Vapor Pressure Measurement for the Water + 1,3-Dimethylimidazolium Chloride System and 2,2,2-Trifluoroethanol + 1-Ethyl-3-methylimidazolium Tetrafluoroborate System

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The combination of ionic liquids (ILs) and refrigerants to be used for absorption cooling has been proposed in recent years. In this paper, the boiling point method was adopted to measure the vapor pressure for water + 1,3-dimethylimidazolium chloride ([DMIm]Cl) and 2,2,2-trifluoroethanol (TFE) + 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm]BF_4) systems. The measured ranges of the vapor pressure and the mass fraction of ILs were from (1 to 100) kPa and from 0.4 to 0.85 for the H_2O + [DMIm]Cl system and from (3 to 100) kPa and from 0.35 to 0.9 for the TFE + [EMIm]BF_4 system, respectively. The Antoine type equation and the NRTL model were selected to correlate the experimental data. For the H_2O + [DMIm]Cl system and the TFE + [EMIm]BF_4 system, the average relative deviations in pressure of the Antoine type equation are 0.84 % and 0.61 % respectively, and the average relative deviations in pressure of the NRTL model are 2.42 % and 1.65 %, respectively. Particularly, the parameters α in the NRTL model for the two systems in this work are minus. The activity coefficients of H_2O and TFE in the liquid phases of H_2O + [DMIm]Cl and the TFE + [EMIm]BF_4 systems are much lower than 1. It shows that the H_2O and TFE are strongly affinitive to the relative ILs selected in this work, and the two systems might be used as alternative working fluids for absorption cooling cycles.

Introduction

As an energy saving and environmentally friendly technology, absorption cooling is attracting more and more attention.[1,2]

Up to now, only two kinds of working fluids, i.e., the H_2O + lithium bromide (LiBr) system and the NH_3 + H_2O system, are widely used in absorption cooling cycles. However, these kinds of working fluids show a number of drawbacks including the corrosiveness of LiBr and the toxicity and flammability of NH_3. So some alternative working fluids of the absorption cooling cycle were proposed, for example, refrigerants with organic absorbents.[3,4] The effort for improving the absorbent has led researchers to consider a recently discovered and vastly expanded class of interesting liquids, known as ionic liquids (ILs).[5]

In the past decade, many scientists had introduced ILs as absorbents to overcome the problems of the existing working fluids and to improve the overall efficiency and operation performance of absorption cooling cycles. Shiflett and Yokozeki[6−8] had thought about H_2O, 2,2,2-trifluoroethanol (TFE), and 1,1,1,2-tetrafluoroethane as refrigerants with ILs as the absorbents for absorption cooling cycles. Kim et al.[9] investigated the TFE + 1-butyl-3- methylimidazolium bromide ([BMIm]Br) system and the TFE + 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF_4) system as potential working fluids for the absorption cycles. The TFE + [BMIm]Br system was found to be more favorable than the TFE + [BMIm]BF_4 system based on the behavior of the vapor pressure.

Usually, it is requisite for an absorption working fluid that the solution should have a much lower vapor pressure than the refrigerant at the same temperature. If the concentration of the absorbent in the vapor phase can be neglected, from the γ/φ formulation of vapor/liquid equilibrium,[10] one can get

$$p = \frac{\gamma_1 x_1 p_1^{\,s}}{\Phi_1} = \frac{\gamma_1 w_1 p_1^{\,s}}{\Phi_1\left(w_1 + w_2\dfrac{M_1}{M_2}\right)} \tag{1}$$

where p is the vapor pressure for the solution; p_1^s is the vapor pressure for the pure refrigerant; γ_1 and x_1 are the activity coefficient and the mole fraction of the refrigerant in the solution, respectively; Φ_1 is the correction factor for the refrigerant (see eq 3); and w_1 and w_2 are the mass fractions of the refrigerant and the absorbent in the solution, as well as M_1 and M_2 are the molecular weights of the refrigerant and the absorbent, respectively. It can be seen from eq 1 that p will be smaller with a smaller γ_1 and a bigger ratio of M_1/M_2, which benefit the absorption cycle performances. The γ_1 is related to the affinity between the refrigerant and the absorbent. Generally speaking, the stronger the affinity is, the smaller the γ_1 will be.

