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An ionic liquid extraction process for the separation of indole from wash oil

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Abstract

Indole is an important industrial substance derived from wash oil, and the traditional alkali fusion method causes serious environmental problems. In this research, imidazolium-based ionic liquids (IBILs) were developed as new extraction agents to separate indole from wash oil with extraction efficiencies more than 90%. The influence of the structure of IBILs was explored. The extraction efficiency and the distribution coefficient of indole were used as the indexes to evaluate the IBILs extraction ability. The key experimental parameters such as initial indole concentration, extraction time, extraction temperature, and volume ratio of IBILs-to-model wash oil were investigated to obtain the optimum condition. The separation mechanism was studied by analyzing the chemical bonds using spectrographic analysis and molecular simulation. IBILs were recycled by back-extraction and exhibited good recycling properties with no obvious reduction and high extraction efficiency. Finally, the optimal process was conducted based on the process simulation.

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Keywords

Indole; wash oil; ionic liquid; extraction; simulation

1. Introduction

Indole is an important industrial chemical and extensively used in the production of spiceries, medicines and exogenous auxins. It can be obtained through two approaches: chemical synthesis and separation. Separation has more economic benefits compared to synthesis. Wash oil is one distillate fraction of coal tar and contains more than 1% of indole [1-3]. In addition, coal tar production is huge, thus, indole derived from coal tar through the separation method is feasible.

Alkali fusion is the traditional separation method, which uses strong alkali (such as KOH) to react with acidulous indole to form rafting [4]. Water is added into the rafting. Then hydrolysis reaction occurs, and indole is transferred into the water solution. A large quality of wastewater is produced during the separation process. Moreover, this process is too complex and have low yield and high cost. Therefore, an environmental and highly efficient method is necessary to fully used indole in wash oil.

A new type of compound called ionic liquids (ILs) has recently emerged. ILs mainly consist of organic cations and inorganic anions. They usually maintain in liquid form at room temperature [5]. They exhibit wide liquid range, high heat capacity, high thermal and chemical stability, and low vapor pressure [6].They are extensively applied as green solvents to a variety of fields, such as organic synthesis,

chromatography analysis, electrochemistry, and separation [7, 8]. ILs gradually became an alternative to conventional organic solvent. They performed well in the separation and extraction of many compounds, such as metal [9, 10], organic acids [11], amino acids [12, 13], biofuels [14], benzene derivatives [15], and phenolic compounds [16-19]. The conventional extraction solvent of indole was changed from one polar solvent (methylacetamide) to two solvents (a polar solvent and non-polar solvent) [20]. The extraction efficiency (EE) of indole using methylacetamide was very low, the manipulation of two solvents was complex, and the recovery of solvent was difficult. Therefore, that the use of ILs in the extraction of indole from wash oil is very promising to be highly efficient and environmentally friendly.

In this study, imidazolium-based ionic liquids (IBILs) were found that can separate indole from model wash oil. Therefore, a series of IBILs was investigated through the extraction efficiency and distribution coefficient of indole, and $BmimBF_4$ was screened out. Moreover, the effects of different experimental conditions such as initial concentration, extraction time, extraction temperature, and volume ratio were studied. The experimental conditions were optimized and the mechanism of the extraction process was explored. The regeneration of ILs and extraction process was also studied, and the whole experiment process was simulated using Aspen Plus.

2. Experimental

2.1 Chemicals

Table 1. Chemicals used in extraction process

The chemicals used in the experiment process are listed in Table 1, in all cases, the percentage purities mentioned previously refer to mass fraction as reported by the suppliers. All the chemical agents were used without further purification. The water was distilled in glass before use.

2.2 Preparation of model wash oil

Due to the complexity of wash oil, indole, naphthalene, quinoline, acenaphthene were chosen as the representative of the low-acid, aromatic, alkaline, and neutral compounds, respectively. Their mass ratio was 1:10:1.67:11.67 in bulk density with the composition of wash oil as a reference. Methylbenzene was selected as the solvent, and 6.025 g of indole, 59.99 g of naphthalene, 10.03 g of quinoline, and 70.02 g of acenaphthene were completely dissolved in methylbenzene by continuous shaking. Then they were diluted to 500 mL in a volumetric flask at room temperature. The concentrations of the model wash oil are 12.05 g/L, 120 g/L, 20.06 g/L, and 140.04 g/L for indole, naphthalene, quinoline, and acenaphthene, respectively. A series of different concentrations of model wash oil was prepared in the same manner.

