Extraction Behavior of Indole from Simulated Wash Oil Using Halogen-Free Ionic Liquids

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ABSTRACT: Indole is an important raw material in the chemical industry, and more than 1 wt % indole is contained in wash oil. Therefore, the extraction of indole from wash oil is of much importance. The conventional separation methods generally cost much money, pollute the environment, and corrode the metallic devices due to the use of large amounts of inorganic acid and alkali solutions, and therefore, new methods should be proposed. In this work, a solvent extraction process for separating indole from simulated wash oil by five halogen-free ionic liquids (HFILs) has been designed, and the extraction behavior of indole has been evaluated. All the studied HFILs presented excellent extraction behavior for indole, and the whole separation process took no more than 5 min. For the same HFIL, the minimum residual indole contents remained the same, even if the initial indole contents changed. Among the HFILs, 1-butyl-3-methylimidazolium dimethyl phosphate ([Bmim][DMP]) has attracted more attention than other HFILs. The results showed that [Bmim][DMP] could extract over 96.9 wt % indole from the simulated wash oil, and the minimum residual indole content was as low as 2.1 g/dm^3. For indole, [Bmim][DMP] presented a maximum distribution coefficient of 201, which was much improved compared to other methods. The HFILs could be regenerated by using diethyl ether with ease. The regenerated HFILs could be reused, and the extraction behavior remained the same as the original HFILs. Based on FT-IR results, a mechanism of hydrogen bonds forming between HFILs and indole was proposed. In addition, the superiorities of HFILs over other separation agents in reusability, amounts needed, distribution coefficient for indole, and chemical structure were proved by comparison.
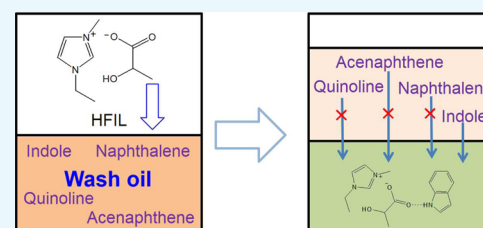
1. INTRODUCTION

Indole is an important raw material in the chemical industry and can be broadly used to synthesize perfume, prepare medicines, and produce plant hormones.[1] Wash oil, which is the distillation fraction of coal pyrolysis oil or petroleum at 230−300 °C, contains more than 1 wt % indole.[2] As reported, the price of wash oil is low, and the output is rich (over 1,000,000 tons/year in China).[3] Therefore, directly separating indole from wash oil is of low cost and has high value, and has become a reliable and sustainable method to obtain indole.[4−6]

The currently used separation techniques to directly separate indole from wash oil in the industry are alkali fusion method and acid polymerization method[4,7,8] because these methods are generally more efficient than the other methods (including supercritical CO_2 method,[9] cyclodextrin method,[10] solvent extraction,[11] and crystallization method[12]). In the alkali fusion method, indole can react with excessive alkali solution (taking KOH solution, e.g., the separation process needs over 120% KOH of the theoretical amount) to form indole potassium salt (as shown in eq 1) at 443.2−513.2 K, and the salt can be

separated from wash oil. Indole can be obtained with separation efficiencies of 25−30 wt % after hydrolysis, distillation, crystallization, and recrystallization treatments of the indole potassium salt. In the acid polymerization method, H_2SO_4 solution is used, and an isomerization reaction occurs. The separation efficiency for indole is about 80 wt %.

As can be seen, KOH solution and H_2SO_4 solution are commonly used in these two processes. These inorganic acid and alkali solutions generally cost much money and pollute the environment. What is more, they can seriously corrode the metallic devices, which threatens our lives and leads to higher costs. In order to overcome the abovementioned shortcomings, a novel physical separation method is badly in need. Actually, real wash oil contains the components that have very close boiling points with indole (such as naphthalene), and these components can form azeotropes with indole. Therefore, the
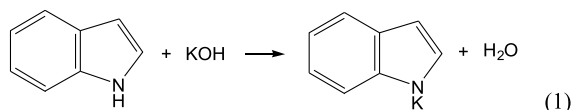
$$\text{indole} + KOH \longrightarrow \text{indole-K} + H_2O \tag{1}$$
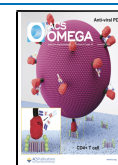
method of distillation has become a challenge of separating indole from wash oil.

