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**Publication date**

2016

**Document Version**

Final published version

**Published in**

Proceedings of the 16th International Refrigeration and Air Conditioning Conference at Purdue

**Citation (APA)**

Wang, M., & Infante Ferreira, C. (2016). Screening criteria for ILs used in NH<sub>3</sub> based absorption heat pump systems. In E. Groll (Ed.), *Proceedings of the 16th International Refrigeration and Air Conditioning Conference at Purdue: IRACC 2016* Article 2285 (Purdue e-Pubs). Purdue University.

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2016

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Wang, Meng and Infante Ferreira, Carlos A., "Screening Criteria for ILs used in NH<sub>3</sub> Based Absorption Heat Pump Systems" (2016).  
*International Refrigeration and Air Conditioning Conference*. Paper 1690.  
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# Screening Criteria for ILs used in NH<sub>3</sub> Based Absorption Heat Pump Systems

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## ABSTRACT

This paper describes a properties-optimization work for the working fluids in NH<sub>3</sub> / ionic liquid (ILs) based single-effect absorption heat pumps. The optimum parameters of the IL can be used as criteria in screening task-specified ILs, which play the role of absorbents, in absorption heat pumps. First, a 8-parameter thermodynamic model to calculate performances of a single-effect absorption heat pump cycle was proposed, which is based on the non-random two-liquid (NRTL) activity coefficient model for the vapor pressure and a linear function for the heat capacity. Then, experimental data on the vapor-liquid equilibrium (VLE) of solutions and heat capacities of the pure ILs were reviewed and fitted to obtain ranges of those parameters. Within certain limits, the values of parameters were optimized in the following step using the above proposed mode. The objective is a maximum system performance. The optimized ILs have low molecular weights, low specific heats and have high absorption capabilities.

## 1. INTRODUCTION

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 (Sözen et al., 2002; Velázquez & Best, 2002; Zaltash et al., 2005; Kim & Infante Ferreira, 2008). Binary mixtures such as H<sub>2</sub>O / LiBr, NH<sub>3</sub> / H<sub>2</sub>O have been widely used in certain applications in absorption systems for centuries, but many challenges do exist (Zheng et al., 2014), such as crystallization possibilities of the H<sub>2</sub>O / LiBr pair and the difficulty in separation of NH<sub>3</sub> / H<sub>2</sub>O pair. Thus, the interest in alternative solvents investigation is renewed (Nowaczyk & Steimle, 1992; Ameen et al., 1995; Donate et al., 2006; Karamangil et al., 2010; J. Sun et al., 2012; Zheng et al., 2014).

Ionic liquids (ILs), as novel absorbents, draw considerable attention for their potential roles in replacing water or LiBr aqueous solutions in conventional absorption refrigeration and heat pump cycles in the past years. In order to preselect promising ILs to be used in absorption systems, many simulations have been conducted. For the NH<sub>3</sub> / ILs based systems, Yokozeki & Shiflett (2007a,b) measured solubility data for NH<sub>3</sub> with some ILs, and calculated their thermodynamic performance in a single-effect cycle. Kotenko et al. (2011) did thermodynamic simulations for an absorption heat pump with 4 NH<sub>3</sub> / ILs mixtures in Aspen Plus and compared their performances with that of the NH<sub>3</sub> / H<sub>2</sub>O system. Chen et al. (n.d., 2014) investigated the vapor-liquid equilibrium (VLE) of metal ion-containing ionic liquid [bmim][Zn<sub>2</sub>Cl<sub>5</sub>] and NH<sub>3</sub>, and compared the thermodynamic performance of the mixture as a working pair with that of NaSCN / NH<sub>3</sub>. Ruiz et al. (2014) modeled NH<sub>3</sub> / IL absorption cycles by COSMO-based Aspen simulation and analyzed cycle performance for conventional and task-specific ILs.

The properties of ILs can be adjusted by the design of anion and cation combination for a task-specified purpose. However, because of the large number of anions and cations, the number of possible combinations is considerable. In this paper, work about the determination of screen criteria of task-specific ILs for absorption heat pump will be discussed. These criteria are determined through the optimization of the performance parameter, i.e. the coefficient of performance (COP) of the single effect absorption heat pump.

