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Articles

Isobaric Vapor−Liquid Equilibrium for Ethyl Acetate + Ethanol + 1-Ethyl-3-methylimidazolium Tetrafluoroborate[†]

Qunsheng Li, Jiguo Zhang, Zhigang Lei,* Jiujuan Zhu, and Fengying Xing

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Box 35,
Beijing, 100029, China

Isobaric vapor−liquid equilibrium (VLE) data for ethyl acetate (1) + ethanol (2) containing ionic liquid (IL) 1-ethyl-3-methylimidazolium tetrafluoroborate ($[EMIM]^+[BF_4]^-$) (3) at atmospheric pressure (101.32 kPa) were measured with a modified Othmer still. It was observed that the VLE data containing the IL were obviously different from that of the IL-free system. The IL investigated showed a notable salting-out effect, which enhanced the relative volatility of ethyl acetate to ethanol and gave rise to the elimination of the azeotropic point at a specific IL mole fraction. It was found that the salting-out effect followed the order of $x_3 = 0.30 > x_3 = 0.20 > x_3 = 0.07$. The measured ternary data were correlated using the NRTL model.

Introduction

Distillation is the most widely utilized separation method. However, when an azeotrope is involved, conventional distillation is not feasible. The distillation processes such as extractive distillation and salt distillation are used in the separation of the azeotropic mixtures. While the circulating solvent in extractive distillation demands high energy, salt distillation requires high quality of equipment because the salt may corrode the plate and deposit in the tower. Ionic liquids might serve as a superior entrainer which can avoid the above disadvantages brought out by traditional distillation and salt distillation. The use of ionic liquids as entrainer in extractive distillation toward azeotrope or close boiling mixtures was first reported by Arlt et al.[1−3] Extractive distillation with ionic liquids toward alkane and alkene was also investigated by Lei et al.[4−7] It was found that ionic liquids offer many excellent properties, such as (1) high chemical stability; (2) less caustic; (3) good solvents for polar and nonpolar compounds; (4) nonvolatile; and (5) good performance in increasing the relative volatility of the mixtures. Therefore, many researchers have studied the phase behavior of the systems containing ionic liquids to select the suitable ionic liquids as the entrainers of extractive distillation.[8−35]

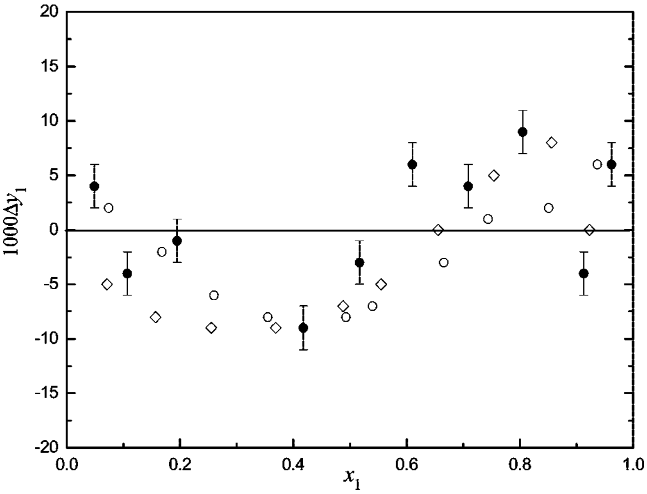

Figure 1. Absolute deviations $\Delta y_1 = y(\text{exptl}) - y(\text{calcd})$ between the calculated and measured mole fractions of ethyl acetate in the vapor phase for the binary system of ethyl acetate (1) + ethanol (2) at 101.32 kPa: ●, this work with error bars representing the extended uncertainty; ◇, ref 49; ○, ref 50.

Ethyl acetate is an important solvent in industry and has promising applications.[36] Ethyl acetate and ethanol form an azeotropic mixture, and thus their separation must depend on special distillation[37−43] or other separation techniques such as solvent extraction and membrane separation.[44−46] However, although extractive distillation with ionic liquids as the entrainers is promising, thermodynamic data are rare. Currently, only a few investigations on vapor−liquid equilibria for ethyl acetate (1) + ethanol (2) containing ionic liquid have been done. In this study, the compositions about vapor−liquid equilibrium of the ternary system of ethyl acetate + ethanol + $[EMIM]^+[BF_4]^-$ were measured at atmospheric pressure (101.32 kPa), which will be the essential data for the purification of ethyl acetate.

