldrich 99%, Reagent Plus, used as received) a 20.964 g of 2bromoethyl acetate (0.1255 mol, 12% excess, Sigma-Aldrich 97%, used as received) and in 100 cm<sup>3</sup> of ethyl acetate (P.O.Ch cz.d.a) was added. The mixture was stirred for 24 h in oil bath at temperature T = 353.2 K. The product precipitates as pink solid. Afterwards the product was filtered and purified by crystallization from acetonitrile and washed with ethyl acetate to give 11.346 g of tan crystalline powder. Reaction yield was 37.61%.

 $^1\text{H}$  NMR  $\delta_{\text{H}}(500$  MHz; D\_2O) ppm: 1.194 (3H, m), 3.191 (3H, s), 3.410–3.570 (4H, m), 3.750–3.790 (2H, m), 3.910–4.010 (4H, m), 4.245–4.500 (2 H, m).

 $^{13}\text{C}$  NMR  $\delta_{\text{C}}(100$  MHz; D\_2O) ppm: 22.704, 50.169, 60.120, 62.882, 62.968, 65.626, 175.604.

# 2.1.3. Synthesis of N-methyl-N-(2-ethoxy-2-oxoethyl)morpholinium bromide, [MOR<sub>1.1(COO)2</sub>][Br]

To a flask containing 10.560 g of methylmorpholine (0.1044 mol, Sigma-Aldrich 99%, Reagent Plus, used as received) in 100 cm<sup>3</sup> of ethyl acetate (P.O.Ch cz.d.a) a 19.441 g of ethyl bromoacetate (0.1164 mol, 11% excess, Sigma-Aldrich 98%, used as received) was added drop wise. Immediately a solid precipitates from the solution. The mixture was stirred for 24 h at room temperature. Afterwards the product was filtered and purified by crystallization from acetonitrile and washed with ethyl acetate to give 23.533 g of crystalline powder. Reaction yield was 84.06%.

<sup>1</sup>H NMR  $\delta_{H}(500 \text{ MHz}; D_2O) \text{ ppm: } 1.194 (3H, tt, {}^{3}J_{H,H} = 7.3 \text{ Hz}, J_{H,H} = 2.1 \text{ Hz}), 3.344 (3H, t, J_{H,H} = 2.1 \text{ Hz}), 3.597-3.711 (4H, m), 3.9535-4.029 (4H, m), 3.253 (2H, m), 4.212 (2H, qt, {}^{3}J_{H,H} = 7.1 \text{ Hz}, J_{H,H} = 2.2 \text{ Hz}), 4.360 (2H, m).$ 

 $^{13}\text{C}$  NMR  $\delta_{\text{C}}(100$  MHz; D\_2O) ppm: 13.135, 48.045, 60.322, 60.735, 62.205, 63.590, 164.727.

2.1.4. Synthesis of 3-(1-methylmorpholinium)propane-1-sulfonate, [MOR<sub>1,3</sub>SO<sub>3</sub>]

To a flask containing 13.417 g of methylmorpholine (0.1196 mol, Sigma-Aldrich 99%, Reagent Plus, used as received) and 20.255 g of 1,3-propanesultone (0.1255 mol, 25% excess, Sigma-Aldrich 98%, used as received) and 200 cm<sup>3</sup> of toluene (P.O.Ch cz.d.a) were added. The mixture was stirred for 24 h in oil bath at temperature T = 388.2 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 26.715 g of white crystalline powder. Reaction yield was 90.20%.

 $^{1}\text{H}$  NMR  $\delta_{\text{H}}(500$  MHz; D\_2O) ppm: 2.117–2.180 (2H, m), 2.889 (2H, t,  $^{3}J_{\text{H,H}}=7.3$  Hz), 3.115 (3H, s), 3.378–3.480 (4H, m), 3.508–3.542 (2H, m), 3.880–4.000 (4H, m).

 $^{13}\text{C}$  NMR  $\delta_{\text{C}}(100$  MHz; D\_2O) ppm: 17.219, 46.785, 47.158, 59.692, 60.322, 63.084.

# 2.1.5. Synthesis of 1-methyl-3-(2-hydroxyethyl)imidazolium bromide, [Im<sub>1,20H</sub>][Br]

To a flask containing 9.909 g of 1-methylimidazole (0.1207 mol, Sigma-Aldrich 98%, used as received), 16.656 g of 2-bromoethanol (0.1333 mol, 10% excess, Sigma-Aldrich 98%, used as received) and 100 cm<sup>3</sup> of ethyl acetate (P.O.Ch for HPLC) were added. The mixture was stirred for 24 h in oil bath at temperature T = 343.2 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 23.110 g of white crystalline powder. Reaction yield was 92.5%.

<sup>1</sup>H NMR  $\delta_{H}$ (500 MHz; D<sub>2</sub>O) ppm: 3.79–3.86 (5H, m), 4.221 (2H, q, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz), 7.33–7.44 (2H, m), 8.659 (1H, m).

 $^{13}\text{C}$  NMR  $\delta_{\text{C}}(100$  MHz; D\_2O) ppm: 35.814, 51.562, 59.817, 122.495, 123.654, 136.375.

## 2.1.6. Synthesis of N-methyl-N-(2-hydroxyethyl)pyrrolidinium bromide, [PYR<sub>1.20H</sub>][Br]

To a flask containing 10.182 g of 1-methylpyrrolidine (0.1196 mol, Sigma-Aldrich 99%, used as received), 16.439 g of 2-bromoethanol (0.1315 mol, 10% excess, Sigma-Aldrich 98%, used as received) and 100 cm<sup>3</sup> of ethyl acetate (P.O.Ch for HPLC) were added. The mixture was stirred for 48 h in oil bath at temperature T = 343.2 K. 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 20.849 g of white crystalline powder. Reaction yield was 82.98%.

<sup>1</sup>H NMR  $\delta_{H}$ (500 MHz; D<sub>2</sub>O) ppm: 2.05–2.15 (4H, m), 2.95–3.05 (3H, m), 3.35–3.55 (6H, m), 3.90–4.00 (2H, m).

 $^{13}\text{C}$  NMR  $\delta_{\text{C}}(100$  MHz; D\_2O) ppm: 21.125, 48.527, 56.235, 65.037, 65.302.

# 2.1.7. Synthesis of 2-hydroxyethypyridinium bromide, [Py<sub>20H</sub>][Br]

To a flask containing 9.699 g of pyridine (0.1226 mol, Sigma-Aldrich 99.9%, used as received), 16.893 g of 2-bromoethanol (0.1352 mol, 10% excess, Sigma-Aldrich 98%, used as received) and 100 cm<sup>3</sup> of ethyl acetate (P.O.Ch for HPLC) were added. The mixture was stirred for 48 h in oil bath at temperature T = 343.2 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 20.614 g of white crystalline powder. Reaction yield was 82.4%.

 $^{1}\text{H}$  NMR  $\delta_{\text{H}}(500$  MHz; D\_2O) ppm: 3.88–4.01 (2H, m), 4.58–4.69 (2H, m), 7.90–8.05 (2H, m), 8.44–8.53 (1H, m), 8.69–8.80 (2H, m).