A genetic algorithm (GA) is a method for solving optimization problems based on a natural selection process that mimics biological evolution, i.e. the survival of the fittest strategy. In general, the fittest individuals of any population tend to reproduce and survive to the next generation, thus improving successive generations (Goldberg, 1989; Houck et

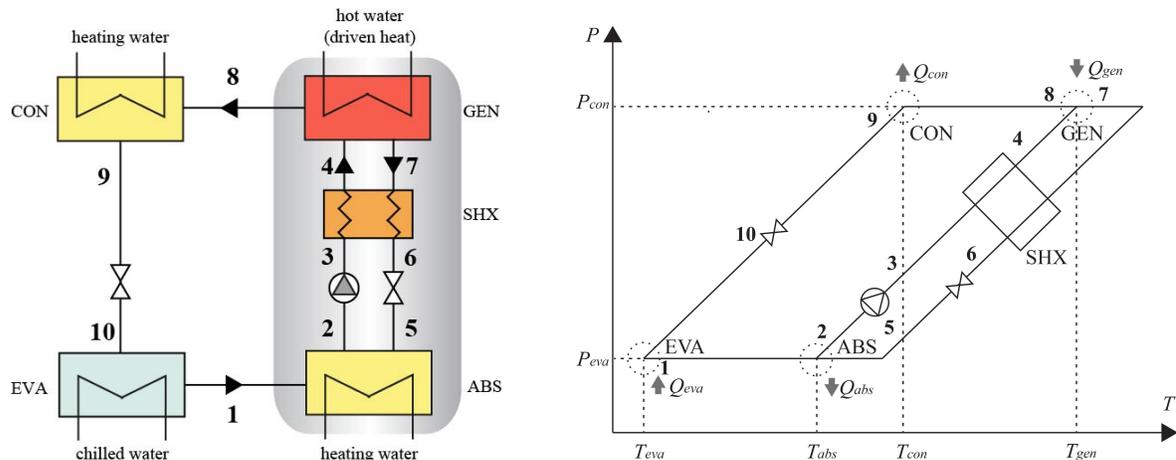
al., 1995). Genetic algorithms have been shown to solve linear and nonlinear problems by exploring all regions of the state space and exponentially exploiting promising areas through mutation, crossover and selection operations applied to individuals in the population (Michalewicz, 1996). The GA has already been used in some related fields such as the correlation works for VLE data (Ortega & Espiau, 2003), optimum work of process parameters in refrigeration process (Dai et al., 2009) and the controller parameters optimization in Heating Ventilating and Air Conditioning (HVAC) systems (Huang & Lam, 1997). In this work, the GA is applied to optimize the parameters in relevant thermodynamic properties, for the determination of the screening criteria.

The outline of the this work can be summarized as: first, a thermodynamic model to calculate performances of a single-effect absorption heat pump cycle is proposed. In this model, the non-random two-liquid (NRTL) activity coefficient model is employed for the vapor pressure to determine state points, and a linear function is used for the ILs' heat capacity to calculate the enthalpies of solutions. In total, 8 parameters are needed to determine the required properties in the model. Then, some experimental data on the vapor-liquid equilibrium (VLE) of solutions and heat capacities of the pure ILs are reviewed and fitted to obtain ranges of these parameters. Within certain limits, the values of parameters are optimized in the following steps based on the above proposed model by a GA method for a maximum system performance.

## 2. OPTIMIZATION PROBLEM DEFINITION

### 2.1 Cycle Description

Fig. 1. depicts a schematic system of a single-effect absorption refrigeration/heat pump cycle. The process is mainly composed of an absorber (ABS), a generator (GEN), a condenser (CON), an evaporator (EVA), along with a solution heat exchanger (SHX), a pump and two throttle valves. To qualitatively illustrate the temperature and pressure relationship of each state, the process is also plotted in a  $\ln P - 1/T$  diagram in Fig. 2.



**Figure 1: Schematic diagram of a absorption system**      **Figure 2: The absorption cycle on a  $\ln P - 1/T$  diagram**

In order to create an integrated model for the thermodynamic analysis of the absorption process, several assumptions have been made to simplify the calculation.

- The system operates in steady state.
- The operating pressures of EVA and ABS are the same, and similarly, the pressures of GEN and CON are also equal.
- The solution is in equilibrium states while leaving ABS and GEN. The refrigerant stream is in a saturated liquid or saturated vapor state in the outlet of CON or EVA, respectively.
- The minimal heat transfer temperature difference of the exchanger SHX is set to 5 K.
- The heat losses, pressure losses and pumping work are neglected.