Experimental Section

Chemicals. The ionic liquid $[EMIM]^+[BF_4]^-$ was provided by Chemical Engineering Institute of the Normal University of Hebei (China), with a mass fraction purity > 98 % observed by liquid chromatography. Furthermore, before the experiments, the IL was dried for 48 h at (363 to 383) K under a vacuum by the rotary evaporator to separate the IL from volatile byproducts and water. After experiments, the IL was reused after the rotary evaporation to eliminate the volatile components. The water mass fraction in IL determined by Karl Fisher titration was less than 0.5 %. Ethanol and ethyl acetate were purchased from

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* To whom correspondence should be addressed. Tel.: +86 10 64433695. E-mail: leizhg@mail.buct.edu.cn.

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Table 1. Vapor−Liquid Equilibrium Data for the Ethyl Acetate (1) + Ethanol (2) System at P = 101.32 kPa

T/K	x_1	y_1
351.46	0.000	0.000
350.13	0.049	0.106
348.85	0.107	0.192
347.04	0.195	0.299
346.13	0.323	0.389
345.46	0.418	0.468
345.06	0.517	0.530
345.00	0.610	0.592
345.36	0.709	0.654
345.94	0.805	0.730
347.55	0.913	0.836
348.86	0.962	0.924
350.25	1.000	1.000

Tianjin Chemical Reagents Company (China) with a purity of above 99.8 %. The purity of reagents was checked by gas chromatography (GC 4000A, China), and they were used without further purification.

Apparatus and Procedure. The VLE data were measured by a circulation vapor−liquid equilibrium still (a modified Othmer still). The details about this apparatus were described in our previous publications.[47,48] The equilibrium temperature was measured by a precision and calibrated thermometer with an uncertainty of 0.1 K. Each solution was prepared gravimetrically using an electronic balance (Satorius, the uncertainty was about 0.1 mg). The uncertainty of the mole fraction of the components in the liquid and vapor phases was 0.002. The equilibrium pressure was kept constant by an on−off pressure controller whose standard uncertainty was 0.10 kPa.

Results and Discussion

To test the performance of the equilibrium apparatus, the binary vapor−liquid equilibria for the system of ethyl acetate + ethanol were measured at 101.32 kPa. The experimental results for the binary system of ethyl acetate (1) + ethanol (2) are listed in Table 1 and compared to the literature as shown in Figure 1. Our experimental data were in good agreement with those reported by Tu et al.[49] and Orchillés et al.[50] with the maximum absolute deviations between the calculated and measured mole fractions of ethyl acetate in the vapor phase of Δy_1 less than 0.010, thus verifying that the experimental apparatus was reliable.

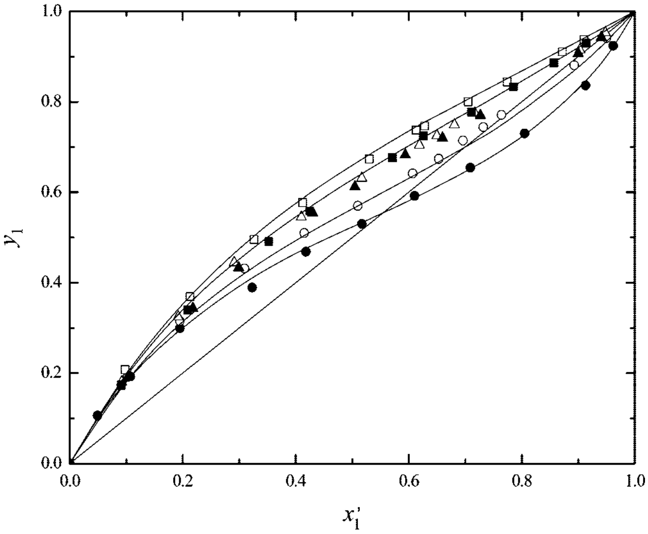

Figure 2. Isobaric VLE diagram for ethyl acetate (1) + ethanol (2) + $[EMIM]^+[BF_4]^-$ (3) system at 101.32 kPa: ●, x_3 = 0 (IL-free); ○, x_3 = 0.07 ($[EMIM]^+[BF_4]^-$); Δ, x_3 = 0.20 ($[EMIM]^+[BF_4]^-$); □, x_3 = 0.30 ($[EMIM]^+[BF_4]^-$); ▲, x_3 = 0.20 ($[EMIM]^+[Triflate]^-$); ■, x_3 = 0.30 ($[EMIM]^+[Triflate]^-$); solid lines, correlated using the NRTL model.