 $^{13}\text{C}$  NMR  $\delta_{\text{C}}(100$  MHz; D\_2O) ppm: 60.346, 63.505, 128.167, 144.638, 146.007.

Since residual water peak overlapped with CH<sub>2</sub> peak of the compound the NMR spectra was redone in acetonitrile. Due to the low solubility of the salt in acetonitrile methanol was added to enhance the solubility.

 $^1H$  NMR  $\delta_{H}(500$  MHz; CD\_3CN) ppm: 3.91–4.05 (2H, m), 4.45–4.60 (1H, m), 4.68–4.79 (2H, m), 8.00–8.1 (2H, m), 8.50–8.58 (1H, m), 8.83–8.95 (2H, m).

 $^{13}\text{C}$  NMR  $\delta_C(100$  MHz; CD\_3CN) ppm: 60.260, 63.621, 127.917, 145.104, 145.742.

# 2.1.8. Synthesis of N-(2-hydroxyethyl)-N,N,N-triethylammonium bromide, [N<sub>2,2,2,0H</sub>][Br]

To a 11.201 g of triethylamine (0.1107 mol, Sigma-Aldrich 98%, Reagent Plus, used as received) 15.360 g of 1-bromoethanol (0.1229 mol, 11% excess, Sigma-Aldrich 95%, used as received) in 100 cm<sup>3</sup> of ethyl acetate (POCh) was added. The mixture was stirred for 48 h in the oil bath at the temperature T = 348 K. Afterwards the product was crystallized from acetonitrile/2-propanol (ratio 10/1 vol/vol) and washed with ethyl acetate to give 20.904 g of crystalline powder. Reaction yield was 83.5%.

<sup>1</sup>H NMR  $\delta_{H}$ (500 MHz; D<sub>2</sub>O) ppm: 1.10–1.25 (9H, m), 3.20–3.30 (8H, m), 3.82–3.90 (2H, m).

<sup>13</sup>C NMR  $\delta_c$ (100 MHz; D<sub>2</sub>O) ppm: 6.864, 53.522, 54.868, 57.568.

# 2.1.9. Synthesis of N-(cyanomethyl)-N,N,N-triethylammonium bromide, [N<sub>2,2,2,1CN</sub>][Br]

To 11.44 g of triethylamine (0.1131 mol, Sigma-Aldrich 98%, Reagent Plus, used as received) in 100 cm<sup>3</sup> of acetonitrile (POCh for HPLC) a 14.24 g of bromoacetonitrile (0.1187 mol, 5% excess, Sigma-Aldrich 97%, used as received) in 100 cm<sup>3</sup> of ethyl acetate (POCh) was added. After few minutes a white solid starts precipitating. The mixture was stirred for 24 h at room temperature. Afterwards the product was filtered and washed with ethyl acetate. The product was purified by crystallization from acetonitrile/2-propanol (ratio 10/1 vol/vol) and washed

with ethyl acetate to give 23.30 g of white crystalline powder. Reaction yield was 92.8%.

<sup>1</sup>H NMR  $\delta_{H}$ (500 MHz; D<sub>2</sub>O) ppm: 1.307 (9H, t, <sup>3</sup>*J*<sub>H-H</sub> = 7.3 Hz), 3.483 (6H, q, <sup>3</sup>*J*<sub>H-H</sub> = 7.3 Hz), 4.50–4.68 (2H, m).

<sup>13</sup>C NMR  $δ_{C}$ (100 MHz; D<sub>2</sub>O) ppm: 7.214, 45.882, 55.693, 111.299.

# 2.1.10. Synthesis of N-(2-hydroxyethyl)-N,N-dimethyl-N-butylammonium bromide, [N<sub>1,120H,4</sub>][Br]

To 10.126 g of dimethylethanolamine (0.1136 mol, Sigma-Aldrich 99.5%, Reagent Plus, used as received) 17.388 g of 1-bromobutane (0.1269 mol, 12% excess, Sigma-Aldrich 98%, used as received) in 100 cm<sup>3</sup> of acetonitrile (POCh) was added. The mixture was stirred for 24 h in the oil bath at the temperature T = 363 K. Afterwards the product was crystallized from acetonitrile and washed with ethyl acetate to give 13.295 g of crystalline powder. Reaction yield was 51.75%.

<sup>1</sup>H NMR  $\delta_{H}(500 \text{ MHz}; D_2O) \text{ ppm: } 0.831 (3H, t, {}^3J_{H,H} = 7.3 \text{ Hz}), 1.263 (2H, h, {}^3J_{H,H} = 7.6 \text{ Hz}), 1.646 (2H, p, {}^3J_{H,H} = 7.6 \text{Hz}), 3.010 (6H, s), 3.253 (2H, m), 3.364 (2H, m), 3.919 (2H, m).$ 

 $^{13}\text{C}$  NMR  $\delta_{\text{C}}(100$  MHz;  $D_2\text{O})$  ppm: 12.753, 19.032, 23.910, 51.305, 55.327, 64.812, 65.286.

# 2.1.11. Synthesis of N,N-di(2-hydroxyethyl)-N,N-dimethylammonium bromide, [N<sub>1,1,20H,20H</sub>][Br]

To a 11.235 g of dimethylethanolamine (0.1260 mol, Sigma-Aldrich 99.5%, Reagent Plus, used as received) 18.020 g of 1-bromoethanol (0.1442 mol, 14% excess, Sigma-Aldrich 95%, used as received) in 100 cm<sup>3</sup> of acetonitrile (POCh) was added. The mixture was stirred for 48 h in the oil bath at the temperature T = 343.2 K. Afterwards the product was crystallized from acetonitrile/2-propanol (ratio 10/1 vol/vol) and washed with ethyl acetate to give 18.518 g of crystalline powder. Reaction yield was 68.6%.

 $^{1}\text{H}$  NMR  $\delta_{\text{H}}(500$  MHz; D\_2O) ppm: 3.01–3.21 (6H, m), 3.40–3.55 (4H, m), 3.85–4.04 (4H, m).

<sup>13</sup>C NMR δ<sub>C</sub>(100 MHz; D<sub>2</sub>O) ppm: 52.176, 55.390, 66.243.

NMR analysis of synthesized compounds is presented in Fig. S2 to S23 in Supplementary materials.

To remove any remaining volatile chemicals and to decrease water content before the experiment, each IL was dried for 48 h in a Vacuum Drying Oven (Binder, model VD 23) at a temperature T = 373 K and under reduce pressure ( $P = 4 \cdot 10^{-4}$  mbar) obtained by vacuum pump (Vacuubrand RZ 6). No decomposition of the tested ILs was observed at the experimental conditions. The structures of the tested ILs are presented in Table 1.

The water content of the dried samples was determined using Karl-Fischer titration (Schott Instruments Titro-Line KF used with CombiTitrant 2 supplied by Merck). The final mass fraction of water was <600 ppm for each IL.