2.3 Extraction process

Figure 1. The concept process of the separation of indole from model wash oil (IBILs: Imidazolium-based ionic liquids)

The extraction processes are performed as Figure 1, a certain amount of model wash oil was put into a tube, and a specific amount of ILs was added into the oil. The

tube was placed in an incubator shaker with a temperature controller within ±0.1 K and 400 rpm for a known time under an appropriate temperature. Two layers clearly appeared in the model wash oil after settling for 30 min, and they were separated by a funnel. The volumes of two layers were measured carefully. The lower layer composed of ILs and indole was fed into a decanter with a given volume of diethyl ether as the back-extraction agent. Two layers were formed after stirring for a certain time, the lower layer was mainly composed of ILs and the upper layer of diethyl ether and indole. A distillation column was used to separate indole from upper layer and recycle diethyl ether. Indole was got from the bottom of the distillation column.

2.4 Analysis methods

EE can be calculated using the concentration of the upper layer, which could be detected using a gas chromatograph (GC) equipped with flame ionization detector (FID). The chromatographic column used in GC was a 30 m × 0.53 mm × 1.5 μm capillary column (Onlysci, ON-1). The chromatographic conditions were as follows: the column temperature, 130 ℃; injector temperature, 250 ℃; and detector temperature, 300 ℃. After extraction, the lower layer and the recycled extraction agents were measured using Fourier transform infrared spectrometer (FT-IR) (Nicolet 380, Thermo Fisher Scientific, America). The spectra were recorded at room temperature.

3. Results and discussion

EE could be calculated through the concentration of the upper layer, which can be detected by using GC. The specific calculation formula is shown as follows:

$$\mathrm{EE}(\%) = \frac{C_o V_o - C_f V_f}{C_o V_o} \times 100 \quad (1)$$

Two layers were carefully separated by using a centrifugal machine, and the volume was measured accurately. The concentration of the lower layer could be calculated by conservation of mass, and the distribution coefficient (D) between the given ILs and oil phases was calculated as follows:

$$\mathrm{D} = \frac{C_{IL}}{C_f} \quad (2)$$

Where C_o and C_f represent the concentration of the original model wash oil and the upper layer after extraction, respectively. V_o and V_f represent the volume of the original model wash oil and the upper layer after extraction, respectively. In Eq. 2, D represents the distribution coefficient, and C_{IL} represents the concentration of the lower layer in the IL phase.

3.1 Selection of IBILs

IBILs were found to be able to separate indole from model wash oil during the experimental process. Thus, several IBILs were used to investigate the influence of the substituents and obtain the optimum IBILs. Different anions, including Cl^-, BF_4^-, PF_6^-, were studied and they were 1-butyl-3-methylimidazolium chloride (BmimCl), 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$), 1-butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$), respectively. The volume ratio of model wash oil-to-IBIL of 1:1 was used in this research. Approximately 10 mL $BmimBF_4$ was added into 10 mL of model wash oil in a test tube. The extraction conducted at temperature of 303.15 K for 60 min and all the experiments were performed under the same conditions. Two layers were observed

after letting the solution stand for a few minutes, and the concentration of the upper layer was detected by GC, EE and D are calculated and shown in Figure 2 and Figure 3. IBILs can separate indole from model wash oil to some extent, and different substitutes exhibited different extraction abilities. The extraction ability of the anions, from greatest to least, follows this order: BF_4^->PF_6^->Cl^-. The extraction efficiencies of indole were 91.36%, 86.47%, and 70.72%. The extraction efficiencies of naphthalene, quinoline, and acenaphthene were less than 60%. The distribution coefficients of indole for $BmimBF_4$, $BmimPF_6$, and BmimCl were 9.51, 6.848, and 5.504, and they were a magnitude higher than the distribution coefficients of naphthalene, quinoline, and acenaphthene. In conclusion, IBILs can be used to separate indole from model wash oil. $BmimBF_4$ performed the highest selectivity among IBILs for the extraction of indole and was thus used as the optimum IBIL in succeeding experiments.