Recently, ionic liquids (ILs) have attracted considerable attention and have been widely applied to many fields, especially in separation of organic chemicals (N-containing compounds,[13−15] O-containing compounds,[16−19] S-containing compounds,[20,21] and so on) from mixtures. Considering the advantages of ILs, such as flexible design, wide operating temperature, and low vapor pressure,[22,23] scientists employed ILs and IL analogues (deep eutectic solvent, DES) to physically separate indole from wash oil and achieved desirable results. Jiao et al.[1] used the solubility difference of indole and other components in the imidazolium-based ILs to separate indole from simulated wash oil. Indole separation efficiency could reach over 90 wt %. However, the IL/indole mole ratio reached as high as 52.2, and the separation time was over 30 min. Also, the distribution coefficient (D) of indole was only about 13. To overcome the abovementioned disadvantages, Wu et al.[24] developed a technique to extract indole from simulated wash oil via forming DES with indole. Three quaternary ammonium salts were employed as extractants. The maximum indole separation efficiency was 96.7 wt %, and the maximum D was largely improved to about 92. Unfortunately, the separation agents contained halogen anion Cl⁻, which might also cause serious corrosion to metallic devices.[25−27] As a result, these separation agents may be undesirable in industry. Given the advantages of ILs, the problem of corrosion can be perfectly solved if we select halogen-free ILs (HFILs) that can interact with indole.

In recent years, HFILs are relatively popular among scientists,[28,29] and especially, their performances in acid gas absorption (such as CO_2, SO_2, and H_2S) are largely reported.[30−35] Compared to normal ILs, HFILs are characterized by low toxicity, biodegradability, and more environment-friendliness, which become the basis to be widely used in separation. From the structure of indole, we find that the N atom in the pyrrole ring is a strongly electronegative atom, and the connected H atom is active. It is expected to find HFILs that can interact with this hydrogen. Zhang et al.[36] studied the separation of indole from oil by HFILs (tetramethylguanidine-based ILs) and pointed out that the driving force for separating indole was the H-bond between indole and the ILs through molecular dynamics simulations and quantum chemical calculations. Then, our aim is to select HFILs with appropriate anions, which may form a hydrogen bond with indole. Except for halogen anions, the common anions can be obtained from L-lactic acid, trifluoromethanesulfonic acid, dimethyl phosphate, acetic acid, and ethyl sulfate. As the selected HFILs have relatively strong alkalinity, chances are that they can interact with hydrogen in N−H of indole. Thus, the abovementioned problems may be solved.

In this work, 1-ethyl-3-methylimidazolium L-lactate ([Emim][LLac]), 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]), 1-butyl-3-methylimidazolium dimethyl phosphate ([Bmim][DMP]), 1-ethyl-3-methylimidazolium ethyl sulfate ([Emim][ES]), and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([Emim][TFMS]) were employed to separate indole from simulated wash oil. The effects of stirring time, separation temperature, HFIL/indole mole ratio, HFIL type, and initial indole content on separation behavior for indole were evaluated. It was found that [Bmim][DMP] can separate indole from simulated wash oil with separation efficiencies up to 96.9 wt %, and the minimum residual indole

content was 2.1 g/dm³. The maximum D of indole was 201 by [Bmim][DMP]. Moreover, The HFILs could be regenerated by using diethyl ether, and the regenerated HFILs could be reused. Based on FT-IR results, we proposed the mechanism of hydrogen bonds forming between HFILs and indole.

2. RESULTS AND DISCUSSION

2.1. Selection of HFILs for Indole Separation. Five HFILs ([Emim][LLac], [Emim][TFMS], [Bmim][DMP], [Emim][Ac], and [Emim][ES]) were designed. Their performances for indole separation from simulated wash oil were generally evaluated to screen out suitable HFILs. A HFIL/indole mole ratio of 2.0 and a simulated wash oil with an initial indole content of 40.0 g/dm³ were selected. The average value of three repeated experiments was used as the final results. The experiments show good repeatability. The separation efficiencies of indole are shown in Figure 1.
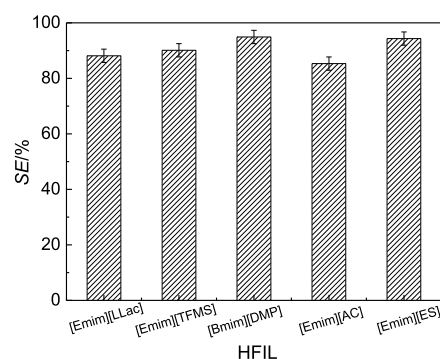

Figure 1. Effect of the HFIL type on indole separation. Conditions: initial indole content, 40.0 g/dm³; temperature, 298.2 K; HFIL/indole mole ratio, 2.0.

As can be seen in Figure 1, all the HFILs can separate indole from simulated wash oil. The separation efficiencies of indole are 88.1, 90.1, 94.9, 85.3, and 94.3 wt % for [Emim][LLac], [Emim][TFMS], [Bmim][DMP], [Emim][AC], and [Emim]-[ES], respectively, under the studied conditions. On the whole, three HFILs ([Emim][LLac], [Emim][TFMS], and [Bmim]-[DMP]) showed relatively high separation efficiencies and were selected as representative separation agents in the following section.