With the given conditions of  $T_{con}$  and  $T_{eva}$ , the pressures  $P_{con}$  and  $T_{eva}$  can be obtained according to the vapor pressure of the pure refrigerant ( $\text{NH}_3$ ), thus, the states 1 and 9 can be determined. Using the pressure equality relationship, the pressure levels for ABS and GEN can be set. Based on the VLE conditions at the outlet of ABS and GEN, the fractions of each component for both strong and weak solutions can be determined, at the given conditions of temperature  $T_{abs}$  and  $T_{gen}$  with the pressure levels obtained above. Thus, states 2 and 7 can be determined, so as for state 8, pure refrigerant vapor from GEN outlet, which is usually at a superheated state. The heat balance of SHX together with the assumption for the valves and pumps (constant enthalpy), states 3, 4, 5, 6 could all be determined.

The enthalpy of each point is obtained according to the state with the help of the enthalpy prediction method discussed in the Section 2.3. The heat exchanged in EVA and GEN is,

$$Q_{eva}/\dot{m}_r = h_1 - h_9 \quad (1)$$

$$Q_{gen}/\dot{m}_r = h_8 + f(h_7 - h_4) - h_7 \quad (2)$$

The performance parameters i.e. coefficient of performance (COP) and circulation ratio ( $f$ ), can be calculated as,

$$COP = \frac{Q_{con} + Q_{abs}}{Q_{gen}} \quad (3)$$

$$f = \frac{\dot{m}_s}{\dot{m}_r} = \frac{1 - w_5}{w_2 - w_5} \quad (4)$$

## 2.2 Vapor Pressure for the $\text{NH}_3$ / ILs Binary Solutions

For the  $\text{NH}_3$  / IL system, due to the non-volatility of ILs, the equilibrium criterion is simplified as,

$$\gamma_{\text{NH}_3} = \frac{P}{x_{\text{NH}_3} P_{\text{NH}_3}^{sat}} \quad (5)$$

here,  $P_{\text{NH}_3}^{sat}$  can be obtained from NIST Refprop (Lemmon et al., 2013). The activity coefficient  $\gamma_{\text{NH}_3}$  can be obtained by the NRTL activity coefficient model,

$$\ln \gamma_i = x_2^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{G_{12} \tau_{12}}{(x_2 + x_1 G_{12})^2} \right] \quad (6)$$

where,

$$\begin{cases} G_{12} = \exp(-\alpha \tau_{12}) \\ G_{21} = \exp(-\alpha \tau_{21}) \\ \tau_{12} = \tau_{12}^{(0)} + \frac{\tau_{12}^{(1)}}{T} \\ \tau_{21} = \tau_{21}^{(0)} + \frac{\tau_{21}^{(1)}}{T} \end{cases} \quad (7)$$

## 2.3 Enthalpies of the Refrigerant and Solution

The enthalpy data of the pure  $\text{NH}_3$  is directly obtained from NIST's Refprop (Lemmon et al., 2013). For a real solution, the total enthalpy can be calculated as the sum of the enthalpy for the ideal solution and the mixing heat, which is expressed as,

$$h = w_{\text{NH}_3} h_{\text{NH}_3} + w_{\text{IL}} h_{\text{IL}} + \Delta h_{\text{mix}} \quad (8)$$

In this preliminary work, the mixing heat part  $\Delta h_{\text{mix}}$  is neglected for a simplification purpose, while only the first 2 terms are taken into consideration. The enthalpy of pure IL can be obtained from the heat capacity of pure IL  $C_p^{\text{IL}}$  as,

$$h_{\text{IL}} = h_0 + \int_{T_0}^T C_p^{\text{IL}} dT \quad (9)$$

## 2.4 Optimization problem and its GA implementation

In this work, the objective is to obtain a maximum COP of a single effect absorption heat pump, thus, the COP described in Section 2.1 is taken as the objective function. The optimal variables are the parameters which give the needed thermodynamic properties (vapor pressure and heat capacity in Section 2.2 and 2.3) of the pseudo working pairs used in the cycle. Constraints for optimal variables are also very critical for a optimization problem in terms of a practical and reasonable result. Thus, they will be determined according to experimental data which already exist in literature. The detailed information is listed in Section 3.1.