Figure 2. The distribution coefficients of naphthalene, quinoline, indole, and acenaphthene for different IBILs;(initial concentration of model wash oil: naphthalene (120.1 g/L), quinoline (20.07 g/L), indole (12.05 g/L), and acenaphthene (140.0 g/L); extraction temperature: 303.15 K; extraction time: 60 min; volume ratio of ILs-to-model wash oil: 1:1)

Figure 3. The extraction efficiency of naphthalene, quinoline, indole, and acenaphthene for different IBILs; (initial concentration of model wash oil: naphthalene (120.1 g/L), quinoline (20.07 g/L), indole (12.05 g/L), and acenaphthene (140.0 g/L); extraction temperature: 303.15 K; extraction time: 60 min; volume ratio of ILs-to-model wash oil: 1:1)

IBILs provide a promising way of separating indole from wash oil. $BmimBF_4$ exhibited high indole EE of more than 90%, with a high value of *D*. However, the effect of different experimental conditions on the extraction process and the

mechanism of the extraction procedure remain unclear. Hence, different parameters were studied, such as initial concentration, volume ratio, extraction temperature, and extraction time.

3.2 Influence of various parameters on the extraction process

3.2.1 Initial concentration

Initial concentration is an important parameter for extraction. Hence, the initial concentration ranges of indole from 48.00 g/L to 12.00 g/L (i.e., 48.00 g/L, 36.00 g/L, 24.00 g/L, and 12.00 g/L) were investigated. The extractions were performed at 303.15 K for 60 min, with a $BminBF_4$-to-wash oil volume ratio of 1:4 to 3:2 (i.e., 1:4, 1:2, 3:4, 1:1, 3:2). Figure 4 shows the results, wherein the concentrations of indole decreased sharply as $BmimBF_4$ increased. The initial concentration had some effect on the indole content of the upper layer. When the $BmimBF_4$-to-wash oil volume ratio was 1:4, the indole contents of the upper layer for initial concentrations of 12.00, 24.00, 36.00, and 48.00 g/L were 2.827, 5.262, 11.06, and 10.69 g/L, respectively. These results suggested that when the initial concentration was low, the indole content of the upper layer resulted in a small value at low $BmimBF_4$-to-model wash oil volume ratio. As the $BmimBF_4$-to-wash oil volume ratio increases, the indole content of the upper layer decreased to a certain concentration of approximately 2.0 g/L to 3.0 g/L. $BmimBF_4$ exhibited significant extraction ability of indole from model wash oil in a high range of the initial concentration, and it can be potentially used in the separation of indole.

Figure 4. The indole content of upper layer for different initial phenols concentration under different volume ratio (initial concentration of model wash oil: naphthalene (120.1 g/L), quinoline (20.07 g/L), indole (12; 24; 36; 48 g/L), and acenaphthene (140.0 g/L); extraction temperature: 303.15 K; extraction time: 60 min)

3.2.2 $BmimBF_4$-to-wash oil volume ratio

Volume ratio is an important parameter for the extraction process, therefore, their affection was thoroughly investigated. The $BmimBF_4$-to-wash oil volume ratios were 1:4, 1:2, 3:4, 1:1, and 2:3. The extractions were performed using model wash oil at 303.15 K for 60 min. Figure 5 shows the results, the EE of indole rapidly increased from 70% to 90% in the volume ratio range of 1:4 to 1:2 and then increased gradually beyond 1:2. D decreased sharply from 13.05 to 10.54 in the range of 1:4 to 1:2, then decreased gently beyond 1:2. The maximum EE of indole was 91.52%, which was obtained at the volume ratio of 1:1, while the value of D was 9.51. The maximum D of 13.05 was obtained at the volume ratio of 1:4, however, the EE of indole was only 76%. To ensure both high EE and D of indole, $BmimBF_4$-to-model wash oil volume ratio of 1:1 was selected and used in the succeeding experiments.