2.2. Effect of Stirring Time on Extraction Behavior. In this subsection, [Emim][LLac], [Emim][TFMS], and [Bmim][DMP] were used to carry out the experiment. An initial indole content of 40.0 g/dm³ was used. Indole content as a function of stirring time is shown in Figure 2.

As can be seen in Figure 2, for the studied HFILs, indole content decreases sharply with the increase of separation time from 0 to 5 min. With the continued extension of separation time, indole content remains basically constant. Results show that the minimum residual contents of indole in the simulated wash oil are 5.2, 4.3, and 2.2 g/dm³, respectively, for [Emim][LLac], [Emim][TFMS], and [Bmim][DMP]. In the following experiments, a stirring time of 30 min was used to ensure adequate time for separation.

2.3. Effect of Temperature on Extraction Behavior. Generally, temperature changes affect physical properties of components. Thus, the separation efficiency of indole is affected. In this subsection, the effect of separation temperature on the separation efficiency of indole was studied. An initial
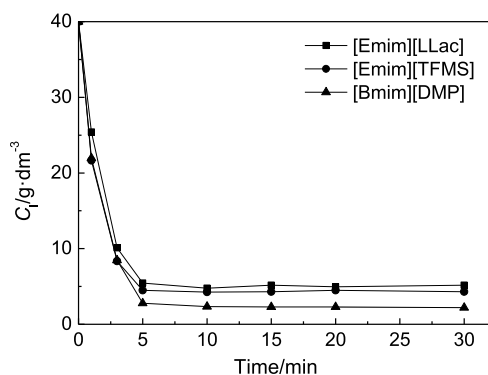
Figure 2. Indole content as a function of stirring time. Conditions: initial indole content, 40.0 g/dm^3; HFIL/indole mole ratio, 2.0; temperature, 298.2 K.

indole content of 40.0 g/dm^3 and a HFIL/indole mole ratio of 2.0 were used. The results are shown in Figure 3.
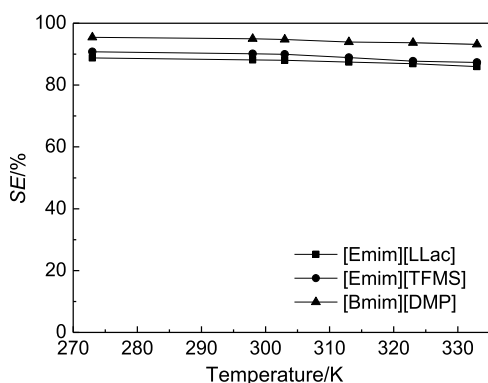

Figure 3. Effect of separation temperature on indole separation efficiency. Conditions: initial indole content, 40.0 g/dm^3; HFIL/indole mole ratio, 2.0.

Figure 3 shows that as temperature increases gradually, indole separation efficiency decreases mildly. With temperature increases from 273.2 to 333.2 K, the separation efficiency of indole decreases from 88.8 to 85.9 wt % for [Emim][LLac] as an extractant, from 90.8 to 87.3 wt % for [Emim][TFMS], and from 95.4 to 93.1 wt % for [Bmim][DMP]. The decrease in the separation efficiency of indole is because the mutual solubility of oil (such as naphthalene and toluene) and indole increases as temperature increases,[37] which is unfavorable for

separation. Also, increase in temperature slightly affects the formation of hydrogen bonds between indole and HFIL negatively.[38] The results of some other separation processes[24,39−41] confirmed this result. On the whole, the decrease of separation efficiency is very slight, which indicates that indole can be separated at room temperature or normal temperature. It is redundant to heat wash oil before separation.

2.4. Effect of the HFIL/Indole Mole Ratio on Extraction Behavior. An appropriate HFIL/indole mole ratio shows much importance during separation, which determines the cost of the separation process and ensures a high separation efficiency of indole. In the subsection, the effect of the HFIL/indole mole ratio on indole separation was evaluated. Wash oil with an initial indole content of 40.0 g/dm^3 was employed. The results are shown in Figure 4.