Water can be regarded as a green refrigerant, which is nontoxic and with high enthalpy of evaporation and excellent thermal characteristics. Hence, water was, is, and will be a good refrigerant in the domain of refrigeration. If the water + ILs are selected as the working fluids, the ILs selected should be very hygroscopic to get a small γ_1; the molecular weight of the ILs should be as small as possible to get a big M_1/M_2 value; and the ILs should be stable with water. The imidazole-based ILs have been researched for its stability with air and water. The experimental results of binary systems indicated that the ILs studied can decrease the vapor pressure of the solvent due to the affinity between the IL and solvent, while the decrease depended on the type and concentration of IL involved.[11,12] Huddleston et al.[13] indicated that for a series of 1-alkyl-3-methylimidazolium cations decreasing the length of the alkyl chain increases the hydrophilicity. For halide salts, they are hydrophilic and miscible with water. 1,3-Dimethylimidazolium chloride ([DMIm]Cl) should be strongly hygroscopic and with

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smaller molecular weight in imidazolium-based ILs, so the water + [DMIm]Cl system was chosen as a potential working fluid in this work.

Even though [DMIm]Cl has smaller molecular weight (132.593) in imidazole-based ILs, it is too big compared with the molecular weight of water (18.015), so the value of the M_1/M_2 ratio is small. To get a bigger M_1/M_2 ratio, the refrigerant should have a large molecular weight. As an environmentally friendly refrigerant with good thermal characteristics, TFE has attracted much attention in the last decades. TFE has a larger molecular weight (100.04) than water and has good affinity with many imidazole-based ILs. So, the solution combined with TFE and imidazole-based ILs can be expected to have a small value of p/p_1^s. Unfortunately, [DMIm]Cl is solid in room temperature and does not have a high solubility in TFE, so 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm]BF_4), which is completely miscible with TFE, was selected to be the absorption working fluid with TFE.

To decide whether a solution is suitable as an alternative working fluid, at first, the basic thermodynamic data must be determined and carefully checked, especially the vapor pressure. In this work, the vapor pressure for the H_2O + [DMIm]Cl and the TFE + [EMIm]BF_4 systems was measured, and the data modeling was studied.

Experimental Section

Materials. The *N*-methylimidazole (≥99 %) was obtained from the ShangHai TitanChem Co. The chloromethane (≥99.98 %) was purchased from Beijing Gaisi Chemical Gases Center. The acetonitrile (≥99 %) was received from Beijing Chemical Co. The 2,2,2-trifluoroethanol (TFE, ≥99.8 %) was supplied by J&K. The 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm]BF_4, ≥99 %) was bought from Henan Lihua Pharmaceutical Co., Ltd. The chloromethane and the acetonitrile were used without any further purification, but the *N*-methylimidazole and the [EMIm]BF_4 were dried at vacuum atmosphere before use.

Synthesis of [DMIm]Cl. The dried *N*-methylimidazole (100 mL) was reacted with excess chloromethane at 0.7 MPa and 75 °C in a reaction kettle (500 mL, 9.8 MPa) for 24 h. The crude product was recrystallized from acetonitrile three times and dried at 180 °C and 1 kPa (absolute pressure). The product was a colorless crystal at 25 °C. The chemical shift for the ^{1}HNMR spectrum (D_2O, δ ppm, 600 MHz) appears as: δ = 8.640 [s, 1H, H2(Im)], 7.410 [s, 2H, H4(Im), H5(Im)], 3.880 [s, 6H, $2NCH_3$]. The chemical shift corresponds to the structure of the [DMIm]Cl. The purity of the product was determined to be more than 0.994 in mass fraction by differential scanning calorimetry (DSC). The detail of the purity determination by the DSC method can be seen in ref 14.

Measurement of Vapor Pressure. The vapor pressure was measured by the boiling point method.[9,12,15−17] This method is valid for the system which contains a volatile species and an involatile species, for example, the ionic liquid aqueous solution in which the vapor pressure of the ionic liquid is negligible as compared to the vapor pressure of water. The boiling point method is usually adopted in a vacuum system. This method has an advantage of fast measurement, and the existence of the inert gases has no effect on the result.