Table 2. Vapor−Liquid Equilibrium Data for the Ternary System Ethyl Acetate (1) + Ethanol (2) + $[EMIM]^+[BF4]^-$ (3) at P = 101.32 kPa

$100x_3$	T/K	x_1'	y_1	γ_1	γ_2	α_{12}
7.198	350.25	0.102	0.191	2.023	1.020	2.079
7.176	348.60	0.195	0.315	1.841	1.029	1.898
7.178	347.35	0.309	0.431	1.657	1.047	1.694
7.232	346.55	0.415	0.510	1.500	1.101	1.467
7.176	346.30	0.510	0.570	1.375	1.165	1.274
7.157	346.36	0.607	0.641	1.296	1.210	1.156
7.235	346.44	0.653	0.674	1.264	1.241	1.099
7.174	346.50	0.696	0.714	1.253	1.239	1.090
7.144	346.94	0.732	0.744	1.223	1.235	1.064
7.099	347.80	0.764	0.771	1.180	1.211	1.040
7.190	349.24	0.893	0.881	1.101	1.311	0.887
7.180	350.15	0.950	0.941	1.073	1.341	0.839
20.110	353.45	0.092	0.180	1.215	1.046	2.166
20.135	351.05	0.192	0.324	2.064	1.066	2.017
20.244	349.73	0.291	0.444	1.950	1.055	1.946
20.262	348.35	0.410	0.545	1.778	1.097	1.724
20.260	347.65	0.517	0.631	1.671	1.118	1.598
20.125	347.27	0.619	0.704	1.574	1.152	1.464
19.938	347.55	0.650	0.725	1.526	1.149	1.420
20.577	348.25	0.681	0.749	1.482	1.128	1.398
20.126	349.50	0.717	0.775	1.390	1.077	1.360
20.012	353.00	0.903	0.915	1.162	1.032	1.156
20.094	354.46	0.948	0.953	1.102	1.007	1.112
29.862	357.54	0.098	0.207	2.396	0.991	2.403
29.748	354.84	0.213	0.369	2.134	1.001	2.161
29.497	353.10	0.326	0.495	1.970	0.997	2.027
28.982	350.75	0.412	0.577	1.945	1.043	1.947
28.516	349.95	0.530	0.673	1.798	1.034	1.825
28.198	349.66	0.613	0.737	1.711	1.018	1.769
28.193	350.15	0.628	0.747	1.666	0.999	1.749
28.065	351.75	0.705	0.800	1.506	0.933	1.674
28.003	354.54	0.774	0.844	1.323	0.850	1.580
27.600	355.55	0.872	0.911	1.221	0.819	1.503
27.510	356.15	0.910	0.937	1.180	0.805	1.471

Table 3. Estimated Values of Binary Interaction Parameters Δg_{ij} and Δg_{ji} in the NRTL Model

i component	j component	α_{ij}	$\Delta g_{ij}/J \cdot mol^{-1}$	$\Delta g_{ji}/J \cdot mol^{-1}$
ethyl acetate (1)	ethanol (2)	0.300	1638.70	971.98
ethyl acetate (1)	$[EMIM]^+[BF_4]^-$ (3)	0.108	10873.30	−1765.11
ethanol (2)	$[EMIM]^+[BF_4]^-$ (3)	0.350	−1319.80	2966.99

Measurements were made for the ternary system of ethyl acetate (1) + ethanol (2) + $[EMIM]^+[BF4]^-$ (3) by keeping the IL mole fraction constant in each set of the experiments. Results of isobaric VLE data for the ethyl acetate + ethanol system containing IL $[EMIM]^+[BF4]^-$ at different IL mole fraction contents (from x_3 = (7 to 30) %) are listed in Table 2. The x, y diagrams are also plotted in Figure 2 in which x_1' is the mole fraction of ethyl acetate in the liquid phase on an IL-free basis.