#### 2.2. Differential scanning calorimetry, DSC measurements

Basic thermophysical characterization of pure additives including: phase transition temperature ( $T_{tr}$ ), enthalpy of phase transition ( $\Delta_{tr}H$ ), as well as temperature  $(T_m)$  and enthalpy of melting  $(\Delta_m H)$  have been measured using differential scanning calorimetry technique (DSC). The experiments were performed with DSC 1 STAR<sup>e</sup> System (Mettler Toledo) calorimeter equipped with liquid nitrogen cooling system and operating in a heat-flux mode. The sample cell was constantly fluxed with high purity nitrogen at constant flow rate of 20 mL·min<sup>-1</sup>. The apparatus was calibrated with the 99.9999 mol% purity indium sample and with high purity ethylbenzene, *n*-octane, *n*-decane, *n*-octadecane, *n*-eicosane, cyclohexane, biphenyl and water. The calibration experiments were carried out with 5 K $\cdot$ min<sup>-1</sup> heating rate in the temperature range from (180 to 430) K. The accuracy of the calibration is u(T) =0.3 K,  $u(\Delta H) = 3.3 \text{ J} \cdot \text{g}^{-1}$ . The sample was sealed in ambient air in hermetic aluminium pans having mass of about 50 mg. An empty hermetic aluminium pan was used as a reference. Sample size of about 10 mg were used throughout this study and the heat flow was normalized by the actual weight of each sample.

The experiments were carried out using 5 K·min<sup>-1</sup> heating rate. The experimental data presented in Table 2 were analyzed using STAR software. Graphical presentation of the experimental data is presented in Figs. S24 to Fig. S34 in Supporting materials.

## 2.3. Solid + Liquid Phase Equilibrium (SLE) measurements

Solutions of lithium bromide were prepared with anhydrous lithium bromide of purity higher than 99% (purchased from Fluka) and deionized water by weighing pure components on Mettler Toledo XA105 balance with an uncertainty of 0.0001 g. The initial concentration was selected to be higher than the solubility data of LiBr at 363.15 K given in the literature. In this study, the mass fraction of LiBr in the solution at the beginning of the solubility measurement was approximately 70 wt%. For the solubility measurements, the solution was placed into the tightly closed cylindrical Pyrex glass with Rotaflo valve, and then heated to temperature of 363.15 K. After that, the solution was cooled and the homogeneous solid phase was obtained. The temperature of last crystal disappearance during a slow increase in temperature  $(< 2 \text{ K} \cdot \text{h}^{-1} \text{ near the equilibrium temperature})$  was detected visually and measured by calibrated electronic thermometer P550 (DOSTMANN electronic GmbH). The visual method can be successfully used in the case of SLE measurements in transparent systems. The decay temperature (the last solid phase crystal disappearance) is visually determined. The errors of this method result from these observations and it is estimated that they do not exceed 0.05 K. The uncertainties of the temperature, and pressure measurements are 0.05 K and 1 kPa. The sample was continuously stirring inside the cell which was placed in the thermostat bath.

Depending on the measurements temperature, water, or ethanol with dry ice was used as

a thermostatic media.

The ternary mixtures of (LiBr + IL / ZI + H<sub>2</sub>O) were prepared by weighing pure components on Mettler Toledo XA105 balance with an uncertainty of 0.0001 g. The IL to LiBr mass ratio for most of the tested ILs was equal to 0.3. For ammonium-based ILs and ZI the experiments were performed also with 0.2 and 0.1 mass ratios. To (LiBr + IL + water) mixture a small amount of water was added and the SLE temperature was visually determined. The measurement procedure was the same as for the measurements of binary solutions of lithium bromide.

#### 3. Results and discussion

#### 3.1.1. Solubility of lithium bromide in water

In this work, the solubility of lithium bromide in water was determined using dynamic method at temperature range from (227 to 350) K. The experimental temperature of last crystal disappearance versus mass fraction of LiBr is presented in Fig.1. and the solubility values are collected in Table 3. For comparison, the literature data of the solubility of LiBr in water [10, 11, 13, 29] are also presented. The solubility of LiBr in water has been widely investigated in a wide temperature and composition range. Linke et al. [9] pointed out that there is poor agreement between published values, especially in the range of the application in refrigeration technologies [30]. Obtained data (Fig. 1) are in good agreement with those by Boryta [10] and Lefebvre et al. [13] within (0.22 to 0.31) mole fraction of LiBr and temperatures from (278 to 363) K. It is well known, that the soluble impurities impact the solubility measurements, due to change in the equilibrium solubility, or the solution structure by adsorption, or chemisorption onto the crystals and by chemical reaction or complex formation in the solution [31]. However, the impact of impurities in LiBr + water system was investigated by Lefebvre et al. [13] where the solubility of lithium bromide with purity of 99 wt% and 99.99 wt% in water were determined. The results indicate that there is

no observable difference between both of these samples hence the conclusion that the dissolved impurities do not significantly affect the solubility in the tested system. As shown in Fig. 1, the solubility curve can be divided into two parts: at temperatures higher than T = 317.67 K, where the lithium monohydrate (LiBr·H<sub>2</sub>O) is the stable form, and the second part at

# Table 1

The structures, names and abbreviations of the compounds under work.

Structure	Name, abbreviation, purity <sup>a</sup> , CAS No.	<i>M</i> [g mol <sup>-1</sup> ]
	N-methyl-N-(2-hydroxyethyl)morpholinium bromide, [MOR <sub>1,20H</sub> ][Br] purity: 20.950 CAS No. —	225.10
	<i>N</i> -(2-acetyloxy)ethyl- <i>N</i> -methylmorpholinium bromide, [MOR <sub>1,2(OOC)1</sub> ][Br] purity: ≥0.950 CAS No. —	268.15
O $BrCH_3 O CH_3 O CH_3 O Br$	N-methyl-N-(2-ethoxy-2-oxoethyl)morpholinium bromide, [MOR <sub>1,1(COO)2</sub> ] [Br] purity: ≥0.950 CAS No. —	268.15
	3-(1-methylpieridinium)propane-1-sulfonate, [MOR <sub>1.3</sub> SO <sub>3</sub> ] purity: ≥0.950 CAS No. —	223.29
	1-methyl-3-(2-hydroxyethyl)imidazolium bromide, [Im <sub>1,20H</sub> ][Br] purity: ≥0.950 CAS No. 97513-90-1	193.04
H <sub>3</sub> C Br Br OH	N-methyl-N-(2-hydroxyethyl)pyrrolidinium bromide, [PYR <sub>1,20H</sub> ][Br] purity: ≥0.950 CAS No. —	196.08
CH <sub>3</sub> Br	2-hydroxyethypyridinium bromide, [Ру <sub>20Н</sub> ][Br] purity: ≥0.950 CAS No. 31678-16-7	204.06
OH HO H <sub>3</sub> C N <sup>+</sup> Br	N-(2-hydroxyethyl)- <i>N,N,N</i> -triethylammonium bromide, [N <sub>2,2,2,20H</sub> ][Br] purity: ≥0.950 CAS No. —	226.15
$N = \underbrace{CH_3}_{CH_3}$ H_3C N Br	N-(cyanomethyl)-N,N,N-triethylammonium bromide, [N <sub>2,2,2,1CN</sub> ][Br] purity: ≥0.950 CAS No. —	221.14
└—СH <sub>3</sub>	N-(2-hydroxyethyl)-N,N-dimethyl-N-butylammonium bromide, [N <sub>1,1,20H,4</sub> ]	226.15