As can be seen in Figure 4, all the studied HFILs show excellent separation performance for indole. For [Bmim]-[DMP] as an extractant, as the [Bmim][DMP]/indole mole ratio increases from 0 to about 1.5, indole content decreases sharply from 40.0 to 3.4 g/dm^3 and indole separation efficiency sharply increases from 0 to 91.9 wt %. Then, as the [Bmim][DMP]/indole mole ratio further increases from 1.5 to about 2.4, indole separation efficiency increases slowly from 91.9 to 95.3 wt %, which may be mainly caused by the solvation of HFILs. Through calculation, the maximum D was 201 ([Bmim][DMP]/indole mole ratio of about 2.40), which is much higher than the results shown in the literature.[1,24] On the one hand, the interaction between indole and HFILs is stronger than the separation agents in the literature, which can be obtained from the SE value and minimum residual indole content under the same conditions. On the other hand, the amount of entrained oily components in this work is smaller. For [Emim][LLac] and [Emim][TFMS] as extractants, similar results are obtained. The maximum separation efficiencies of indole are 90.4 and 92.2 wt %, respectively. Indole separation from simulated wash oil was mainly because of the formation of hydrogen bonds between HFILs and indole (described in the Section 2.7). When HFILs were added to wash oil drop by drop, more HFILs can form hydrogen bonds with indole. Indole content in simulated wash oil thus decreases gradually. As shown in eq 2, when indole content decreases, SE increases. When the HFIL/indole mole ratio was more than about 1.5, due to the low indole content, more added HFILs could not lead to more interaction (with indole), but could lead to reach a new phase equilibrium between simulated wash oil and HFILs, which revealed the reason for the slow increase of SE.
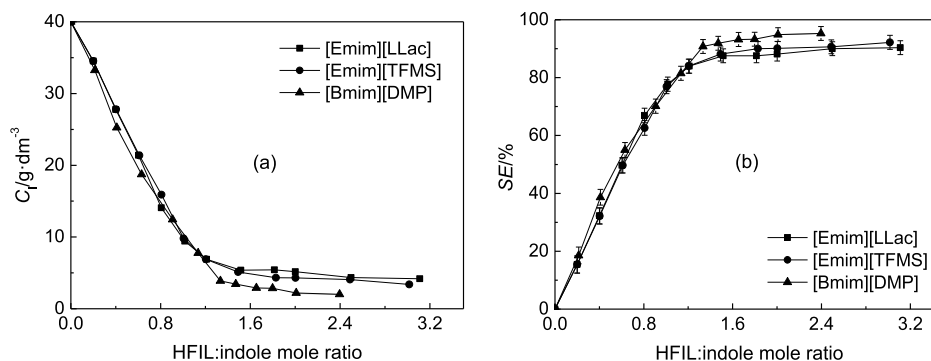

Figure 4. Effect of the HFIL/indole mole ratio on (a) indole content and (b) indole separation efficiency. Conditions: initial indole content, 40.0 g/dm^3; temperature, 298.2 K.

2.5. Effect of Initial Indole Content on Extraction Behavior. The indole quantity in wash oil determines the amount of HFILs needed to separate indole. For different wash oils with various indole contents, in order to separate indole, a proper amount of HFILs is especially needed. Therefore, the effect of initial indole content on indole separation is necessary. In this subsection, [Bmim][DMP] was selected as the extractant. The results are shown in Figure 5.
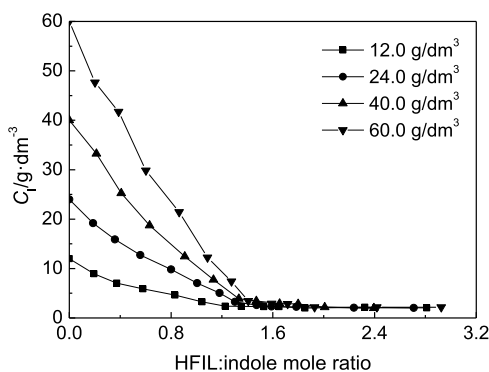

Figure 5. Effect of indole initial content on indole separation. Conditions: initial indole content, 12.0, 24.0, 40.0, and 60.0 g/dm^3; separation agent, [Bmim][DMP]; temperature, 298.2 K.

As can be seen in Figure 5, indole content in simulated wash oils decreases from their initial contents (12.0, 24.0, 40.0, and 60.0 g/dm^3) to minimum residual contents, as the [Bmim]-[DMP]/indole mole ratio increases from 0 to about 1.5. Interestingly, the minimum residual contents are the same, even if the initial indole contents have changed. Indole content decreases with the increase of the [Bmim][DMP]/indole mole ratio and reaches an minimum residual content of 2.1 g/dm^3. The maximum SE can reach as high as 96.9 wt %. Also, as can be seen from Figure 5, wash oil with higher initial indole content needs more amount of HFILs to achieve the minimum residual indole content than wash oil with lower initial indole content. Therefore, the amount of HFILs needed mainly depends on the amount of indole contained in wash oil.