The effect of IL on the solution nonideality could be expressed by the activity coefficient of component i, γ_i, which could be calculated by the following equation

$$\gamma_i = \frac{y_i \varphi_i P}{x_i \varphi_i^s P_i^s} \tag{1}$$

where y_i represents mole fraction of component i in the vapor phase; x_i is the mole fraction of component i in the liquid phase containing IL; P is the total pressure of the equilibrium system, 101.32 kPa; P_i^s is the vapor pressure of pure component i at system temperature, which could be calculated by the Antoine equation using the Antoine constants from the literature;[51] φ_i

is the fugacity coefficient of component i in the vapor mixture; and φ_i^{s} is the fugacity coefficient of pure component i in its saturated state. To simplify, the IL is treated as a nondissociating component, and the assumption of an ideal behavior is adopted for the vapor. The fugacity coefficients φ_i and φ_i^{s} are equal to unity at a low pressure. Therefore, eq 1 could be rewritten as

$$\gamma_i = \frac{y_i P}{x_i P_i^{\mathrm{s}}} \qquad (2)$$

It should be noted that IL does not appear in the vapor phase due to its nonvolatility. However, its mole fraction in the liquid phase is considered when calculating activity coefficients of ethyl acetate or ethanol. In addition to activity coefficients, the relative volatility of ethyl acetate to ethanol is also calculated as follows

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} \qquad (3)$$

where x_1 and x_2 are mole fractions of ethyl acetate and ethanol in the liquid phase containing IL, respectively. The calculated activity coefficients and relative volatilities are also given in Table 2.

As suggested in previous works,[5,6] the NRTL, Wilson, and UNIQUAC models are commonly used to correlate the vapor−liquid equilibrium data of the systems containing ILs because their binary interaction parameters can be input into some famous simulation programs such as ASPEN PLUS, PROII, etc., and the thermodynamic behavior of multicomponent systems can be deduced from binary systems. However, in most cases, the NRTL model gives better agreement with the experimental results. So in this work, the binary interaction parameters of the NRTL model were first obtained from the vapor−liquid equilibrium data of the ethyl acetate (1) + ethanol (2) system, and then other binary interaction parameters were obtained from ternary vapor−liquid equilibrium data. The Marquardt method as in Press et al[52] was used for data correlation, and the correlated results are given in Table 3, where the average relative deviation (ARD) is defined as

$$\mathrm{ARD}(\%) = \frac{1}{n}\sum_{n}\left|\frac{\gamma_i^{\mathrm{exptl}} - \gamma_i^{\mathrm{calcd}}}{\gamma_i^{\mathrm{exptl}}}\right| \cdot 100 \qquad (4)$$

In the NRTL model, the nonrandomness parameters α are set to be the same as those in ref 50. In this case, the ARD is 1.60 % for the ethyl acetate (1) + ethanol (2) system and 4.66 % for

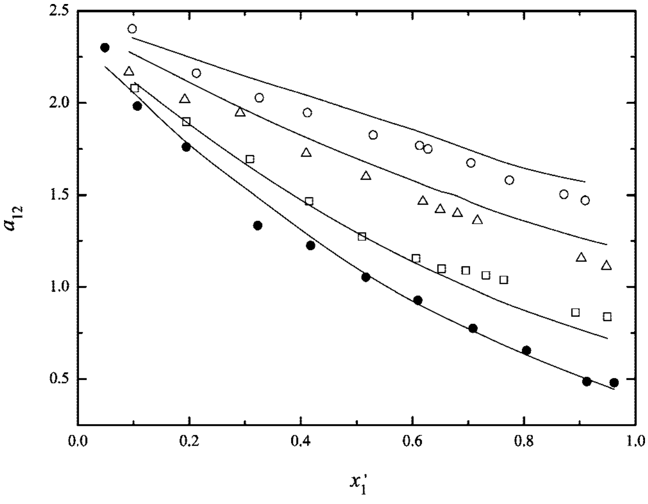

Figure 3. Relative volatility of ethyl acetate (1) to ethanol (2) at 101.32 kPa: ●, x_3 = 0 (IL-free); □, x_3 = 0.07 ([EMIM]$^+$[BF$_4$]$^-$); Δ, x_3 = 0.20 ([EMIM]$^+$[BF$_4$]$^-$); ○, x_3 = 0.30 ([EMIM]$^+$[BF$_4$]$^-$); solid lines, correlated using the NRTL model.