The apparatus for vapor pressure measurement was provided by Tokyo Rika Kikai Co. Ltd. The schematic diagram of the apparatus is shown in Figure 1. This apparatus primarily consisted of an equilibrium vessel (500 cm^3), an oil bath, a condenser cooled by refrigerant, a temperature sensor, and a temperature transmitter calibrated with the uncertainty of ± 0.05 °C, a U-tube mercury manometer with the minimum calibration of 1 mm, a magnetic stirrer, and a set of vacuum systems. The atmospheric pressure was measured with a calibrated barometer with minimum calibration of 0.1 kPa, which is comparable with the accuracy of the U-tube mercury manometer. The acceleration of gravity in Beijing is 9.8012 $m \cdot s^{-2}$ from ref 18, and the density of mercury at a given temperature can be found from ref 19. So, the pressure of the system can be determined by the reading of the U-tube mercury manometer and the reading of the atmospheric barometer.

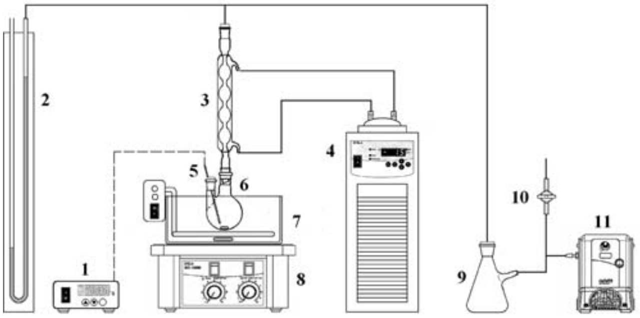

Figure 1. Schematic diagram of the experimental apparatus for the measurement of vapor pressure: 1, temperature transmitter; 2, U-tube mercury manometer; 3, condenser; 4, refrigerator; 5, temperature sensor; 6, equilibrium vessel; 7, oil bath; 8, magnetic stirrer; 9, pressure buffer; 10, vacuum control valve; 11, vacuum pump.

A sample solution with a desired concentration was prepared with an electronic balance with an uncertainty of ± 0.01 g. The sample solution with an approximate volume of 250 cm^3 was placed in the equilibrium vessel and evacuated to a proper vacuum degree of pressure which was controlled by the operation of the vacuum control valve and the vacuum pump. A pressure buffer was used to suppress pressure fluctuations. The sample solution was then heated by the oil bath and stirred well by the magnetic stirrer to prevent superheating. After thermal equilibrium is reached, the solution is boiling. The temperature of the sample solution and the pressure of the apparatus were measured. Adjusting the vacuum degree can control the equilibrium temperature to a given value. The condenser was worked with sufficiently chilled ethanol (the chilled ethanol temperature which is controlled by the refrigerator is about 1 °C for the H_2O + [DMIm]Cl system and is below −10 °C for the TFE + [EMIm]BF_4 system) to minimize the amount of condensed vapor liquid (<0.5 g) because this refrigerant-rich vapor and liquid can vary the initial concentration of the sample solution. The mass fraction change of the sample solution, because of the refrigerant-rich vapor, was less than 0.002. Thus, the concentration prepared for each sample solution was scarcely varied by the increase of less than 0.001 in mass fraction of absorbate compared with the composition desired. Because the vapor pressure of ILs can be neglected compared with the pressure of the refrigerants,[9] the vapor pressure of the solutions can be considered the partial pressure of the vapor refrigerants only.

Validity of the Method. To confirm the validity of the method used in this work, the vapor pressure of pure water and the NaCl aqueous solution with 0.25 mass fraction of NaCl were measured. The results are compared with the data from refs 20 and 21, and the deviations are shown in Figure 2. It can be seen that the relative deviation of the result is higher at lower pressure and lower at higher pressure. But generally speaking, the data measured in this work accord with those from the literature very well. The average relative deviations are 0.41 %

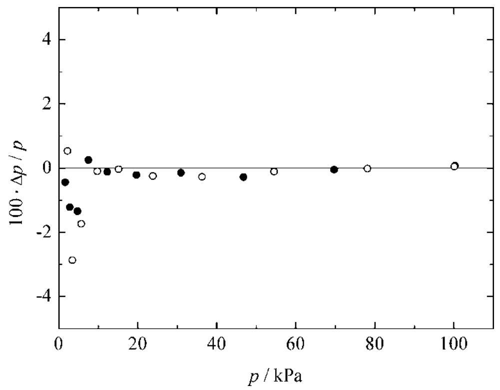

Figure 2. Deviations of the experimental vapor pressure for H_2O and the H_2O + NaCl system (0.25 mass fraction of NaCl) $\Delta p = p(\text{exptl}) - p(\text{literature})$. p(literature) for H_2O is from ref 20. p(literature) for H_2O + NaCl is from ref 21. ●, H_2O; ○, H_2O + NaCl.

and 0.60 % in vapor pressure for water and the NaCl aqueous solution, respectively.