## 3. RESULTS AND DISCUSSION

### 3.1 Constraints of variables

In order to limit the search domain and make the optimization reasonable and reliable (more close to the reality), constraints of optimal variables are collected based on the experimental data of relevant properties.

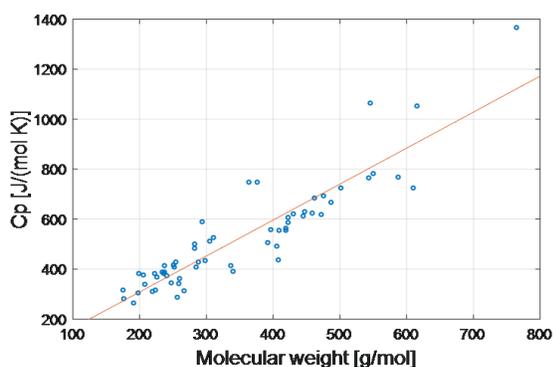
Experimental VLE data of  $\text{NH}_3$  / ILs binary systems are collected from literature (G. Sun et al., 2012; Li et al., 2010; Yokozeki & Shiflett, 2007a,b). Based on those data, the fitted binary parameters in NRTL model (Eq. 6 and 7) are listed in Table 1.

**Table 1: Correlated binary parameters in NRTL model**

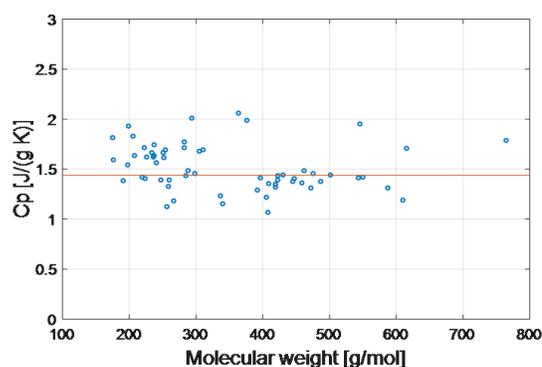
Working pairs*	$\alpha$	$\tau_{12}^{(0)}$	$\tau_{12}^{(1)}$	$\tau_{21}^{(0)}$	$\tau_{21}^{(1)}$
$\text{NH}_3$ / [mmim][DMP] <sup>1</sup>	0.24	7.82	-2300.68	-4.43	1000.39
$\text{NH}_3$ / [emim][BF <sub>4</sub> ] <sup>2</sup>	1	-0.01	236.41	-1.26	164.59
$\text{NH}_3$ / [hmim][BF <sub>4</sub> ] <sup>3</sup>	1	-14.8	5081.74	-2.67	478.85
$\text{NH}_3$ / [omim][BF <sub>4</sub> ] <sup>4</sup>	0.91	-7.01	2690.74	-2.4	283.17
$\text{NH}_3$ / [bmim][BF <sub>4</sub> ] <sup>5</sup>	-0.013	-48.23	8961.06	32.62	-5490.64
$\text{NH}_3$ / [bmim][PF <sub>6</sub> ] <sup>6</sup>	0.33	3.73	-509.57	-4.19	643.5
$\text{NH}_3$ / [emim][Tf <sub>2</sub> N] <sup>7</sup>	0	-100	14710.17	71.51	-9046.21
$\text{NH}_3$ / [emim][EtSO <sub>4</sub> ] <sup>8</sup>	0.72	11.17	-4089.25	-7.53	2451.46
$\text{NH}_3$ / [emim][SCN] <sup>9</sup>	-0.27	-10.66	3120.01	5.6	-1967.71

\* The experimental VLE data used are from, 1 (G. Sun et al., 2012), 2, 3 and 4 (Li et al., 2010), 5, 6 and 7 (Yokozeki & Shiflett, 2007a), 8 and 9 (Yokozeki & Shiflett, 2007b).

Experimental heat capacity ( $C_p$ ) data of 61 ILs at 298.15 K from a review (Paulechka, 2010) are plotted in Fig. 3 and 4 respectively in mole-based and mass-based units. It's quite interesting to find the molar based  $C_p$  data are distributed in a linear trend with respect to the molecular weight. And the mass-based  $C_p$  data are centralized near  $1.44 \text{ J g}^{-1} \text{ K}^{-1}$  in a nearly constant range between  $1\text{-}2 \text{ J g}^{-1} \text{ K}^{-1}$ . These trends provide simple relationships between the  $C_p$  value with molecular weight. Based on that, we assume the mass-based  $C_p$  value at 298.15 K is in a range of  $1.3$  to  $2.0 \text{ J g}^{-1} \text{ K}^{-1}$  in the following optimization.