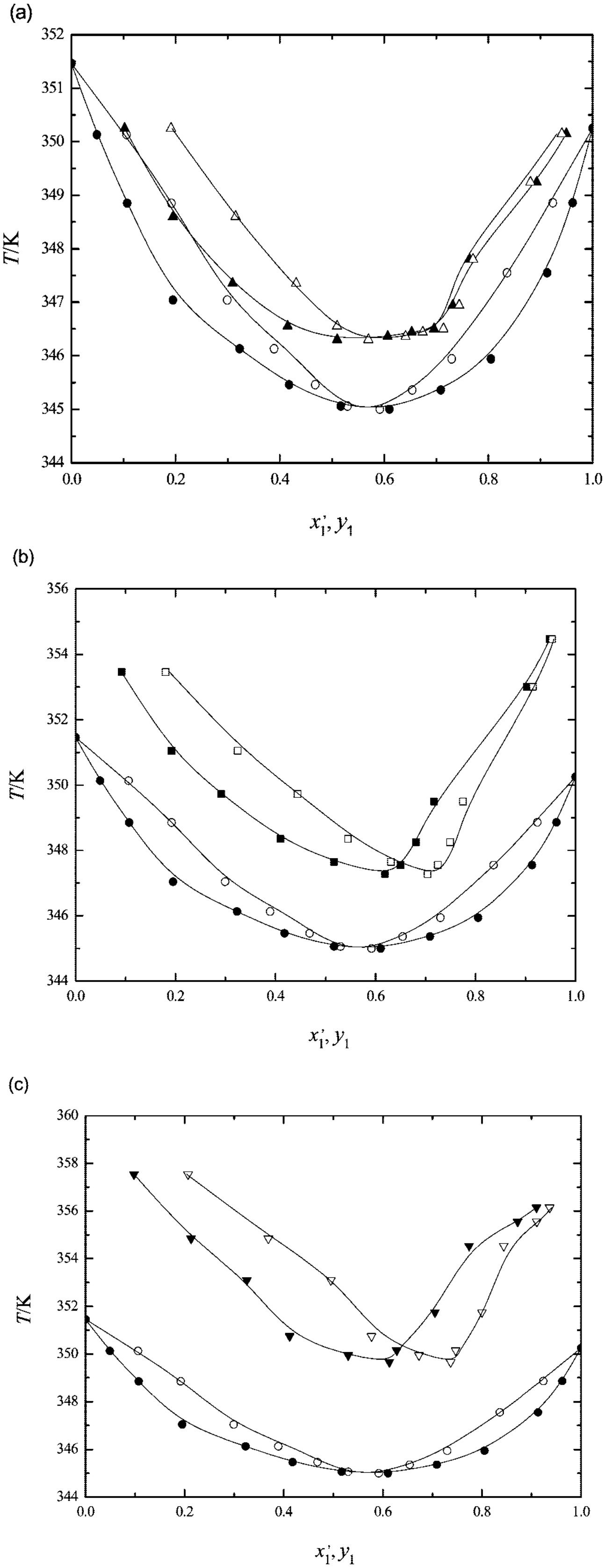

Figure 4. T, x, y diagram for the ternary system of ethyl acetate (1) + ethanol (2) containing [EMIM]$^+$[BF$_4$]$^-$ (3) at different contents of IL: ●, $x_1 = x_1'$ (x_3 = 0); ○, y_1 (x_3 = 0); ▲, x_1' (x_3 = 0.07); Δ, y_1 (x_3 = 0.07); ■, x_1' (x_3 = 0.20); □, y_1 (x_3 = 0.20); ▼, x_1' (x_3 = 0.30); ▽, y_1 (x_3 = 0.30); solid lines, correlated using the NRTL model.

the ethyl acetate (1) + ethanol (2) + $[\text{EMIM}]^+[\text{BF4}]^-$ (3) system.