2.6. Reuse of HFILs. The abovementioned results show that the HFILs have good separation performance for indole from simulated wash oil. It is required to reduce the separation cost and protect the environment as much as possible. Therefore, whether the extractants can be reused or not is of great significance. It is predicted that these HFILs can be regenerated without changing their properties. For most extractants, diethyl ether is commonly considered to be an effective antisolvent.[1,24] For the present separation process, indole is easily soluble in diethyl ether. The polarity of the studied HFIL is relatively strong, while that is relatively weak for diethyl ether. According to the principle of "like dissolves like", HFILs are probably insoluble in diethyl ether (the results showed that the solubility of HFIL in diethyl ether was less than 0.05 g·dm^{-3}). Therefore, HFILs can also be regenerated by diethyl ether, which is finally proved to be an effective way. In this subsection, [Emim][TFMS], [Bmim][DMP], and [Emim][ES] were used to study the effect of cycle times on the separation process. The separation efficiency of indole as a function of cycle time is shown in Figure 6.

As shown in Figure 6, for any one of the three HFILs ([Emim][TFMS], [Bmim][DMP], and [Emim][ES]), the
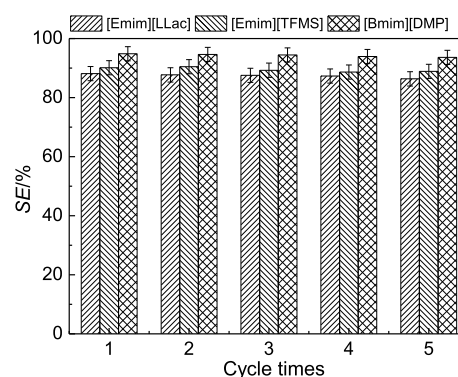

Figure 6. Indole separation efficiency as a function of cycle times. Conditions: initial indole content, 40.0 g/dm^3; HFIL/indole mole ratio, 2.0; temperature, 298.2 K.

separation efficiency of indole remains nearly constant with the increase of cycle times.

As reported in the literatures,[1,2,24] NMR has strong authority and accuracy in characterization properties of separation agents. Therefore, the properties of the regenerated HFIL and original HFIL were characterized by ^{1}H NMR. The ^{1}H NMR spectra of the original and regenerated HFILs are shown in Figure 7. The peak positions and other information were
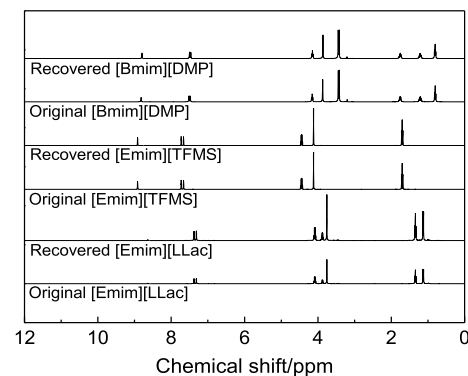

Figure 7. ^{1}H NMR spectra of the original and regenerated [Emim][LLac], [Emim][TFMS], and [Bmim][DMP].

listed as follows. [Bmim][DMP] (400 MHz, D$_2$O): δ = 0.80 ppm (3H, CH$_3$N), δ = 1.22 ppm (2H, CH$_3$CH$_2$), δ = 1.75 ppm (2H, CH$_2$CH$_2$), δ = 3.44 ppm (6H, 2CH$_3$ in DMP), δ = 3.87 ppm (3H, CH$_3$CH$_2$), δ = 4.15 ppm (2H, CH$_2$N), δ = 7.48 ppm (1H, CHNCH$_3$), δ = 7.51 ppm (1H, CHN), δ = 8.82 ppm (1H, NCHN); [Emim][TFMS] (400 MHz, D$_2$O): δ = 1.70 ppm (3H, CH$_3$CH$_2$), δ = 4.12 ppm (3H, CH$_3$N), δ = 4.44 ppm (2H, CH$_2$CH$_2$), δ = 7.66 ppm (1H, CHNCH$_3$), δ = 7.72 ppm (1H, CHN), δ = 8.92 ppm (1H, NCHN); [Emim][LLac] (400 MHz, D$_2$O): δ = 1.12 ppm (3H, CH$_3$N), δ = 1.34 ppm (3H, CH$_3$C), δ = 3.75 ppm (3H, CH$_3$CH$_2$), δ = 3.86 ppm (1H, CH$_3$CH), δ = 4.09 ppm (2H, CH$_3$CH$_2$), δ = 7.31 ppm (1H, CHNCH$_3$), δ = 7.37 ppm (1H, CHN), δ = 8.63 ppm (1H, NCHN). As can be seen, the chemical shifts of the original HFIL are the same as those of the regenerated HFIL, which reveals that the regenerated HFIL do not change compared to the original one in properties. Also, their ability to extract indole remains nearly unchanged. Therefore, these HFILs can be reused.