#### Table 1 (continued)



<sup>a</sup> Purity analysis method: NMR and Karl-Fischer.

temperatures lower than 317.67 K, where the dihydrate form (LiBr  $\cdot$  2H<sub>2</sub>O) becomes the stable crystalline form. Lefebvre et al. [13] presented the *in situ* video capture of LiBr xH<sub>2</sub>O (where x is 1, 2 or 3) suspension solutions. It was clearly shown that above 318.15 K, the LiBr  $\cdot$  H<sub>2</sub>O crystals nucleate with flocculent shape, in dendritic crystals, whereas under this temperature, the crystals transformed to LiBr  $\cdot$  2H<sub>2</sub>O are in a tetragonal structure.

In the available literature many different values of transition temperature between lithium bromide dihydrate and trihydrate are reported. Boryta [10] shows that the break in the solubility curve due to the transition between LiBr  $\cdot$  2H<sub>2</sub>O and LiBr  $\cdot$  3H<sub>2</sub>O is at *T* = 276.05 K (at 58.2 wt% of LiBr), whereas the temperature reported by Duvall et al. [12] was 278.85 K. Data presented in this work show a metastable region of dihydrate phase below the transition temperature. Phase transition was estimated to be 274 K based on the trend of liquidus curve below and above the metastable region. Lefebvre et al. [13] observed no transition between the two hydrate forms above 267.15 K and confirmed that the LiBr · 3H<sub>2</sub>O crystals nucleate only below that temperature. It was also mentioned, that due to the slow kinetics of nucleation of LiBr  $\cdot$  3H<sub>2</sub>O only the LiBr  $\cdot$  2H<sub>2</sub>O crystals are present above 267.15 K. The transition temperature between LiBr $\cdot$ 5H<sub>2</sub>O and LiBr $\cdot$ 3H<sub>2</sub>O (T =221.95 K and 45.7% of LiBr) is presented by Boryta [10] but due to the temperature limit of the dynamic method it was impossible to determine it

The solubility data can be interpreted using the Van't Hoff equation [31, 32] by the following equation:

$$\left(\frac{\partial lnx}{\partial T^{-1}}\right) = \frac{-\Delta H^{\nu H}}{R} \tag{1}$$

Table 2	
Thermophysical properties	of pure ILs determined by DSC technique. <sup>a</sup>

Ionic liquid	$T_{\rm tr,1}/({\rm K})$	$\Delta_{\mathrm{tr},1}H/(\mathrm{kJ}\cdot\mathrm{mol}^{-1})$	$T_{\rm m}/({\rm K})$	$\Delta_{\rm m} H/(kJ \cdot { m mol}^{-1})$
[MOR <sub>1,20H</sub> ][Br]	390.00	14.20	419.21	0.932
[MOR <sub>1,2(OOC)1</sub> ][Br]	-	_	406.35	19.77
[MOR <sub>1,1(COO)2</sub> ][Br]	-	-	424.71	23.80
$[MOR_{1,3}SO_3]$	-	-	602.73	167.63
[Im <sub>1,20H</sub> ][Br]	-	-	373.14	18.07
[PYR <sub>1,2OH</sub> ][Br]	-	-	527.06	7.74
[Py <sub>2OH</sub> ][Br]	-	-	379.02	18.25
[N <sub>2,2,2,20H</sub> ][Br]	394.25	18.13	538.77	79.30
[N <sub>2,2,2,1CN</sub> ][Br]	-	-	465.04	15.38
[N <sub>1,1,2OH,4</sub> ][Br]	371.49	4.95	385.08	15.98
[N <sub>1,1,20H,20H</sub> ][Br]	354.30	1.04	527.64	5.59

<sup>a</sup> Standard uncertainties *u* are as follows:  $u(T_{\text{fus}}) = 0.1 \text{ K}$ ;  $u(\Delta_{\text{fus}}H) = 0.5 \text{ kJ} \cdot \text{mol}^{-1}$ .

where: x is the LiBr mole fraction, T is the temperature of last crystal disappearance, *R* is the gas constant,  $\Delta H^{\nu H}$  is the van't Hoff enthalpy which is often interpreted as the dissolution enthalpy. As a first approximation, enthalpy of crystallization can be estimated as the opposite of the Van't Hoff enthalpy of dissolution. Eq. (1) leads to a linear relationship between lnx and  $T^{-1}$  from which it is possible to determine the value of  $\Delta H^{\nu H}$ . At narrow temperature range, this linearity is used in this work to precisely evaluate the transition temperature between the different hydrated crystalline forms of lithium bromide monohydrate and dihydrate. In order to obtain the transition temperature between lithium dihydrate and monohydrate forms, the two branches of curve around the transition point were linearized. From the intersection of two straight lines the transition temperature was determined (see Fig. S35 in SI). The experimental and literature characterization of the  $(LiBr \cdot H_2O)$  to  $(LiBr \cdot 2H_2O)$  transition including: temperature and enthalpy of the transition as well as the lithium bromide mass fraction are collected in Table 4. It can be noticed that in comparison with the literature results, the values obtained in this work are in good agreement with that presented by Kessis [33] and Lefebvre et al. [13] but significantly different from the values presented by other investigators. The



**Fig. 1.** The comparison of the experimental and literature data on solubility of lithium bromide with water: ( $\blacklozenge$ ) experimental data; ( $\diamondsuit$ ) Boryta [10]; ( $\blacktriangle$ ) Lefebvre et al. [13]; ( $\bigtriangleup$ ) Knoxville and Dean [11]; ( $\times$ ) Seidell [29].

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# Table 3

The experimental solid–liquid (SLE) phase equilibria measurements for {LiBr (1) + water (2)} binary system at pressure p = 100 kPa.<sup>a</sup>

<i>w</i> <sub>1</sub>	<i>x</i> <sub>1</sub>	<i>T</i> /(K)	<i>w</i> <sub>1</sub>	<i>x</i> <sub>1</sub>	<i>T</i> /(K)
0.6722	0.2984	349.16	0.5823	0.2212	276.23
0.6608	0.2879	334.33	0.5749	0.2155	268.74
0.6564	0.2839	325.26	0.5718	0.2112	264.85
0.6513	0.2793	317.54	0.5664	0.2066	258.73
0.6460	0.2746	314.89	0.5552	0.1946	265.04
0.6417	0.2709	312.86	0.5542	0.1911	264.13
0.6334	0.2639	309.83	0.5465	0.1837	261.11
0.6249	0.2568	305.51	0.5375	0.1754	254.09
0.6171	0.2506	301.87	0.5297	0.1686	249.28
0.6083	0.2437	296.70	0.5207	0.1606	243.73
0.6012	0.2376	292.01	0.5129	0.1533	237.71
0.5942	0.2319	286.94	0.4984	0.1441	227.00
0.5898	0.2266	282.75			

<sup>a</sup> Standard uncertainties *u* are as follows:  $u(x_1) = 0.0001$  and u(T) = 0.05 K, u(p) = 1 kPa.

discrepancies result directly from discrepancies in solubility of lithium bromide in water presented in Fig. 1.