Results and Discussions

The vapor pressures for the H_2O + [DMIm]Cl and the TFE + [EMIm]BF_4 systems were measured, and experimental data were listed in Tables 1 and 2, respectively. For the H_2O + [DMIm]Cl system, the range of the mass fraction of [DMIm]Cl is from 0.4 to 0.85, and the range of measured pressure is from (1 to 100) kPa. For the TFE + [EMIm]BF_4 system, the range of the mass fraction of [EMIm]BF_4 is from 0.35 to 0.9, and the range of measured pressure is from (3 to 100) kPa.

The Antoine equation is usually used to correlate the vapor pressure of the pure component system. Because of the nonvolatility of the ILs, the IL-containing binary system can be considered a pseudo one-component system with a given composition, so the data in Tables 1 and 2 can be correlated with an Antoine type equation.[9,15−17] The correlation was shown as eq 2

$$\log(p/\text{kPa}) = \sum_{i=0}^{4}\left[A_i + \frac{1000B_i}{T/\text{K} - 43.15}\right]w^i \qquad (2)$$

where p is vapor pressure in kPa; T is the temperature in K; and w is the mass fraction of the ILs. The parameters A_i and B_i in eq 2 are listed in Table 3 for the two systems, respectively. The average relative deviations (ARD) for pressure between experimental and calculated values are also listed in Table 3.

Besides the Antoine type equation, activity coefficient models are also used to correlate the data of vapor−liquid equilibrium at low and medium pressure. The correction factor Φ_1 in eq 1 can be calculated by[10]

$$\Phi_1 = \exp\left[\frac{(B_1 - V_1^{L})(p - p_1^{s})}{RT}\right] \qquad (3)$$

where V_1^{L} is the saturated liquid molar volume at the system temperature and B_1 is the second virial coefficient which can be calculated by[10]

$$B_1 = (B^{(0)} + \omega B^{(1)})\frac{RT_c}{p_c} \qquad (4)$$

$$B^{(0)} = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad (5)$$

$$B^{(1)} = 0.139 - \frac{0.172}{T_r^{4.2}} \qquad (6)$$

where T_c and p_c are the critical temperature and the critical pressure, respectively; T_r is the reduced temperature; and ω is the acentric factor defined by[10]

$$\omega \equiv -1.0 - \log\left(\frac{p^{s}_{1,T_r=0.7}}{p_c}\right) \qquad (7)$$

where $p^{s}_{1,T_r=0.7}$ is the vapor pressure of component 1 at the reduced temperature of 0.7.

The saturated liquid molar volumes of TFE can by calculated by the density data in ref 22. The saturated liquid molar volumes of H_2O are from ref 20. The saturated vapor pressures of H_2O and TFE are from ref 20 and ref 23, respectively. In the range of the experimental data, the largest Φ_1 values calculated for H_2O and TFE are 1.00005 and 1.349, respectively; so, the effect of Φ_1 on the H_2O (1) + [DMIm]Cl (2) system can be neglected, but the effect of Φ_1 on the TFE (1) + [EMIm]BF_4 (2) system should be considered.

The general nonrandom two-liquid (NRTL) equation usually was used to correlate the vapor−liquid equilibrium of IL-containing systems.[24,25] The activity coefficients, γ_i, were correlated by the following equations based on the NRTL model

$$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right] \qquad (8)$$

$$\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right] \qquad (9)$$

$$G_{12} = \exp(-\alpha\tau_{12}) \qquad (10)$$

$$G_{21} = \exp(-\alpha\tau_{21}) \qquad (11)$$

$$\tau_{12} = \tau_{12}^{(0)} + \frac{\tau_{12}^{(1)}}{T} \qquad (12)$$

$$\tau_{21} = \tau_{21}^{(0)} + \frac{\tau_{21}^{(1)}}{T} \qquad (13)$$

where γ_1 and γ_2 are the activity coefficient of component 1 and component 2, respectively; x_1 and x_2 are the mole fraction of component 1 and component 2, respectively; and α, $\tau_{12}^{(0)}$, $\tau_{12}^{(1)}$, $\tau_{21}^{(0)}$, and $\tau_{21}^{(1)}$ are the parameters of the NRTL model. These parameters are listed in Table 4 for the two systems, respectively. The ARDs for pressure between experimental and calculated values are also listed in Table 4. It can be seen that the ARDs of the NRTL model are larger than those of the Antoine type correlation. This may be because more parameters are involved in the Antoine type equation.