2.7. Mechanism of Indole Separation by HFILs. The mechanism of the present separation process is helpful for us to solve other separation problems. Scheme 1 shows that the H

Scheme 1. Structural Schemes of Indole and HFILs Used in This Experiment

[Emim][Ac]   [Emim][LLac]   [Bmim][DMP]

[Emim][TFMS]   [Emim][ES]   Indole
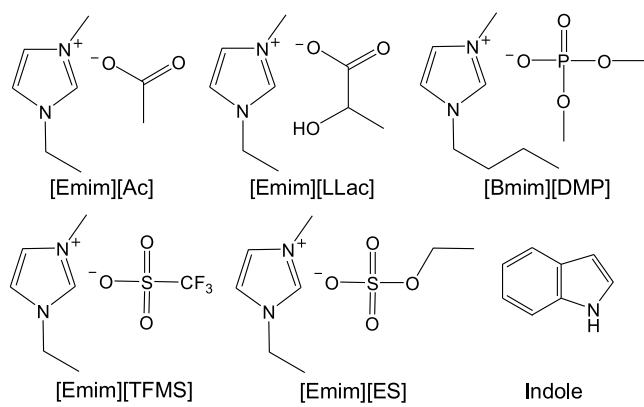
atom in indole N−H is an active H because of the strongly electronegative atom of N. Therefore, oxygen in the −COO⁻ −PO₄⁻ or −SO₃⁻ group of HFILs may share electrons with the active H atom of indole to form hydrogen bonds. Based on the previous literatures,[42] FT-IR is excellent in obtaining hydrogen bond information. FT-IR can detect the information of the chemical bond or functional group. Therefore, the mechanism of the present work was explored by FT-IR. Figure 8 shows the FT-IR spectra of indole, HFILs, and HFIL + indole mixtures.

The v-NH stretching vibration of indole can be generally observed in wavenumbers ranging from 3300 to 3500 cm⁻¹.[1]

Figure 8 shows that the stretching vibration of v-NH occurs at 3401 cm⁻¹. Taking [Emim][TFMS] for example, as shown in Figure 8b, in the FT-IR spectrum of the mixture formed by [Emim][TFMS] and indole, the stretching vibration of v-NH shifts from 3401 to 3329 cm⁻¹, which reveals the existence of hydrogen bonds. This is because stretching vibration of v-NH can be weakened through the formation of hydrogen bonds, thus leading to the decrease of absorption frequency. In the FT-IR spectra of [Emim][LLac] and [Bmim][DMP], similar phenomena can also be observed. As shown in Figure 8a,c, the stretching vibration of v-NH shifts from 3401 to 3256 and 3103 cm⁻¹, respectively. Other components in the simulated wash oil (naphthalene, quinoline, acenaphthene, and toluene) cannot form hydrogen bonds with HFILs, and therefore, they cannot be separated.

2.8. Comparison between This Method with Other Methods. Both inorganic acid and alkali are not used in the present method in comparison with conventional methods,[4,5] and thus, no corrosion will be caused to the container or equipment. No waste water is used, and both the extractant and solvent can be recycled. What is more, the present method is easily operated, which shows superiority to the supercritical CO₂ method.[9]