Figure 5. Indole EE and D from model wash oil at different volume ratio (initial concentration :(initial concentration of model wash oil: naphthalene (120.1 g/L), quinoline (20.07 g/L), indole (12.05 g/L), and acenaphthene (140.0 g/L); extraction temperature: 303.15 K; extraction time: 60 min)

3.2.3 Extraction temperature

Figure 6. EE and D of indole from model wash oil at different extraction temperature (initial concentration: naphthalene (120.1 g/L), quinoline (20.07 g/L), indole (12.05 g/L), and acenaphthene (140.0 g/L); volume ratio: 1:1; extraction time: 60 min)

Extraction temperature is an important parameter; therefore, it was thoroughly

investigated in this study. The extraction temperature varied from 303.15 K to 333.15 K, that is, 303.15, 313.15, 323.15, and 333.15 K. The extraction was performed at $BmimBF_4$-to-wash oil volume ratio of 1:1 for 60 min in the model wash oil. The results are shown in Figure 6. As the extraction temperature increased, the EE of indole increased at the range of 303.15 K to 313.15 K, and then decreased beyond 313.15 K. The D of indole had the same trend as the EE. The maximum EE and the D of indole were obtained at 313.15 K, that is, 90.71% and 12.77, respectively. This trend was caused by the solubility of indole in methylbenzene, and $BmimBF_4$ increased as temperature increased. The optimum temperature was obtained when the EE and the distribution coefficient reached the maximum value. Therefore, increasing the temperature had a certain effect on the extraction process, and 313.15 K was suitable for the extraction process.

3.2.4 Extraction time

Figure 7. EE and distribution ratio of indole from model wash oil at different extraction time (initial concentration: naphthalene (120.1 g/L), quinoline (20.07 g/L), indole (12.05 g/L), and acenaphthene (140.0 g/L); volume ratio: 1:1; extraction temperature: 303.15 K)

Extraction time was investigated thoroughly from 5 min to 90 min, that is, 5, 10, 30, 60, and 90 min. The extractions were performed as follows: extraction temperature, 303.15 K; and $BmimBF_4$-to-model wash oil volume ratio, 1:1. The result is shown as Figure 7. The EE of indole increased as extraction time increasing. The EE and the distribution coefficient of indole increased sharply from 45.18% and 0.942 to 90.40% and 12.324 in the range of 5 min to 60 min, respectively. Then the variation trend turned to be stable beyond 60 min. The distribution coefficient value had a slight

decrease from 60 min to 90 min, which may cause by the evaporation of the solvent. Every experiment data point in this article, thrice repeated experiments were did and the average value was used as the final result. According to the results, the extraction process required a certain time to reach equilibrium. To ensure the sufficient of the extraction process, 60 min was chosen as the suitable extraction time.

3.3 Mechanism of the extraction process

Figure 8. FT-IR spectra of $BmimBF_4$, Indole, and ILs layer

Figure 9. Structure of the stable indole-$BmimBF_4$ complex

ILs could separate indole from model wash oil because the intermolecular forces between ILs and indole are stronger than methylbenzene and indole. The chemical bonds between indole and $BmimBF_4$ were analyzed through FT-IR. The FT-IR spectra of $BmimBF_4$, indole, and the ILs layer are shown in Figure 8. In general, the **ν-**NH stretching vibration can be observed between wavenumbers of 3300 cm^{-1} and 3500 cm^{-1}. The **ν-**NH stretching vibration in indole was observed at 3400 cm^{-1}, and this vibration peak disappeared after extraction in the ILs layer. This change in the absorption bonds is mainly due to the changes between different vibrational states of bond in molecules, and a portion of the electron cloud in a nitrogen atom migrated to higher wavenumbers. These results suggested the existence of hydrogen bond between $BmimBF_4$ and indole after extraction [21]. Then, DFT calculation using Gaussian 09 program[22] and experiment with FT-IR were carried out to explain the mechanism. The geometric optimizations of extraction monomers, indole and $BmimBF_4$, and their complex (indole-$BmimBF_4$) were performed at

B3LYP/6–311+g(d, p) level. The final obtained geometries were recognized as local minima without any negative vibrational frequency. Meanwhile, the solvent effect was introduced by using the polarized continuum model (PCM) [23]. The solvent methylbenzene was used, ε= 2.4 (20 ^{o}C). The result is shown in Figure 9, it depicted that two hydrogen bonds formed between $BmimBF_4$ and indole. Besides the hydrogen bond N-H···F that was indicated by FT-IR spectrum, there was another hydrogen bond C-H···F that appeared between the benzene ring of indole and $BmimBF_4$. The bond lengths were 1.92 Å and 2.55 Å for N-H···F and C-H···F, respectively. It was confirmed that there were hydrogen bonds existed during the extraction process.