It should be particularly mentioned that the parameters α in the NRTL model for the two systems are minus. This may not be common for the NRTL model. In ref 26, the value scale of α was discussed in detail for several considerations, and the minus α value is also involved in it. In a sense, the α is just an empirical parameter however.

Figures 3 and 4 show the experimental and the correlated results for the H_2O + [DMIm]Cl and the TFE + [EMIm]BF_4 systems, respectively. It is shown that the correlated results of the two models adopted in this work agree with the experimental results very well. The correlated result of the Antoine type equation is slightly better than that of the NRTL model.

In the foregoing section, a smaller activity coefficient of the refrigerant component is expected in an absorption working fluid. Figure 5 shows the γ_1 of the H_2O (1) + [DMIm]Cl (2) system and the TFE (1) + [EMIm]BF_4 (2) system at the temperature of 80 °C. For comparison, the γ_1 of the H_2O (1) + 1-butyl-3-methylimidazolium bromide ([BMIm]Br) (2) system, the H_2O (1) + 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF_4) (2) system, and the H_2O (1) + 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([HydMIm]BF_4) (2) sys-

Table 1. Experimental Data of the Vapor Pressure for the H_2O (1) + [DMIm]Cl (2) System

$w_2 = 0$		$w_2 = 0.40$		$w_2 = 0.55$		$w_2 = 0.65$		$w_2 = 0.75$		$w_2 = 0.80$		$w_2 = 0.85$	
$x_1 = 1$		$x_1 = 0.9169$		$x_1 = 0.8576$		$x_1 = 0.7985$		$x_1 = 0.7104$		$x_1 = 0.6479$		$x_1 = 0.5650$	
t	p	t	p	t	p	t	p	t	p	t	p	t	p
°C	kPa	°C	kPa	°C	kPa	°C	kPa	°C	kPa	°C	kPa	°C	kPa
14.0	1.64	17.8	1.66	25.0	1.98	25.0	1.43	30.7	1.10	40.0	1.17	48.7	1.13
23.2	2.81	25.8	2.70	30.0	2.64	30.0	1.91	40.0	1.88	50.0	2.09	60.0	1.97
32.2	4.74	30.0	3.39	40.0	4.62	40.0	3.45	50.0	3.21	60.0	3.45	70.0	3.20
40.3	7.51	40.0	6.02	50.0	8.04	50.0	5.86	60.0	5.40	70.0	5.67	80.0	5.29
49.9	12.26	50.0	10.22	60.0	13.06	60.0	9.66	70.0	8.79	80.0	8.93	90.0	8.14
59.8	19.69	60.0	16.29	70.0	20.39	70.0	15.03	80.0	13.46	90.0	13.66	100.0	12.31
69.9	30.94	70.0	25.46	80.0	31.19	80.0	23.15	90.0	20.28	100.0	19.97	110.0	17.78
79.7	46.73	80.0	38.71	90.0	46.23	90.0	34.32	100.0	29.88	110.0	28.98	120.0	25.41
89.9	69.75	90.0	57.13	100.0	67.18	100.0	49.85	110.0	42.99	120.0	41.01	130.0	35.28
99.7	100.32	100.0	82.80	111.7	100.37	110.0	70.89	120.0	60.23	130.0	56.88	140.0	49.26
		105.5	100.41			120.8	101.25	130.0	83.03	140.0	77.77	150.0	67.36
								136.5	101.32	148.7	100.98	160.0	89.95
												164.3	100.25

Table 2. Experimental Data of the Vapor Pressure for the TFE (1) + [EMIm]BF_4 (2) System