When compared with the method proposed by Jiao et al.,[1] the best D of indole in this work is 201 for [Bmim][DMP], while that is only about 13 for [Bmim]BF₄. In addition, the amount of [Bmim][DMP] used to separate indole from simulated wash oil is just 2.0 times of indole in the mole ratio, while that of [Bmim]BF₄ is 52.2 times of indole in the mole ratio. For the DES method proposed by Wu et al.,[24] the extractants used in this work are halogen-free ionic liquids, which prevent damaging metal containers or equipment.
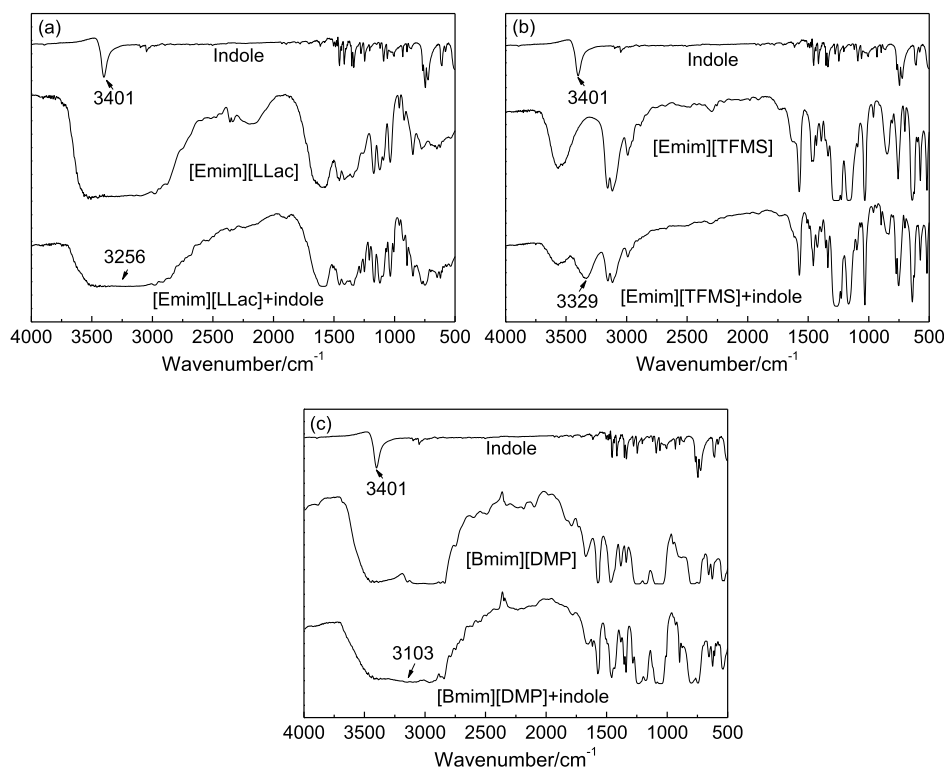

Figure 8. FT-IR spectra of (a) indole, [Emim][LLac], and their mixture; (b) indole, [Emim][TFMS], and their mixture; (c) indole, [Bmim][DMP], and their mixtures.

3. CONCLUSIONS

A solvent extraction process for separating indole from simulated wash oil by five HFILs has been designed, and the extraction behavior has been evaluated. The whole separation process took no more than 5 min. Among the HFILs, [Bmim][DMP] attracted more attention than other HFILs. The results showed that [Bmim][DMP] could extract over 96.9 wt % indole from simulated wash oil, and the minimum residual indole content was as low as 2.1 g/dm³. For indole, [Bmim][DMP] presented a maximum distribution coefficient of 201. Based on FT-IR results, a mechanism of hydrogen bonds forming between HFILs and indole was proposed. In addition, the superiority of the HFIL method over other methods was proved by comparison.

4. EXPERIMENTAL SECTION

4.1. Chemicals. The chemical reagents employed in this work were provided by Aladdin Chemical Co., Ltd. (Shanghai, China, including indole, acenaphthene, naphthalene, and quinoline), Beijing Tongguang Fine Chemicals Co., Ltd. (Beijing, China, including diethyl ether, and toluene), and Shanghai Chengjie Chemical Co., Ltd. (Shanghai, China, including [Emim][LLac], [Emim][Ac], [Bmim][DMP], [Emim][ES], and [Emim][TFMS]). The specifications of the chemicals are listed in Table 1. The purities are in mass

Table 1. Chemical Materials Used in the Experiments

chemical name	CAS number	purity (%)	density (g/cm³)	viscosity (mPa·s)
Indole	120-72-9	99		
Naphthalene	91-20-3	98		
quinolone	91-22-5	99		
Acenaphthene	83-32-9	98		
Toluene	108-88-3	98		
diethyl ether	60-29-7	98		
[Emim][LLac]	888320-07-8	99	1.15	170.0
[Emim][Ac]	143314-17-4	99	1.10	115.0
[Bmim][DMP]	891772-94-4	99	1.16	584.7
[Emim][ES]	342573-75-5	99	1.24	97.6
[Emim][TFMS]	145022-44-2	99	1.38	42.7

fraction (provided by suppliers). The density and viscosity values were obtained at 298.2 K and provided by the suppliers. All the chemical reagents (analytical reagent grade) were directly used for the separation process without any treatment.

4.2. Preparation of Simulated Wash Oils. Wash oil, yellowish brown to brown oily liquid, is mainly used to wash benzene from coke oven gas or to prepare cold oil injection or fuel oil in industry. It contains quinoline, isoquinoline, indole, biphenyl, acenaphthene, fluorene, naphthalene compounds, azaaromatic compounds, and so on. As can be seen, the composition of a real wash oil is very complex. In general, the components of wash oil are mainly aromatic component, alkaline component, and neutral component. In this subsection, naphthalene (aromatic component), quinoline (simulated alkaline component), and acenaphthene (simulated neutral component) were selected as representative components of real wash oil. The simulated wash oils were prepared based on the previous literature.[24] First, 20.0 g of indole was added to a 500 cm³ beaker containing enough toluene. Then, 60.0 g of naphthalene, 10.0 g of quinoline, and 70.0 g of

acenaphthene were successively added to this beaker. Then, the mixture was mechanically stirred for at least 20 min until a homogeneous solution was formed. Finally, the mixture was poured out to a 500 cm³ volumetric bottle and diluted to the calibration line by using toluene. Like that, a simulated wash oil was prepared. The contents of indole, naphthalene, quinoline, and acenaphthene were 40.0, 120.0, 20.0, and 140.0 g/dm³, respectively. For other specifications of simulated wash oil (containing 12.0, 24.0, or 60.0 g/dm³ indole), the same approach was employed. The prepared simulated wash oils were kept in a volumetric bottle for use.

