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Absorption heat pump cycles with NH_3 – ionic liquid working pairs

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HIGHLIGHTS

- Nine NH_3/IL pairs are investigated in AHPs for building heating.
- COP of four NH_3/IL pairs beats that of the NH_3/H_2O.
- Idealized NH_3/IL mixture can reach a COP of 1.84.
- [Emim][SCN] is currently a feasible candidate to be used in AHPs with PHX.

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ABSTRACT

Ionic liquids (ILs), as novel absorbents, draw considerable attention for their potential roles in replacing water or LiBr aqueous solutions in conventional NH_3/H_2O or H_2O/LiBr absorption refrigeration or heat pump cycles. In this paper, performances of 9 currently investigated NH_3/ILs pairs are calculated and compared in terms of their applications in the single-effect absorption heat pumps (AHPs) for the floor heating of buildings. Among them, 4 pairs were reported for the first time in absorption cycles (including one which cannot operate for this specific heat pump application). The highest coefficient of performance (COP) was found for the working pair using [mmim][DMP] (1.79), and pairs with [emim][Tf_2N] (1.74), [emim][SCN] (1.73) and [bmim][BF_4] (1.70) also had better performances than that of the NH_3/H_2O pair (1.61). Furthermore, an optimization was conducted to investigate the performance of an ideal NH_3/IL pair. The COP of the optimized mixture could reach 1.84. Discussions on the contributions of the generator heat and optimization results revealed some factors that could affect the performance. It could be concluded that the ideal IL candidates should show high absorption capabilities, large solubility difference between inlet and outlet of the generator, low molecular weights and low heat capacities. In addition, an economic analysis of the AHP using NH_3/[emim][SCN] working pair with plate heat exchangers was carried out based on heat transfer calculations. The results indicated that the NH_3/IL AHP is economically feasible. The efforts of heat transfer optimization in the solution heat exchanger and a low expense of ILs can help the IL-based AHP systems to become more promising.

1. Introduction

The Paris Agreement adopted by 195 countries in the 2015 Paris climate conference (COP 21) reset the global ambition: limiting the temperature rise from pre-industrial levels well below 2 K. Efforts responding to climate change are also accelerating the way the energy sector is developing [1]. Heating and cooling, especially for buildings take up the majority of the energy consumption and the greenhouse gases emission. According to the European Commission, heating and cooling consumed 50% (22.85 EJ) of the final energy consumption in the EU in 2012. 45% of energy for heating and cooling in the EU was used in the residential sector, 37% in industry and 18% in services [2]. In the US, 41% (42.2 EJ) of the primary energy in 2010 was consumed by the buildings sector, compared to 30% by the industrial sector and 29% by the transportation sector. Heating and cooling took 59% of the buildings energy consumption [3]. As an increasingly significant energy consumer in the buildings sector, China is the largest energy-consuming economy in the world, and buildings energy used in China was the second-largest in the world after the US, representing nearly 16% of total global energy consumption in buildings in 2012 (more than 18 EJ) [4].

Absorption refrigeration and heat pump cycles are drawing considerable attention because they can take effective advantage of low-grade heat from concentrating solar collectors or waste heat, providing opportunities for clean and sustainable energy utilizations [5–8]. Working pairs H_2O/LiBr and NH_3/H_2O have been widely used in

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Nomenclature

A	area (m^2)
C	cost (k€)
C_p	heat capacity (kJ kg^{-1} K^{-1}/kJ $kmol^{-1}$ K^{-1})
c	coefficient in heat capacity (–)
f	circulation ratio (–)
G	parameters in NRTL model (–)
h	specific enthalpy (kJ kg^{-1})
$\dot{m}$	mass flow rate (kg s^{-1})
Mw	molecular weight (kg $kmol^{-1}$)
P	pressure (Pa)
Q	heat flow (W)
q	quality (kg kg^{-1})
T	temperature (K/°C)
w	mass concentration (kg kg^{-1})
x	molar concentration (kmol $kmol^{-1}$)

Greek letter

α	parameter in NRTL model (–)
γ	activity coefficient (–)
τ	parameter in NRTL model (–)

Subscript and superscript

0	reference state
1,2 …	state point
abs	absorber
c	critical (property)
con	condenser
E	excess (enthalpy)
eva	evaporator
gen	generator
NH_3	species of NH_3
IL	species of IL
phx	plate heat exchanger
r	refrigerant stream
s	strong solution stream
sat	saturated state
sol	solution
sthx	shell-and-tube heat exchanger
vap	vapor

