



Performance of a vapour absorption refrigeration system operating with ionic liquid-ammonia combination with water as cosolvent



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HIGHLIGHTS

- Ionic liquids have favourable properties for use in absorption refrigerators.
- The mass circulation ratio is high because of their large molecular weight.
- Water is an excellent cosolvent when ammonia is used as the refrigerant.
- A new method is developed to optimize systems with water as cosolvent.

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ABSTRACT

Ionic liquids are ideal absorbents for vapour absorption refrigeration systems because of their low volatility, and good solubility with different natural refrigerants such as ammonia, water, carbon dioxide, etc. However, the high circulation ratio and viscosity of ionic liquids pose many problems such as high pumping power and low absorber efficiency. One possibility is to use water as a cosolvent to overcome these drawbacks. The results of our study on the performance of a vapour absorption refrigerator operating with ammonia as the refrigerant and different ionic liquids and water as solvent and cosolvent respectively are presented in this paper. The results show that the use of water as a co-solvent results in a large decrease in circulation ratio, and hence the size of equipment, while the coefficient of performance decreases slightly.

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1. Introduction

Water–LiBr vapour absorption refrigeration systems (VARs) that operate with a variety of heat inputs are widely used for cooling applications above 4 °C. The size of these systems is generally large due to the sub-atmospheric operating pressures. More importantly, the heat addition temperature is limited because of the possibility of crystallization of the solution. VARs that operate with ammonia–water combination do not have these limitations. However, an additional distillation column is required to separate ammonia from water which decreases the efficiency while increasing the complexity and cost of the system. There have been

many attempts to find working fluid pairs that overcome the limitations of the widely used LiBr–H₂O and NH₃–H₂O pairs.

Ionic liquids (IL) are designer salts that are in a liquid phase at ambient as well as higher operating temperatures. The cation and anion of the salt can be chosen independently to form a salt that meets a specific requirement. Recently, there has been a great interest worldwide to design ionic liquids for different applications [1]. Ionic liquids are molten salts or electrolytes at room-temperature, composed entirely of ions, but physically neutral. Ionic liquids are composed of mostly organic cations and organic or inorganic anions with alkyl chain [2–5]. There is a worldwide interest in the use of VARs operating with ionic liquids to overcome some of the limitations of LiBr–H₂O systems.

One of the major drawbacks with most ILs is the high viscosity, which is several times higher than (in some cases even hundreds of times) that of water. The high viscosity results in poor diffusion of the refrigerant in the IL solution, leading to poor overall system

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efficiencies. The ideal solution is to design an IL with an appropriate combination of cation and anion pairs that results in lower viscosity. While the search is on for the right IL, a more convenient engineering solution is to use water as a cosolvent with known ILs.

Since ammonia has high solubility with water, water is an excellent co-solvent with ionic liquid as the absorbent and ammonia as the refrigerant. The addition of water also reduces the viscosity of the solution considerably. To the best of our knowledge, there is little information in literature on the use of a co-solvent in these systems to reduce the circulation ratio.

The results of our study with ammonia as the refrigerant, water as the co-solvent and the following absorbents (solvents) are presented in this paper:

- 1-ethyl-3-methylimidazolium Ethylsulfate ([emim][EtSO₄])
- 1-ethyl-3-methylimidazolium Acetate ([emim][Ac])
- 1-hexyl-3-methylimidazolium Chloride ([hmim][Cl])

A new optimisation based method has been developed for choosing the different process parameters of the VARS including the equilibrium concentration of ammonia at a given ratio of concentration of the solvent and co-solvent entering the solution pump.

2. Review of literature

A large amount of literature exists on fundamental studies on the preparation, thermophysical properties and vapour–liquid equilibria of a variety of ILs. Specialized databases also exist on the thermophysical properties. Significant interest has been shown in the use of VARS operating with ionic liquids as the absorbent and R-134a, H₂O, NH₃ and CO₂ as the refrigerant [6–9].

Sen and Paolucci [1] proposed the use of ionic liquid as the absorbent and carbon dioxide as the refrigerant in a VARS. Yokozeki and Shiflett [10] patented a vapour absorption refrigerator operating with ionic liquids and water as the refrigerant. They suggest the use of Redlich–Kwong equation of state (RK EoS) with modifications for estimating the properties of ionic liquid and refrigerant combinations. They also proposed the use of a generic van der Waals equation of state for estimating the gas solubility in ionic liquids [13].