$w_2 = 0$		$w_2 = 0.35$		$w_2 = 0.55$		$w_2 = 0.70$		$w_2 = 0.80$		$w_2 = 0.90$	
$x_1 = 1$		$x_1 = 0.7861$		$x_1 = 0.6182$		$x_1 = 0.4589$		$x_1 = 0.3310$		$x_1 = 0.1802$	
t	p	t	p	t	p	t	p	t	p	t	p
°C	kPa	°C	kPa	°C	kPa	°C	kPa	°C	kPa	°C	kPa
10.0	3.96	20.0	3.97	30.0	3.50	40.0	3.06	60.0	4.20	90.0	5.48
20.0	7.25	30.0	6.91	40.0	5.93	50.0	4.88	70.0	6.40	100.0	8.06
30.0	12.82	40.0	11.65	50.0	9.60	60.0	7.78	80.0	9.55	110.0	11.44
40.0	21.83	50.0	18.84	60.0	15.10	70.0	11.91	90.0	14.00	120.0	15.97
50.0	36.10	60.0	29.49	70.0	22.90	80.0	17.61	100.0	20.10	130.0	21.74
60.0	57.08	70.0	45.01	80.0	33.99	90.0	25.52	110.0	28.00	140.0	29.19
70.0	87.31	80.0	66.48	90.0	48.79	100.0	36.26	120.0	38.47	150.0	39.19
73.5	100.80	91.4	100.70	100.0	68.94	110.0	50.42	130.0	51.99	160.0	51.71
				111.8	100.82	120.0	68.84	140.0	69.91	170.0	67.22
						130.0	92.36	150.0	91.41	180.0	84.45
						133.0	100.90	153.7	100.98	187.7	101.02

Table 3. Parameters of the H_2O + [DMIm]Cl and the TFE + [EMIm]BF_4 Systems Correlated by Equation 2

parameters	H_2O (1) + [DMIm]Cl (2)	TFE (1) + [EMIm]BF_4 (2)
A_0	6.63792	7.07169
A_1	1.98185	2.21272
A_2	−2.56594	−12.26637
A_3	0.39046	16.30294
A_4	0	−7.42051
B_0	−1.25369	−1.55649
B_1	−2.42824	−0.36505
B_2	4.49655	1.19880
B_3	−2.91009	−1.05059
B_4	0	−0.07484
$100 \cdot \text{ARD}^a$ for p	0.84	0.61
application range of eq 2	$0.4 \le w_2 \le 0.85$	$0.35 \le w_2 \le 0.9$

[a] ARD = $100\Sigma_{i=1}^{N}|(\text{exptl}_i - \text{calcd}_i)/\text{expt;}_i|/N$; N = number of measurement points, exptl =experimental value, calcd = calculated value.

Table 4. Parameters of the H_2O + [DMIm]Cl and the TFE + [EMIm]BF_4 Systems Correlated by Equation 8

parameters	H_2O (1) + [DMIm]Cl (2)	TFE (1) + [EMIm]BF_4 (2)
α	−0.08636	−0.2611
$\tau_{12}^{(0)}$	0	−8.348
$\tau_{12}^{(1)}$/K	−25000	1000
$\tau_{21}^{(0)}$	0	3.810
$\tau_{21}^{(1)}$/K	−1644	−17841
$100 \cdot \text{ARD}^a$ for p	2.42	1.65

[a] ARD = $100\Sigma_{i=1}^{N}|(\text{exptl}_i - \text{calcd}_i)/\text{expt;}_i|/N$; N = number of measurement points, exptl = experimental value, calcd = calculated value.

tem from ref 27 are also shown in Figure 5. It is shown that the γ_1 of the two systems in this work are all lower than 1, and the γ_1 decrease with the decrease of x_1. It is also shown that the γ_1 for the H_2O (1) + [DMIm]Cl (2) system and the TFE (1) + [EMIm]BF_4 (2) system are lower than those of the H_2O (1) + IL (2) systems from ref 27. This means that the H_2O and TFE are strongly affinitive to the relative ILs selected in this work and shows the potential of the two systems to be used as alternative working fluids.