**Figure 3: Mole-based  $C_p$  values of 61 selected ILs at 298.15 K**



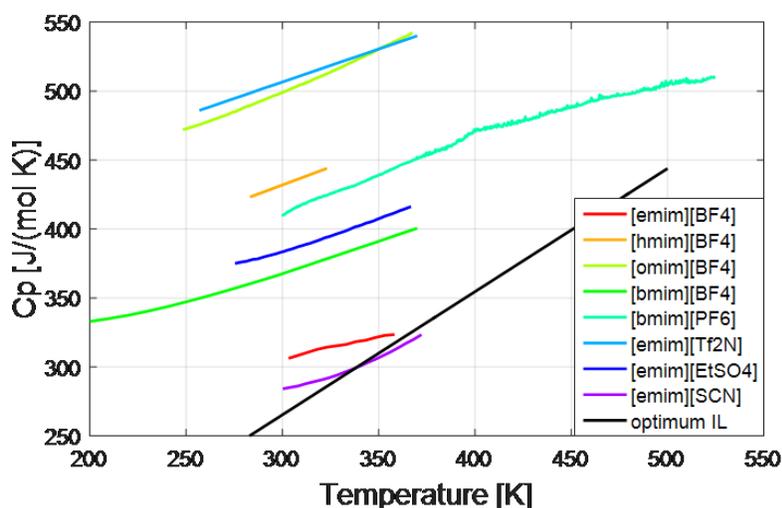
**Figure 4: Mass-based  $C_p$  values of 61 selected ILs at 298.15 K**

For the same ILs involved in the NRTL fitting in Table 1, the molar based  $C_p$  values of them are plotted along temperature in Fig. 5. With respect to the temperature, the  $C_p$  values of different ILs also show linear trends. Thus, the molar  $C_p$  value can be represented by a linear expression. Table 2 lists the fitted parameters of the linear expression from the experimental  $C_p$  data from literature (Ren et al., 2011; Yu et al., 2009; García-Miaja et al., 2008; Paulechka et al., 2015; Kabo et al., 2004; Paulechka et al., 2007; Navarro et al., 2013) and the molecular weight data.

**Table 2: Correlated parameters in  $C_p = c_0 + c_1 T$  for mole-based  $C_p$  and molecular weight**

ILs*	$c_0$	$c_1$	$M_w$ [ $\text{g mol}^{-1}$ ]
[mmim][DMP] <sup>1</sup>	-153.898	1.476	222.18
[emim][BF <sub>4</sub> ] <sup>2</sup>	214.067	0.308	197.97
[hmim][BF <sub>4</sub> ] <sup>3</sup>	275.962	0.520	254.08
[omim][BF <sub>4</sub> ] <sup>4</sup>	323.894	0.588	282.13
[bmim][BF <sub>4</sub> ] <sup>5</sup>	250.201	0.397	226.02
[bmim][PF <sub>6</sub> ] <sup>6</sup>	282.070	0.452	284.18
[emim][Tf <sub>2</sub> N] <sup>7</sup>	363.188	0.478	391.31
[emim][EtSO <sub>4</sub> ] <sup>8</sup>	245.526	0.462	236.29
[emim][SCN] <sup>9</sup>	116.474	0.547	169.25

\* The experimental  $C_p$  data used are from, 1 (Ren et al., 2011), 2 (Yu et al., 2009), 3 (García-Miaja et al., 2008), 4, 5 and 8 (Paulechka et al., 2015), 6 (Kabo et al., 2004), 7 (Paulechka et al., 2007) and 9 (Navarro et al., 2013).



**Figure 5: Experimental  $C_p$  (molar based) values with respect to temperature**

Besides, the molecular weight in this optimization is set in a range of 200 - 400. In all, up and low limits of optimum variables and some properties (mass-based  $C_p$  and molecular weight) are summarised in Table 3. With this, constraints of search domain can be built.