3.1.2. Solubility of lithium bromide in water in presence of anticrystallization additive

The solubility of the {lithium bromide + ionic liquid, or zwitterionic compound + water} system (IL, or ZI to LiBr mass fractions = 0.1 to 0.3) were measured using dynamic method in the temperature range (240 to 360) K and in the concentration range (0.56 to 0.80) mole fraction of LiBr. The experimental results are listed in Tables 5 to 7 and Tables S1 to S5 in SI and graphically presented in Figs. 2 to 4 and Fig. S36 to S39 in SI. The IL structures were selected to determine the influence of cation core structure and the impact of functional groups on solubility of lithium bromide with water. The experiment clearly shows a large enhancement in solubility of lithium bromide in water was obtained by addition of ionic liquid, or zwitterionic compound to the lithium bromide + water solution. It was observed that, the temperature of transition between lithium bromide dihydrate and monohydrate has not changed due to addition a small amount of IL. This observation is true for all the additives tested in this work.

It is generally known that, for the absorption refrigeration machines, the coefficients of performance (COP) strongly depend of the properties of working fluids. As was mentioned, various new working fluids have been developed to improve the performance characteristics of the conventional (lithium bromide + water) system. General procedure for checking the validity includes the measurements of various basic thermodynamic and physicochemical properties of the solution, which are required for the proper design of absorption refrigerators and heat pumps. 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. Yokozeki [34] reported theoretical performances of various refrigerant-absorbent pairs and calculated values of the COP for different working fluids. The specified temperatures for the cycle condition were:  $T_g/T_{con}/T_a/T_{eva} = 100/40/30/10$  °C, where  $T_g$ ,  $T_{con}$ ,  $T_a$ ,  $T_{eva}$  is the temperature of generator, condenser, absorber and evaporator, respectively. To address the crystallization problem solubility of lithium

#### Table 5

The experimental solid–liquid (SLE) phase equilibria measurements for {LiBr (1) + morpholinium - based IL (2) + water (3)} binary system (IL:LiBr = 1:2.33 mass fraction) at pressure p = 100 kPa.<sup>a</sup>

$w_{1+2}$	<i>x</i> <sub>1+2</sub>	<i>T</i> /(K)	$W_{1+2}$	<i>x</i> <sub>1+2</sub>	<i>T</i> /(K)
LiBr (1) + $[MOR_{1.20H}][Br]$ (2) + water (3) ( $w_2 = 0.3005$ )					
0.7728	0.3651	341.47	0.7066	0.2894	291.79
0.7643	0.3541	327.35	0.6951	0.2783	284.49
0.7562	0.3440	315.34	0.6850	0.2688	276.76
0.7436	0.3290	309.54	0.6733	0.2584	266.12
0.7377	0.3223	306.86	0.6616	0.2485	254.51
0.7303	0.3140	303.57	0.6526	0.2410	243.51
0.7198	0.3028	299.49			
LiBr(1) + [M]	IOR <sub>1.2(00C)1</sub> ][Br	(2) + water	(3) $(w_2 = 0.30)$	02)	
0.7893	0.3826	357.80	0.7197	0.2981	299.82
0.7821	0.3725	350.51	0.7096	0.2878	294.83
0.7758	0.3639	344.90	0.6972	0.2758	288.26
0.7696	0.3558	337.02	0.6843	0.2639	280.36
0.7605	0.3443	324.25	0.6732	0.2541	271.01
0.7515	0.3334	314.35	0.6664	0.2483	264.18
0.7427	0.3232	309.78	0.6606	0.2435	258.12
0.7357	0.3152	307.36	0.6541	0.2383	251.20
0.7277	0.3064	303.12			
LiBr(1) + [M]	IOR <sub>1.1(COO)2</sub> ][Br	(2) + water	(3) $(w_2 = 0.30)$	03)	
0.7614	0.3454	332.28	0.7095	0.2877	296.00
0.7583	0.3416	327.26	0.7028	0.2812	291.99
0.7545	0.3369	321.35	0.6947	0.2734	287.66
0.7504	0.3320	316.31	0.6841	0.2637	280.08
0.7428	0.3232	310.86	0.6765	0.2570	273.62
0.7352	0.3146	308.41	0.6701	0.2514	268.19
0.7278	0.3066	305.41	0.6615	0.2443	259.02
0.7182	0.2965	300.21	0.6498	0.2348	246.86

<sup>a</sup> Standard uncertainties *u* are as follows:  $u(x_1) = 0.0001$  and u(T) = 0.05 K, u(p) = 1 kPa.

bromide in water at the absorber's working temperature (T = 303.15 K) was compared to the values in the presence of anticrystallization additive. The composition range of the binary and ternary mixtures at the absorber's working temperature is shown in Fig. 5 and S40 in SI. Addition of a small amount of IL, or ZI significantly improves the solubility of lithium bromide in water.

For the binary (LiBr + water) system, a narrow range of composition for the liquid state at temperature 303.15 K was found. Above LiBr mole fraction,  $x_{\text{LiBr}} = 0.2549$  the aqueous solution of lithium bromide crystallizes. Based on comparison of the experimental data on solubility of lithium bromide without additives, and these data in presence of different IL, or ZI as anti-crystallization additives, it was shown that in the second case, the mutual solubility increases. In this work, eleven different additives were tested. The greatest increase in solubility of LiBr in water was observed when [MOR<sub>1,3</sub>SO<sub>3</sub>] was added. It was possible to determine the liquidus curve for ZI to LiBr mass fraction up to 0.2. For the mass fraction of 0.3 the system supercools and does not crystallize, after cooling to 223.15 K the sample undergoes vitrification. From comparison of the solubility curves for the same IL to LiBr mass fraction, it can be noticed that in the case of [MOR<sub>1,3</sub>SO<sub>3</sub>] the highest composition range for the liquid state at T = 303.15 K, equal to  $x_{1+2} = 0.3209$  was observed (for IL to LiBr mass fraction of equal to 0.2). The solubility of lithium bromide in water decreases in the following order:  $[MOR_{1,3}SO_3] (x_{1+2} =$  $(0.3209) > [N_{1,1,20H,20H}][Br] (x_{1+2} = 0.2949) > [N_{2,2,2,20H}] (x_{1+2} = 0.2949) > [N_{2,2,20}] (x_{1+2} = 0.2949) > [N_{2,2$ 

Table 4

Characterization of the (LiBr·H<sub>2</sub>O) to (LiBr·2H<sub>2</sub>O) transition. The van't Hoff linearization given by Eq. (1) are used to determine the temperature and enthalpy of crystallization.