3.4 Recycle of IBILs

The recycle of IBILs is crucial for the extraction process, so the cyclicity was investigated. Diethyl ether (DE) was used as an efficient back-extraction agent to recycle $BmimBF_4$. It was selected to recycle $BmimBF_4$ because of the significant solubility difference between $BmimBF_4$ and indole in DE. When DE was added in the $BmimBF_4$ layer, two layers were formed clearly after stirring for a certain time. The lower layer was identified as $BmimBF_4$, and the upper layer was mainly composed of DE, indole and a small amount of model wash oil. The specific separation process was performed as follows: 10 mL of $BmimBF_4$ was added in 10 mL model wash oil, and the extraction was performed at temperatures lower than 313.15 K with 60 min of stirring to mix them thoroughly. Then 20 mL of DE was added to the lower layer after the extraction process, and two layers were formed after stirring. The two layers were separated accurately using a separating funnel, and the lower layer was washed using

DE. The lower layer was placed in a vacuum drier at 333.15 K to remove DE and the model wash oil. The upper layer was composed of DE, model wash oil, and indole. DE can be removed through distillation. The recycled $BmimBF_4$ was weighed until the mass was constant. The same processes were repeated thrice under the same conditions. The extraction efficiencies of indole were calculated to evaluate the extraction ability of the recycled $BmimBF_4$. Multiple recycle masses were also weighed to evaluate the recycle efficiency of $BmimBF_4$. Figure 10 shows that the recycled $BmimBF_4$ still maintained considerably high EE, which was 89.96% after reusing thrice and the recycle efficiency of $BmimBF_4$ maintained high value of more than 94%.

The recycled $BmimBF_4$ was confirmed by qualitative analysis through FT-IR. The spectra of the standard and recycled $BmimBF_4$ are shown in Figure 11. The characteristic absorption peaks of the recycled $BmimBF_4$ were identical to those of standard $BmimBF_4$. The FT-IR spectra suggested that the recycled lower layer was $BmimBF_4$.

Figure 10. Indole extraction efficiency and $BmimBF_4$ recycle efficiencies versus regeneration cycles

Figure 11.FT-IR spectra of recycled $BmimBF_4$ and standard $BmimBF_4$

3.5 Process design and simulation

Figure 12. Flowsheet of the separation of indole from model wash oil.

B1. Extraction column, B2. Back-extraction column, B3. Flash separator, B4. Heater, B5. ILs tank. DE: diethyl ether; IL: ionic liquid

A specific process was designed on the basis of the previously mentioned experiment as shown in Figure 12. This separation process mainly involved an extraction column, a back-extraction column, a rectifying column, a heater, and an IL tank. First, the IL (stream 1) and the wash oil were added into the extraction column (B1), and two layers were formed with an extraction efficiency of indole of more than 90%. Stream 3, which flowed from the top of the extraction column, was the wash oil after the extraction of indole. The IL layer from the bottom of the extraction column flowed to the back-extraction column (B2) with the back-extraction agent DE (streams 5 and 10). Two layers were formed, the upper layer (stream 6) was mainly composed of DE and indole, and the lower layer (stream 7) was composed of IL, which could be recycled to the separation process. Stream 6 was moved to a rectifying column (B3), DE was steamed from the top, and the lower layer was mainly composed by indole and little wash oil that needed further separation. The recycled ILs (stream 7) and the new supplementary ILs (stream 11) were stored in an IL tank (B5) and flowed to the extraction column. The entire extraction process was conducted under ambient pressure and normal temperature. This process provided a significant approach for the environmental separation of indole.

Afterward, a preliminary simulation of the experimental process was carried out using Aspen Plus in this article. The flow diagram was built in user interface with Figure 1 as a reference, Decanter was chosen as the extraction and back-extraction units, and Radfrac was chosen as the separation unit of the distillation column.