The IL investigated increased the relative volatility of ethyl acetate to ethanol and thus showed a salting-out effect for ethyl acetate, as shown in Figures 2 to 4. Moreover, the azeotropic point at $x_1 = 0.550$ for the ethyl acetate + ethanol binary mixture is shifted upward with the addition of IL, and even the azeotropic phenomena could be totally eliminated at a specific IL content. In addition, the comparison of separation ability between $[\text{EMIM}]^+[\text{BF4}]^-$ and $[\text{EMIM}]^+[\text{Triflate}]^-$ (1-ethyl-3-methylimidazolium trifluoromethanesulfonate) was also made. It can be found from Figure 2 that $[\text{EMIM}]^+[\text{BF4}]^-$ exhibits a little higher selectivity at $x_3 = 0.20$ and 0.30 than $[\text{EMIM}]^+$-$[\text{Triflate}]^-$ as proposed by Orchillés et al.[50] Moreover, $[\text{EMIM}]^+[\text{BF4}]^-$ is much easier to be obtained from chemical markets at a lower price.

Figures 2 to 4 also indicate the complex effect of IL on the VLE of the ethyl acetate + ethanol system. An increase of the IL content leads to a higher ethyl acetate content in the vapor phase and, therefore, to a larger relative volatility of ethyl acetate to ethanol. This may be due to the strong selective interaction between the IL and ethanol molecule.

To further investigate the salt effect of IL on ethyl acetate + ethanol, relative volatilities of ethyl acetate to ethanol were plotted in Figure 3 where the system contains (7 to 30) % mole fraction of IL. With an increase in the IL component, the relative volatility of ethyl acetate to ethanol increases. So the salting-out effect follows the order: 30 % > 20 % > 7 %.

The measured VLE containing the azeotropic system ethyl acetate + ethanol and the IL $[\text{EMIM}]^+[\text{BF4}]^-$ are presented in a pseudobinary way in Figure 2, where the liquid-phase composition of the low-boiling component is the amount of this substance in the volatile part of the liquid phase. The IL component is demonstrated for each curve separately. The x, y diagram is shown in Figure 2, and the T, x, y diagram is shown in Figure 4. Figure 4 shows that the equilibrium temperatures increase at higher mole fractions of the IL, which indicates that higher heating temperatures on the reboiler of the extractive distillation column are needed to reach the new equilibrium at higher contents of the IL. On the other hand, for a given purity of the distillate, the reflux ratio of the extractive distillation column can be reduced when the relative volatility of the low-boiling component to high-boiling component becomes higher, which means that the heat demand for the extractive distillation column decreases with the increase of relative volatility, but the heat quality increases.

Conclusions

ILs are becoming new alternative entrainers in special distillation processes. The isobaric VLE data for ethyl acetate + ethanol containing $[\text{EMIM}]^+[\text{BF4}]^-$ were measured at atmospheric pressure (101.32 kPa) and correlated using the NRTL model with an ARD of 1.60 % for the ethyl acetate (1) + ethanol (2) system and of 4.66 % for the ethyl acetate (1) + ethanol (2) + $[\text{EMIM}]^+[\text{BF4}]^-$ (3) system. The mole fraction of ethyl acetate in the vapor phase increases with the increase of the concentration of $[\text{EMIM}]^+[\text{BF}_4]^-$ in the liquid phase. The results indicated that the IL studied showed a salting-out effect, which led to an elimination of the azeotropic phenomenon at a specific IL content. Moreover, the IL exhibits a little higher selectivity than $[\text{EMIM}]^+[\text{Triflate}]^-$. Therefore, the results implied that $[\text{EMIM}]^+[\text{BF4}]^-$ is a promising additive for special distillation processes due to its notable salt effect and desirable properties, such as nonvolatility, nonflammability, and chemical stability. Moreover, because of its nonvolatility, the IL can be regenerated by different methods such as stripping, evaporating, or drying.

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