**Table 3: Limits of optimum variables and properties in the optimization**

Variable	$\alpha$	$\tau_{12}^{(0)}$	$\tau_{12}^{(1)}$	$\tau_{21}^{(0)}$	$\tau_{21}^{(1)}$	$c_0$	$c_1$	$C_p$ [ $\text{J g}^{-1}\text{K}^{-1}$ ] at 298.15 K	$M_w$ [ $\text{g mol}^{-1}$ ]
Low limit	-1	-200	-5000	-10	-10000	-1000	0	1.3	200
Up limit	2	100	15000	100	2500	100	1000	2	400

### 3.2 Optimization results

The property optimization work is conducted under a specified case which is a common working condition in applications, the generating temperature  $T_{gen}$ , condensing temperature  $T_{con}$ , absorbing temperature  $T_{abs}$  and evaporating

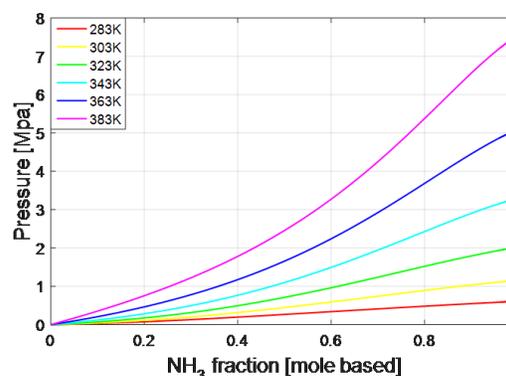
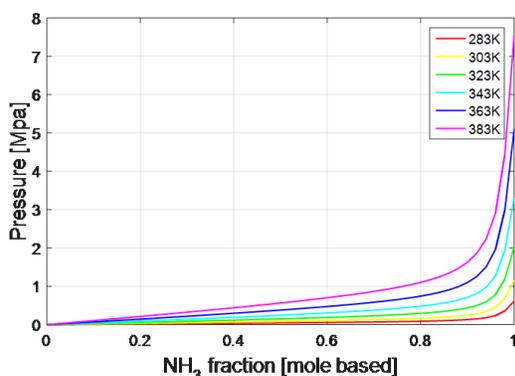
temperature  $T_{eva}$  are set to be 100 °C, 40 °C, 30 °C and 10 °C, respectively.

With a GA method, the optimized performance and corresponding optimum variables are obtained and listed in Table 4. The maximum COP under above constraints could reach 1.81 and the circulation ratio is 1.83.

**Table 4: Optimized performance & optimum variables**

performance		NRTL					$C_p$		$M_w$
COP	$f$	$\alpha$	$\tau_{12}^{(0)}$	$\tau_{12}^{(1)}$	$\tau_{21}^{(0)}$	$\tau_{21}^{(1)}$	$c_0$	$c_1$	
1.81	1.83	1.91	1.63	2.11	-2.05	-0.71	-2.62	0.89	201.50

The P-T-x diagram of the optimum IL with  $\text{NH}_3$  described by the parameters in NRTL model is shown in Fig. 6. As a comparison, the P-T-x diagram of  $\text{NH}_3$  / [emim][SCN] is also plotted in Fig. 7. The vapor pressure of the optimum pair is quite lower than that of the  $\text{NH}_3$  / [emim][SCN] pair.  $\text{NH}_3$  solubility data of the listed working pairs and optimum one are listed in Table 5 at a randomly chosen condition of 383 K and 1 MPa. Compared with the others, the optimum pair shows the highest value. This means the optimized IL holds a better absorption capability.



**Figure 6: Optimized P-T-x diagram of  $\text{NH}_3$  / IL pair**      **Figure 7: P-T-x diagram of  $\text{NH}_3$  / [emim][SCN] pair**

**Table 5: Solubility of  $\text{NH}_3$  in ILs at 383K and 1MPa**

ILs	Solubility [ $\text{mol mol}^{-1}$ ] of $\text{NH}_3$
[mmim][DMP]	0.2112
[emim][BF <sub>4</sub> ]	0.2007
[hmim][BF <sub>4</sub> ]	0.4637
[omim][BF <sub>4</sub> ]	0.4397
[bmim][BF <sub>4</sub> ]	0.1448
[bmim][PF <sub>6</sub> ]	0.3451
[emim][Tf <sub>2</sub> N]	0.1768
[emim][EtSO <sub>4</sub> ]	0.2486
[emim][SCN]	0.2541
Optimum IL	0.7652

The black line in Fig. 5 depicts the  $C_p$  data of the optimum IL. Compared with the others, this optimum one occupies relatively lower  $C_p$ . Since the molecular weight  $M_w$  has a linear ascending relationship with molar based  $C_p$ , the optimum  $M_w$  is also very close to the low limit, which is 201.50.