	Transition temperature/(°C)	Mass fraction of LiBr/(%)	van't Hoff enthalpy of (LiBr $\cdot 2H_2O$ )/(kJ $\cdot mol^{-1}$ )	Temperature range/(°C)
This work	44.52	65.10	5.24	23.6-44.4
Lefebvre et al. [13]	45.0	65.0	5.43	25.1-45.0
Duvall et al. [12]	34.3	67.66	7.69	21.3-34.3
Knoxville and Dean [11]	39.8	67.85	7.64	19.7-39.8
Kessis [33]	44.2	64.32	6.13	24.3-44.2

#### Table 6

The experimental solid-liquid (SLE) phase equilibria measurements for {LiBr (1) + IL (2) + water (3)} binary system (IL:LiBr = 1:2.33 mass fraction) at pressure p = 100 kPa.<sup>a</sup>

$w_{1+2}$	<i>x</i> <sub>1+2</sub>	<i>T</i> /(K)	$W_{1+2}$	<i>x</i> <sub>1+2</sub>	<i>T</i> /(K)	
LiBr (1) + $[Im_{1,20H}][Br]$ (2) + water (3) ( $w_2 = 0.2998$ )						
0.7685	0.3651	345.12	0.6945	0.2826	287.79	
0.7602	0.3545	333.68	0.6883	0.2767	283.64	
0.7524	0.3449	322.61	0.6827	0.2716	279.17	
0.7469	0.3383	314.63	0.6744	0.2641	273.67	
0.7379	0.3278	309.57	0.6667	0.2573	266.64	
0.7298	0.3188	307.09	0.6571	0.2492	257.51	
0.7185	0.3067	301.78	0.6498	0.2433	248.51	
0.7051	0.2929	294.54				
LiBr(1) +	[PYR <sub>1.20H</sub> ][Br]	(2) + water (3	) $(w_2 = 0.3009)$	9)		
0.7722	0.3695	352.20	0.7111	0.2984	298.67	
0.7655	0.3607	343.00	0.6979	0.2853	290.60	
0.7591	0.3526	335.14	0.6897	0.2775	285.66	
0.7521	0.3440	324.28	0.6755	0.2646	276.17	
0.7419	0.3320	312.45	0.6691	0.2590	271.00	
0.7324	0.3211	308.04	0.6605	0.2517	264.20	
0.7226	0.3104	303.58	0.6533	0.2457	257.12	
LiBr(1) +	[Py <sub>20H</sub> ][Br] (2)	+ water (3) (	$w_2 = 0.3000$ )			
0.7778	0.3754	350.30	0.7047	0.2907	293.06	
0.7704	0.3656	341.02	0.6974	0.2835	289.16	
0.7634	0.3565	331.75	0.6891	0.2757	284.09	
0.7541	0.3449	317.37	0.6790	0.2664	277.62	
0.7451	0.3342	311.83	0.6671	0.2561	268.04	
0.7358	0.3235	307.27	0.6558	0.2465	258.29	
0.7274	0.3142	303.91	0.6458	0.2385	248.15	
0.7155	0.3016	298.66	0.7047	0.2907	293.06	

<sup>a</sup> Standard uncertainties *u* are as follows:  $u(x_1) = 0.0001$  and u(T) = 0.05 K, u(p) = 1 kPa.

0.2809 > [N<sub>1,1,20H,4</sub>][Br] ( $x_{1+2} = 0.2775$ ) > [N<sub>2,2,2,1CN</sub>][Br] ( $x_{1+2} = 0.2541$ ).

In the case of [MOR<sub>1,3</sub>SO<sub>3</sub>] the negatively charged sulfonyl group can form ionic pair with the lithium cation thus creating a new moiety in the liquid phase [MOR<sub>1,3</sub>SO<sub>3</sub>Li][Br] which increases solubility of LiBr in water.

It is clearly shown that zwitterionic additives seem to be a promising alternative to IL. Further work is planned in this topic, on the possibility of using ZI as anti-crystallization additives.

A broader comparison of the effects for different types of IL was possible on the basis of solubility measurements with the IL to LiBr equal to 0.3. In this case, the maximum measured composition range for the liquid state at T = 303.15 K, that is  $x_{1+2} = 0.3251$  was determined with  $[N_{1,1,2OH,2OH}]$ . The influence of the tested IL on solubility of (LiBr + water) binary system show that the solubility of LiBr in water decreases in the following order:  $[N_{1,1,2OH,2OH}][Br]$  ( $x_{1+2} = 0.3251$ ) >  $[Py_{2OH}][Br]$  ( $x_{1+2} = 0.3136$ ) ~  $[MOR_{1,2OH}][Br]$  ( $x_{1+2} = 0.3135$ ) >  $[Im_{1,2OH}][Br]$  ( $x_{1+2} = 0.3114$ ) >  $[PYR_{1,2OH}][Br]$  ( $x_{1+2} = 0.3098$ ) >  $[MOR_{1,2(OOC)1}][Br]$  ( $x_{1+2} = 0.3071$ ) >  $[N_{2,2,2OH}][Br]$  ( $x_{1+2} = 0.3043$ ) >  $[MOR_{1,1(COO)2}][Br]$  ( $x_{1+2} = 0.3039$ ) >  $[N_{1,1,2OH,4}][Br]$  ( $x_{1+2} = 0.3012$ ). A decrease in solubility of LiBr in water was observed when  $[N_{2,2,2,1CN}][Br]$  was used as an additive; in this case, the range of the liquid phase composition at the absorber's working temperature is 0.2245, whereas for (LiBr + water) binary system  $x_{LiBr} = 0.2549$ .

The hydroxyl group in the additive increases the solubility of the LiBr. The best results were observed for the cation with two hydroxyl groups  $[N_{1,1,2OH,2OH}]$ [Br] ( $x_{1+2} = 0.3251$ ). When comparing the mono-hydroxy additives the more polar the compound the better. Additional interactions with the oxygen in morpholinium as well as  $\pi$  interactions in the case of pyridinium and imidazolium salts both enhance the solubility comparing to more aliphatic pyrrolidinium and ammonium. The increase in the aliphatic character of the IL by increasing the aliphatic side chain length decreases the solubility. Generally, groups within the structure that promote hydrogen bonding or allow for favorable solvation will increase the solubility of LiBr.