Conclusions

On the consideration that p will be lower with a smaller γ_1 and a bigger ratio of M_1/M_2 for a binary working fluid, which benefit the absorption cycle performances, the H_2O + [DMIm]Cl and TFE + [EMIm]BF_4 systems were selected as potential working fluids to investigate in this work. The boiling point method was used to measure the vapor pressure for the two systems. The measured ranges of the vapor pressure and the mass fraction of ILs were from (1 to 100) kPa and from 0.4 to 0.85 for the H_2O + [DMIm]Cl

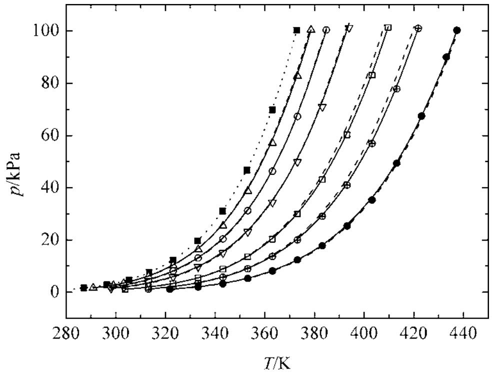

Figure 3. Vapor pressure for the H_2O (1) + [DMIm]Cl (2) system versus temperature: ■, $w_2 = 0$; Δ, $w_2 = 0.4$; ○, $w_2 = 0.55$; ▽, $w_2 = 0.65$; □, $w_2 = 0.75$; ⊕, $w_2 = 0.8$; ●, $w_2 = 0.85$; —, calculated by the Antoine type equation; - - -, calculated by the NRTL model; ····, ref 20.

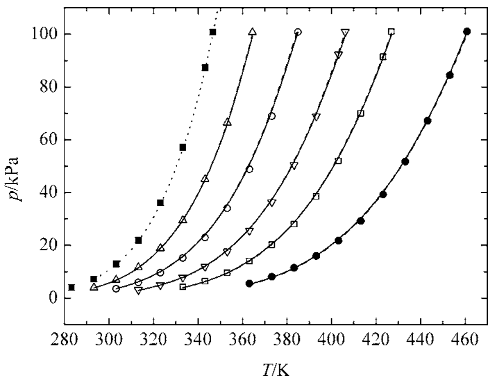

Figure 4. Vapor pressure for the TFE (1) + $[EMIm]BF_4$ (2) system versus temperature: ■, $w_2 = 0$; Δ, $w_2 = 0.35$; ○, $w_2 = 0.55$; ▽, $w_2 = 0.7$; □, $w_2 = 0.8$; ●, $w_2 = 0.9$; —, calculated by the Antoine type equation; - - -, calculated by the NRTL model; ••••, ref 23.

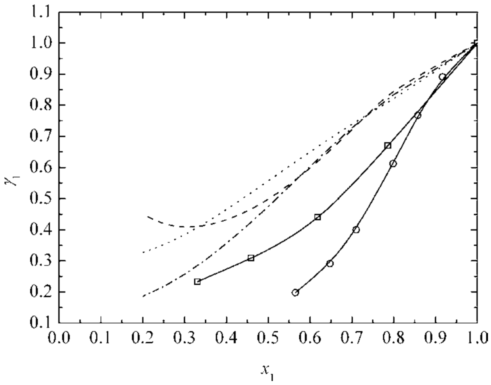

Figure 5. Activity coefficient of component 1 versus mole fraction of component 1 in the liquid phase at a temperature of 80 °C. The symbols were the experimental data: ○, H_2O (1) + [DMIm]Cl (2); □, TFE (1) + $[EMIm]BF_4$ (2); —, results of smoothing processing; - - -, H_2O (1) + [BMIm]Br (2);[27] ••••, H_2O (1) + $[HydEMIm]BF_4$ (2);[27] -•-•-•-, H_2O (1) + $[BMIm]BF_4$ (2).[27]

system and from (3 to 100) kPa and from 0.35 to 0.9 for the TFE + $[EMIm]BF_4$ system, respectively.

The Antoine type equation and the NRTL model were selected to correlate the experimental data. For the H_2O + [DMIm]Cl system and the TFE + $[EMIm]BF_4$ system, the average relative deviations in pressure of the Antoine type equation are 0.84 % and 0.61 %, respectively, and the average relative deviations in pressure of the NRTL model are 2.42 % and 1.65 %, respectively. Particularly, the parameters α in the NRTL model for the two systems in this work are minus. The activity coefficients of H_2O and TFE in the liquid phases of H_2O + [DMIm]Cl and the TFE + $[EMIm]BF_4$ systems are much lower than 1. It shows that the H_2O and TFE are strongly affinitive to the relative ILs selected in this work, and the potential of the two systems might be promising alternative working fluids for improving the performances of the absorption cooling cycle.

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