The optimum properties including vapor pressure and  $C_p$  allow us to screen the ideal IL for absorption heat pump cycle. The challenge for future work is identifying ILs which show properties close to the  $C_p$  and vapor pressure of the optimized ideal mixture. It is clear that a low molecular weight, low  $C_p$  and high absorption capability are essential requirements.

## 4. CONCLUSIONS

A property-optimization work has been introduced in this paper. The following has been concluded:

- A 8-parameter thermodynamic model for generic NH<sub>3</sub> / ILs working fluids applied in single-effect absorption heat pumps has been developed.
- The mole-based  $C_p$  values at a certain temperature were found almost in linear trend with respect to the molecular weights for various ILs. While for a certain IL, the  $C_p$  also showed a linear dependence with temperature.
- With the constrains, a GA method was implemented with the COP as objective function, which indicated that the optimum COP is 1.81. From the work it could be concluded that the ideal IL candidates should show high absorption capabilities, low heat capacities and low molecular weights.

## NOMENCLATURE

$C_p$	Heat capacity	(J mol <sup>-1</sup> K <sup>-1</sup> )	$M_w$	Molecular weight	(g mol <sup>-1</sup> )
$c$	Coefficient in heat capacity	(-)	$P$	Pressure	(Pa)
$f$	Circulation ratio	(-)	$Q$	Heat flow	(W)
$G$	Parameters in NRTL model	(-)	$T$	Temperature	(K)
$h, \Delta h$	Enthalpy	(J kg <sup>-1</sup> )	$w$	Mass concentration	(kg kg <sup>-1</sup> )
$\dot{m}$	Mass flow rate	(kg s <sup>-1</sup> )	$x$	Molar concentration	(mol mol <sup>-1</sup> )

### Greek letter

$\alpha$	Parameter in NRTL model	(-)	$\tau$	Parameter in NRTL model	(-)
$\gamma$	Activity coefficient	(-)			

### Subscript and superscript

0	Reference state	NH <sub>3</sub>	Species of NH <sub>3</sub>
1,2 ...	State point	<i>IL</i>	Species of IL
<i>abs</i>	Absorber	<i>i</i>	Species of <i>i</i> -th component
<i>con</i>	Condenser	<i>r</i>	refrigerant stream
<i>eva</i>	Evaporator	<i>s</i>	strong solution stream
<i>gen</i>	Generator	<i>sat</i>	Saturated state
<i>mix</i>	Mixing heat		

### Abbreviation

ABS	Absorber	HVAC	Heating ventilating and air conditioning
CON	Condenser	IL / ILs	Ionic liquid(s)
COP	Coefficient of performance	NRTL	Non-random two-liquid activity coefficient model
EVA	Evaporator	SHX	Solution heat exchanger
GA	Genetic algorithm	VLE	Vapor-liquid equilibrium / vapor-liquid equilibria
GEN	Generator		
[mmim][DMP]	1,3-dimethylimidazolium dimethyl phosphate		
[emim][BF <sub>4</sub> ]	1-ethyl-3-methylimidazolium tetrafluoroborate		
[hmim][BF <sub>4</sub> ]	1-hexyl-3-methylimidazolium tetrafluoroborate		
[omim][BF <sub>4</sub> ]	1-methyl-3-octylimidazolium tetrafluoroborate		
[bmim][BF <sub>4</sub> ]	1-butyl-3-methylimidazolium tetrafluoroborate		
[bmim][PF <sub>6</sub> ]	1-butyl-3-methylimidazolium hexafluorophosphate		
[emim][Tf <sub>2</sub> N]	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide		
[emim][EtSO <sub>4</sub> ]	1-ethyl-3-methylimidazolium ethylsulfate		
[emim][SCN]	1-ethyl-3-methylimidazolium thiocyanate		

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## ACKNOWLEDGMENT

The authors would like to acknowledge the financial support of the China Scholarship Council.