#### Table 7

The experimental solid–liquid (SLE) phase equilibria measurements for {LiBr (1) + ammonium–based IL (2) + water (3)} binary system (IL:LiBr = 1:2.33 mass fraction) at pressure p = 100 kPa.<sup>a</sup>

$w_{1+2}$	<i>x</i> <sub>1+2</sub>	<i>T</i> /(K)	$w_{1+2}$	$x_{1+2}$	<i>T</i> /(K)
LiBr(1) + [1]	N22220H][Br] (2	2) + water (3	3) $(w_2 = 0.3004)$	1)	
0.7691	0.3603	348.69	0.7049	0.2877	295.07
0.7647	0.3546	341.57	0.7007	0.2836	292.75
0.7605	0.3493	336.30	0.6970	0.2801	290.48
0 7562	0 3440	330.03	0.6926	0 2758	287 65
0.7512	0 3380	322.86	0.6886	0 2722	284 90
0.7312	0.3326	316 33	0.6848	0.2686	204.50
0.7400	0.3320	211.25	0.0040	0.2000	201.33
0.7425	0.3276	210.42	0.0614	0.2030	279.57
0.7367	0.5255	310.42	0.0771	0.2017	274.01
0.7341	0.3182	309.24	0.6736	0.2587	2/1.38
0.7292	0.3129	307.55	0.6701	0.2557	267.49
0.7248	0.3081	305.82	0.6652	0.2514	263.30
0.7212	0.3043	303.58	0.6608	0.2478	259.80
0.7176	0.3005	301.83	0.6549	0.2429	254.36
0.7138	0.2966	299.66	0.6502	0.2392	250.11
0.7094	0.2922	297.55	0.7049	0.2877	295.07
LiBr (1) + []	N <sub>2,2,2,1CN</sub> ][Br] (2	2) + water (3	( $w_2 = 0.3000$	))	
0.7578	0.3467	348.15	0.6572	0.2455	312.17
0.7534	0.3414	338.18	0.6498	0.2394	310.38
0.7465	0.3331	324.75	0.6429	0.2340	308.49
0.7417	0.3276	319.91	0.6343	0.2274	305.59
0.7376	0.3230	318.47	0.6309	0.2248	303.96
0.7329	0.3177	317.39	0.6235	0.2193	300.66
0.7284	0.3127	317.83	0.6161	0.2140	296.86
0.7238	0.3078	318.30	0.6095	0.2094	293.50
0 7194	0 3031	318 56	0.6027	0 2047	289 52
0.7147	0.2083	318.96	0.5071	0.2009	286.52
0.7147	0.2303	210.27	0.5571	0.2005	200.52
0.7039	0.2094	210.07	0.5908	0.1908	282.07
0.0905	0.2805	210.07	0.5850	0.1950	279.50
0.6878	0.2721	318.16	0.5788	0.1891	275.65
0.6792	0.2643	317.44	0.5734	0.1857	2/1.9/
0.6/1/	0.25//	315.37	0.5677	0.1822	269.24
0.6647	0.2517	314.11	0.5622	0.1789	265.75
LiBr(1) + [1]	N <sub>1,1,20H,4</sub> ][Br] (2	2) + water (3	B) $(w_2 = 0.2996)$	5)	
0.7703	0.3620	351.93	0.7168	0.2998	302.77
0.7650	0.3552	345.92	0.7112	0.2942	300.78
0.7590	0.3476	337.87	0.7070	0.2899	298.18
0.7540	0.3415	332.44	0.6994	0.2824	293.09
0 7483	0 3346	322.92	0.6912	0 2747	287 77
0 7425	03279	312.7	0.6829	0.2671	280.89
0.7369	0.3215	311.28	0.6754	0.2604	273.04
0.7317	0.3158	309.22	0.6687	0.2546	266.33
0.7271	0.2107	207.21	0.6614	0.2494	250.55
0.7271	0.5107	205.20	0.0014	0.2464	256.50
0.7215	0.3048	505.20	0.0343	0.2427	230.29
LiBr(1) + [1]	N <sub>1,1,20H,20H</sub> ][Br	] (2) + water	$(3) (w_2 = 0.30)$	004)	
0.7822	0.3797	351.15	0.7278	0.3131	298.94
0.7743	0.3690	336.18	0.7237	0.3086	296.78
0.7711	0.3647	330.15	0.7194	0.3041	294.61
0.7673	0.3598	324.38	0.7097	0.2941	289.59
0.7625	0.3537	316.69	0.7019	0.2864	283.93
0.7570	0.3468	309.65	0.6931	0.2780	276.95
0.7519	0.3406	308.68	0.6876	0.2728	272.03
0 7460	0 3336	306 36	0.6821	0.2678	266.69
0 7414	0 3283	304 59	0.6769	0.2631	260.00
0.7360	0.3203	307.55	0.6714	0.2001	200.50
0.7305	0.3231	302.00	0.6640	0.2303	233.04
0.7520	0.5165	500.20	0.0049	0.2327	247.04

<sup>a</sup> Standard uncertainties *u* are as follows:  $u(x_1) = 0.0001$  and u(T) = 0.05 K, u(p) = 1 kPa.

Among ammonium-based ILs, the greatest improvement in solubility in the discussed working pair, was observed with the use of  $[N_{1,1,2OH,2OH}][Br]$ . Moreover, an increase of the alkyl chain length results in a decrease in solubility, thus a narrower composition range at the absorber's working temperature was observed for  $[N_{1,1,2OH,4}][Br]$  than for  $[N_{2,2,2OH}][Br]$ . Additionally, it was observed that when the amount of IL increases (the IL to LiBr ratio increases), the solubility of LiBr in water increases, excluding  $[N_{2,2,2,1CN}][Br]$ . In the case of the  $[N_{2,2,2,1CN}]$ [Br] we observe a positive effect in higher temperatures (above the hydrate-dihydrate transition). In the lower temperatures when



**Fig. 2.** The solid–liquid (SLE) phase equilibrium data for {LiBr (1) + morpholinium-based IL (2) + water (3)} ternary systems, IL to LiBr mass fraction is equal to 0.3: ( $\bullet$ ) [MOR<sub>1,2(0H</sub>] [Br]; ( $\blacktriangle$ ) [MOR<sub>1,1(COD)2</sub>][Br]; ( $\bigstar$ ) [MOR<sub>1,2(OOC)1</sub>][Br]; ( $\bullet$ ) the experimental data for {LiBr (1) + water (2) binary system. Points: experimental results; solid lines: guide to the eye; dotted line: experimental temperature of transition between lithium bromide dihydrate and monohydrate forms.

dihydrate form is present, the IL allows for stabilization of the crystalline phase and the solubility decreases. It is worth mentioning that the mass fraction 0.2 has an influence on the transition temperature decreasing it by 12.5 K (from 317.7 K to 305.2 K). This may be the result of inclusion of the cation into the solid hydrate phase. Surprisingly this behavior is not observed in mass fraction 0.3.

Morpholinium-based ILs without functionalization were tested in our previous study [35]. The solubility of LiBr in water with all of the tested morpholinium additives decreases in the following order: [MOR<sub>1,3</sub>SO<sub>3</sub>] (supercooled) > [MOR<sub>1,2OH</sub>][Br] (0.3135) > [MOR<sub>1,2</sub>][Br] (0.3123) [35] > [MOR<sub>1,2(OOC)1</sub>][Br] (0.3071) > [MOR<sub>1,1(COO)2</sub>][Br] (0.3039)  $\approx$  [MOR<sub>1,4</sub>][Br] (0.3031) [35] > [MOR<sub>1,6</sub>][Br] (0.2910) [35].