Abbreviation

ABS	absorber
AHP	absorption heat pump
CON	condenser
COP	coefficient of performance
EOS	equation of state
EVA	evaporator
GA	genetic algorithm
GAX	generator/absorber heat exchanger
GEN	generator
HC	hydrocarbon
HFC	hydrochlorofluorocarbon
HX	heat exchangers
IL	ionic liquid
NRTL	non-random two-liquid activity coefficient model
OHTC	overall heat transfer coefficient
PHX	plate heat exchanger
REC	rectifier
RMSD	root-mean-square deviation
RK	Redlich-Kwong (equation of state)
SHX	solution heat exchanger
VLE	vapor-liquid equilibrium/vapor-liquid equilibria
[mmim][DMP]	1,3-dimethylimidazolium dimethyl phosphate
[emim][BF_4]	1-ethyl-3-methylimidazolium tetrafluoroborate
[hmim][BF_4]	1-hexyl-3-methylimidazolium tetrafluoroborate
[omim][BF_4]	1-methyl-3-octylimidazolium tetrafluoroborate
[bmim][BF_4]	1-butyl-3-methylimidazolium tetrafluoroborate
[bmim][PF_6]	1-butyl-3-methylimidazolium hexafluorophosphate
[emim][Tf_2N]	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide
[emim][$EtSO_4$]	1-ethyl-3-methylimidazolium ethylsulfate
[emim][SCN]	1-ethyl-3-methylimidazolium thiocyanate

certain applications in absorption systems, while many challenges do exist, such as crystallization possibilities of the H_2O/LiBr pair and the difficulty in the separation of the NH_3/H_2O pair [9]. Thus, the investigation of alternative solvents is still a relevant topic [10–14,9].

Ionic liquids (ILs), whose properties can be adjusted by the design of anion and cation combination for a task-specified purpose, have drawn considerable attention for their potential roles in replacing conventional absorbents used in absorption refrigeration and heat pump cycles in the past years. Researchers recognized the strengths of ILs in applications, such as high boiling point, good affinity with refrigerants, and high chemical and thermal stabilities [9]. Nevertheless, there are also some challenges related to the technical feasibility and costs when introducing them, thus many efforts are still needed before the ILs are accepted in practice.

In order to preselect promising ILs to be used in absorption systems, many researchers did performance investigations. The majority of investigations were focused on performance predictions, in which the frequently studied refrigerants include H_2O [15,16], hydrocarbons (HCs) [17], hydrofluorocarbons (HFC) [18,19] and CO_2 [20]. Since NH_3 based absorption systems hold strengths such as sub-zero degree applications and free of air infiltration, research related to these mixtures is most relevant. Nevertheless, there is only limited work which has been reported. Yokozeki and Shiflett [21,22] measured solubility data for NH_3 with a set of ILs, and calculated the thermodynamic performance of these mixtures in a single-effect cycle. Kotenko [23] also developed thermodynamic simulations for absorption heat pumps (AHPs) with 4 NH_3/ILs mixtures in Aspen Plus, and compared their performances with that of the NH_3/H_2O system. Their results showed that the efficiency of some of the investigated NH_3/IL AHP processes, at specified operating conditions, was higher than that of conventional NH_3/H_2O systems. Chen et al. [24,25] investigated vapor-liquid equilibria (VLE) for metal ion-containing ionic liquid [bmim][Zn_2Cl_5] with NH_3, and compared the thermodynamic performance of this mixture with that of the NH_3/NaSCN pair. The performance of the former system is better than that of the latter one when the generator temperature is high and the absorber and the condenser temperatures are low. Ruiz et al. [26] modeled NH_3/IL absorption using COSMO-based Aspen simulations and analyzed cycle performance for conventional and task-specific ILs.

In these performance prediction studies of absorption systems, the enthalpy of the NH_3/IL solution is always an essential thermodynamic property. Most researchers obtained this property by adding an excess enthalpy to the sum of enthalpies of the two pure components. The excess enthalpy could be obtained from the VLE data via a variety of models. Some researchers [27,15,28] used the non-random two-liquid (NRTL) activity coefficient model to predict it. However, Shiflett and Yokozeki [27] found that an accurate prediction of the mixing enthalpy with NRTL is very difficult, because the excess enthalpy is derived from