4.3. Separation Procedure and Analysis Methods. The whole separation process was performed in a fume hood. HFILs with a certain HFIL/indole mole ratio were added to a graduated test tube with 10 cm³ simulated wash oil, and the indole content was recorded as C_0. Then, the tube was mechanically stirred at constant temperature. After resting for 5 min, two liquid phases appeared. The lower phase and the upper phase were the HFIL phase containing indole (indole-rich phase) and wash oil phase removing indole, and the volumes were recorded as V_L and V_U, respectively.

After reaching a phase equilibrium, a sample was taken from the wash oil phase by a sampler and diluted with dichloroethane. The results given in some refs 1 2 24, and 27 show that gas chromatography (GC) exhibits the accuracy and feasibility for content analysis. According to the detected contents, SE can be calculated. Therefore, the samples were tested by GC (Shimadzu GC-2014, Japan, RTX-5 capillary column, flame ionization detector), and the indole content tested by GC was recorded as C_I. A liquid separatory funnel was then employed to separate the HFIL phase from the wash oil phase. The separation efficiency of indole (SE) was obtained by eq 2, and D (distribution coefficient of indole) was obtained by eq 3.

$$SE = \frac{V_0 C_0 - V_U C_I}{V_0 C_0} \times 100 \tag{2}$$

$$D = \frac{C_L}{C_U} = \frac{V_0 C_0 - V_U C_I}{V_L C_I} \tag{3}$$

where V_U and V_L are the volumes of the oil phase and the HFIL phase, respectively, dm³, when a phase equilibrium is reached; V_0 is the volume of the initial simulated wash oil and is 0.010 dm³; C_0 is the initial indole content, g/dm³; C_I refers to the indole content after reaching a phase equilibrium, g/dm³; C_U and C_L in g/dm³ refer to the indole contents of the upper wash oil phase and lower HFIL phase, respectively, after reaching the phase equilibrium.

As described above, a mixture of HFILs rich in indole was obtained after separation. Diethyl ether was added to this mixture to recover HFILs and indole. The volume ratio of diethyl ether to HFILs was about 10. After mechanically stirring for 30 min, indole easily dissolved in diethyl ether, but HFILs hardly. Then, two phases clearly appeared. Through analysis, the upper phase was proved to be diethyl ether-containing indole, and the lower phase was the regenerated HFIL. After phase separation, the regenerated HFIL was used for the next cycle, and the upper phase was treated with distillation to obtain indole.

4.4. Characterization. The structural schemes of indole and HFILs used in this experiment are shown in Scheme 1. To analyze the separation mechanism, we collected Fourier transform infrared (FT-IR) spectra of indole, HFILs, and

HFIL + indole mixture using a Bruker TENSOR II spectrophotometer (DTGS KBr detector, scanning region ranging from 4000 to 400 cm^{-1}). In addition, we employed a nuclear magnetic resonance spectrometer (Avance III, Bruker, Germany, 400 MHz, D$_2$O, Bruker 5 mm BBO probe) to determine the ^{1}H NMR spectra of the original and regenerated HFILs. The number of scanning samples during ^{1}H NMR characterization is 16. The mass of each HFIL sample is 20 mg.

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Notes

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■ NOMENCLATURE

IL	ionic liquids
DES	deep eutectic solvent
D	distribution coefficient
HFIL	halogen-free ionic liquids
C_0	initial indole concentration
V_U	the volume of the upper oil phase
V_L	the volume of the lower HFIL phase
GC	gas chromatography
C_I	indole content detected by GC
SE	the indole separation efficiency
[Emim][LLac]	1-ethyl-3-methylimidazolium L-lactate ionic liquid
[Emim][Ac]	1-ethyl-3-methylimidazolium acetate ionic liquid
[Bmim][DMP]	1-butyl-3-methylimidazolium dimethyl phosphate ionic liquid
[Emim][ES]	1-ethyl-3-methylimidazolium ethyl sulfate ionic liquid
[Emim][TFMS]	1-ethyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid

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