**Fig. 3.** The solid–liquid (SLE) phase equilibrium data for {LiBr (1) + IL (2) + water (3)} ternary systems, IL to LiBr mass fraction is equal to 0.3: ( $\blacktriangle$ ) [PYR<sub>1,20H</sub>][Br]; ( $\circlearrowright$ ) [Im<sub>1,20H</sub>][Br]; ( $\circlearrowright$ ) [MOR<sub>1,20H</sub>][Br]; ( $\bigcirc$ ) [Py<sub>20H</sub>][Br]; ( $\bigstar$ ) the experimental data for {LiBr (1) + water (2)} binary system. Points: experimental results; solid lines: guide to the eye; dotted line: experimental temperature of transition between lithium bromide dihydrate and monohydrate forms.



**Fig. 4.** The solid–liquid (SLE) phase equilibrium data for {LiBr (1) + ammonium – based IL (2) + water (3)} ternary systems, IL to LiBr mass fraction is equal to 0.3: ( $\blacktriangle$ ) [N<sub>2,2,20H</sub>][Br]; ( $\bigcirc$ ) [N<sub>1,1,20H,4</sub>][Br]; ( $\diamondsuit$ ) the experimental data for {LiBr (1) + water (2)} binary system. Points: experimental results; solid lines: guide to the eye; dotted line: experimental temperature of transition between lithium bromide dihydrate and monohydrate forms.

From this comparison, we can observe that the impact of the ethylhydroxyl group comparing to the ethyl group is not significant. It suggested that the ionic interactions play the dominant role in the inhibition of crystallization. The influence of ester functionality on the solubility is low, although it is possible to observe the impact of different group position (ethyl ester *vs.* morpholinium ester). This probably the result of less steric hindrance for electrostatic interactions with lithium cation. Only the alkyl chain length significantly influences the solubility with the increase in the alkyl chain decreasing solubility. Since tested IL have the same ion as the LiBr we should expect the salting out phenomena to decrease the solubility of LiBr in aqueous solution, surprisingly we observe the opposite. This could be explained by formation of the IL ionic pairs within the solution and interaction of said ionic pairs with lithium and bromide ions.

The mole fraction analysis allows for better insight into molecular interactions, although for the technological point of view the weight fractions are more interesting. The weight fraction comparison is presented on the Fig. 5. Most of the ILs exhibit similar weight fraction at the absorber temperature on the level of  $w_{1+2} = 0.72$ . Compared to LiBr aqueous solution alone (w = 0.6225) the results obtained in this work are promising from the point of view of future use of IL, except  $[N_{2,2,2,1CN}]$ [Br] as an anti-crystallization additive in absorption refrigeration technology. However, the literature review shows that some additives that significantly improve the solubility of lithium bromide in water (thus the wider range of composition for the liquid state at absorber's working temperature) have been proposed, for example, when ethanolamine was added (ethanolamine to LiBr mass fraction w = 0.3) the  $w_{1+2}$  is equal to 0.8285 [17]. The results obtained in this study select  $[N_{1,1,2OH,2OH}][Br]$  as the best additive ( $w_{1+2} = 0.7386$ ) and are worse than literature data for ethanolamine or 1,2-propanediol ( $w_{1+2} =$ 0.8112) [36].

It is worth to mention, that zwitterionic additive ([MOR<sub>1,3</sub>SO<sub>3</sub>]) prevented crystallization in the whole range. The sulfonyl group in [MOR<sub>1,3</sub>SO<sub>3</sub>] can form ionic pair with the lithium cation thus creating a new moiety in the liquid phase [MOR<sub>1,3</sub>SO<sub>3</sub>Li][Br] with increased solubility. The zwitterionic compounds can be a promising alternative to IL and further work with this class of compounds will be continued.



Fig. 5. The comparison of the composition range of binary and ternary systems at the absorber's working temperature (T = 303.15 K) for IL to LiBr mass fraction 0.3.

SLE measurements show that the addition of 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 in turn will increase the COP. The experimental data presented in this article are the first step in the search for the best additives that reduce the crystallinity of (LiBr + water) binary system. Such data, supplemented by (vapor + liquid) phase equilibria measurements and physicochemical properties such as density and dynamic viscosity of the (LiBr + IL + water) ternary systems will allow selecting the best anticrystallization additives for conventional working fluid in absorption refrigeration technology.

### 4. Conclusion

In this work the solubility of lithium bromide in water was determined at wide temperature and concentration range. The experimental results were compared with the literature data which exhibit a wide disparity. It was presented that the experimental SLE data are in good agreement with those presented by Boryta [10] and Lefebvre et al. [13]. Van't Hoff dissolution enthalpy was calculated from experimental solubility data, and compared with the literature values.

The (solid + liquid) phase equilibria of lithium bromide in water in the presence of IL, or ZI as anti-crystallization additives were presented. Significant solubility enhancement of lithium bromide in water was obtained by adding ionic liquid, or zwitterionic compound to the lithium bromide + water solution, which could increases the working liquid composition range at the absorber's working temperature. For the binary (LiBr + water) system, a narrow range of composition for the liquid state at temperature 303.15 K was found. The experiment shows, that the greatest increase in solubility of LiBr in water was observed when [MOR<sub>1,3</sub>SO<sub>3</sub>], or [N<sub>1,1,2OH,2OH</sub>][Br] were added (the IL to LiBr mass fraction = 0.3). In the case of  $[MOR_{1,3}SO_3]$  the solution did not crystallize and maintained in liquid form even after prolonged cooling. As for  $[N_{1,1,2OH,2OH}][Br]$  the maximum composition range for the liquid state at T = 303.15 K, that is  $x_{1+2} = 0.3251$  whereas for aqueous solution of lithium bromide without any additives, the maximum range of the liquid state,  $x_{\text{LiBr}} = 0.2549$  was determined. Similar results were obtained from weight fraction analysis.

Most of the ILs have similar positive effect and the effect of functionalization is not significant. Since the temperatures of the corresponding hydrate transformation temperatures are not influenced by the ILs, we conclude that the IL rather stabilize the LiBr in the aqueous than disrupt the solid phase. The [N<sub>1.1.2OH.2OH</sub>][Br], IL with two hydroxyl groups has significantly higher solubility. It may be a result of complexation of LiBr in aqueous phase by hydrogen bonding and donor – acceptor interactions. In the case of [MOR<sub>1.3</sub>SO<sub>3</sub>] the sulfonyl group can form ionic pair with the lithium cation thus creating a new moiety in the liquid phase [MOR<sub>1.3</sub>SO<sub>3</sub>Li][Br] with increased solubility. Zwitterionic additives seem to be a promising alternative to IL, although vapor pressures of these mixtures should be investigated in order to verify that the increase in the solubility does not negatively influence the VLE properties. The solubility measurements together with vapor pressure data and physicochemical properties of the working fluid are essential for the optimum design of an absorption heat pump. This work is the first step of the experimental work in this area and further research will be carried out.

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#### Appendix A. Supplementary data

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