Yokozeki and Shiflett [11] also measured the solubility of ammonia in ionic liquids and calculated thermodynamic performance of the cycle using NH₃ as the refrigerant with [emim][EtSO₄], [emim][Ac], [DMEA][Ac] and [emim][SCN] as the absorbents [11]. The solubility of ammonia with ionic liquid was measured at different temperatures by the same authors [12]. The RK EoS was used to calculate the binary interaction parameters for ionic liquid–refrigerant combinations to model the properties of both liquid and vapour phases. The coefficient of performance of ILs–NH₃ system is about 9–18% lower than that of conventional NH₃–H₂O system and the circulation ratio of ILs–NH₃ system was calculated to be 10 times higher than that of the conventional NH₃–H₂O system. According to their observation the solubility of NH₃ in ionic liquid is even better than the solubility of HFCs in ILs [13].

The thermophysical properties of ILs have been measured by many authors. He et al. [14] measured the properties of combinations of ionic liquids and water, ethanol, and methanol. Their investigations confirmed that while ionic liquids have high viscosity, the viscosity of ionic liquid mixtures also decreases markedly with an increase in temperature. Kim et al. [15] investigated new working pairs for vapour absorption refrigeration system using TFE–[bmim][BF₄] and TFE–[bmim][Br] as the working fluids. They measured thermophysical properties of TFE and ionic liquid

mixtures. The solubility of TFE was found to be higher in [bmim][Br] than [bmim][BF₄]. Hence [bmim][Br] is a favourable absorbent for vapour absorption systems.

Yokozeki and Shiflett [16] measured the solubility of water with twelve ionic liquids and studied the theoretical performance of single effect VARS. They used the RK EoS to estimate the vapour–liquid equilibria of ionic liquid and water in order to understand the solubility behaviour of water in ionic liquids. The COP of [mmim][(CH₃)₂PO₄]-water and [emim][(CH₃)₂PO₄]-water was estimated at 0.662 and 0.691 respectively, which is about 85–88% of that of conventional LiBr–H₂O system. Martin and Bermejo [17] used the group contribution equation of state by Jorgensen [18] to model vapour–liquid equilibria of ionic liquid and CO₂ mixture up to a pressure of 30 MPa. Their result shows that the circulation ratio was the lowest with [Alkyl-mim][NO₃] and [Alkyl-mpyr][Tf₂N], and the highest with [Alkyl-mpy][Tf₂N]. The theoretical coefficient of performance was estimated to be 0.21 at temperatures $T_g/T_c/T_a/T_e = 393/313/310/278$ K with [bmpyr][Tf₂N]-CO₂ combination. The circulation ratio was estimated to be 24, which is very high in comparison to conventional NH₃–H₂O system.

Cai et al. [19] developed a model for a vapour absorption refrigeration system using lumped-parameter approach. They successfully demonstrated the usefulness of the RK EoS model to predict the thermodynamic properties of ionic liquids. The coefficient of performance with [bmim][PF₆]-CO₂ as the working fluid was calculated as 0.0722, which is much lower than that of conventional systems. Zuo et al. [20] published the results of measured vapour pressure, heat capacity and density of 1-ethyl-3-methylimidazolium ethyl sulfate-water mixture at a temperature range of 300–373 K. They correlated the vapour pressure data with NRTL model and heat capacity data with polynomial equation which is a function of temperature and concentration. The relative average deviation between experimental and regressed data for vapour pressure, heat capacity and density was 1.9%, 1.2%, and 0.8% respectively. Ren et al. [21] suggested [emim][DMP] ionic liquid as a new absorbent for absorption heat pumps. They investigated the vapour–liquid equilibria of binary mixtures of [emim][DMP] with water, ethanol and methanol as the refrigerants. The average deviation between the experimental and predicted values of bubble pressure using the NRTL model for H₂O-IL, methanol-IL and ethanol-IL was 1.44%, 1.98% and 1.54% respectively.

Zhang and Hu [22] carried out the thermodynamic simulations of vapour absorption refrigeration system using water and [emim][DMP] as the working pair. They used activity coefficient model (NRTL method) to estimate the vapour pressure of water and ionic liquid. The coefficient of performance of the [emim][DMP]-H₂O system was estimated to be lower than that with LiBr–H₂O system by 7%. However, the coefficient of performance with the [emim][DMP]-H₂O system was still higher at 0.7. Most of the studies have been conducted with imidazolium based ionic liquids, mainly with ammonia, and water as the refrigerant [13,20–23], and a few with carbon dioxide [17,24,25].

The review of literature on VARS operating with ionic liquids shows that there is little information on the use of a cosolvent in these systems, which is the focus of this paper.

3. Analysis

The vapour absorption refrigeration system shown in Fig. 1 was simulated with different working pairs and water as the cosolvent. The simulation was carried out using Aspen Plus[®] process simulator [26]. The properties of ionic liquid were determined using activity coefficient Non-Random Two Liquid (NRTL) model [27,28] and that of the vapour phase using the Soave–Redlich–Kwong (SRK) equation of state [29]. The parameters of the NRTL methods were

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