Because of the applicability of the NRTL property method in miscibility system and the calculation of the physical properties of liquid-liquid stratification system, it is particularly suitable for the extraction process and is used in the following simulation process [24]. $BmimBF_4$ was selected as the typical ILs, but it could not be found in the built-in database of Aspen Plus. So we input it as the user defined compound, and its physical property data were directly input in parameters of pure component. The Binary interaction parameters of NRTL involve $BmimBF_4$ were determined through the regression of liquid-liquid equilibrium data. During the simulation, indole was chosen to be the only solute of the model wash oil in order to simplify the separation process. The operation conditions were as follow: the extraction temperature was 313.15 K under atmospheric pressure, the volume ratio of $BmimBF_4$ to model wash oil was 1:1, and the concentration of indole was 12.00 g/L.

Table 2. The simulation results of the experimental process by Aspen Plus

The simulation results are shown in Table 2, approximately 91% of indole was extracted by $BmimBF_4$ from model wash oil, and 96.54% of indole was separated from $BmimBF_4$ using DE. About all of the $BmimBF_4$ could be recycled through back-extraction with the mass fraction of 99.75%. At last indole with the mass fraction of 91.06% was got after the removal of DE. The simulation results were in a good accordance with those experimental data. It is a fine reference to predict the extraction efficiency under different experimental conditions. And through the simulation of the experimental process, the extraction efficiency and the indole purity could be easily optimized by regulating the experimental conditions.

4. Conclusion

IBILs were found to be able to separate indole from model wash oil as a kind of successful extraction medium. The effects of different extraction conditions, such as different anions, initial concentration, $BmimBF_4$-to-model wash oil volume ratio, extraction temperature, and extraction time were investigated in this research. The EE and the distribution coefficient of indole were selected as the indexes to evaluate the extraction ability of IBILs. The anions had significant influence on the extraction process, and $BmimBF_4$ was screened as the suitable extraction agent. The different extraction conditions were investigated and the optimum extraction conditions were obtained. When the $BmimBF_4$-to-model wash oil volume ratio was 1:1, the indole EE of 91.52% and the distribution coefficient of 9.51 were obtained as comparatively good results. The extraction needed a certain time to reach equilibrium, and an extraction time of 60 min was selected as the appropriate value. This extraction process is not very sensitive to the change of extraction temperature, and 313.15 K was selected as the optimum temperature. $BmimBF_4$ was recycled by back-extraction agent DE, and the EE of indole remained at approximately 90% after three recycles without an obvious decrease in mass. And the simulation of the extraction process had been carried out using Aspen Plus, the simulation results were in a good accordance with those experimental data. The FT-IR spectrum of the lower layer after extraction and the molecule simulation results using GAUSSIAN 09 both suggested the formation of the hydrogen bond between $BmimBF_4$ and indole. The proposed extraction process has the important reference significance to the separation of indole

from wash oil. This method is environmentally-friendly compared with the traditional method because it can avoid the use of strong alkaline and acidic aqueous solutions and the production of large amount wastewater.

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Notations

List of symbols

C_o	Original concentration ($g \cdot L^{-1}$)
V_o	Originalvolume(mL)
C_f	Concentration after reaction($g.L^{-1}$)
V_f	Volume after reaction (mL)
C_{IL}	Concentration of ILs layer ($g \cdot L^{-1}$)

Abbreviations

ILs	Ionic liquids
IBILs	Imidazolium-based ionic liquids
FID	Flame ionization detector
D	Distribution coefficient
EE	Extraction efficiency
FT-IR	Fourier transform infrared spectrometer
GC	Gas chromatograph
DE	Diethyl ether

Subscripts

o	original data
f	data after reaction

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Table captions:

Table 1. Chemicals used in extraction process

Table 2. The simulation results of the experimental process by Aspen Plus

Figure captions:

Figure 1. The concept process of the separation of indole from model wash oil (IBIL: Imidazolium-based ionic liquid)

Figure 2. The distribution coefficients of naphthalene, quinoline, indole, and acenaphthene for different IBILs;(initial concentration of model wash oil: naphthalene (120.1 g/L), quinoline (20.07 g/L), indole (12.05 g/L), and acenaphthene (140.0 g/L); extraction temperature: 303.15 K; extraction time: 60 min; volume ratio of ILs-to-model wash oil: 1:1)

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Figure 4. The indole content of upper layer for different initial phenols concentration under different volume ratio (initial concentration of model wash oil: naphthalene (120.1 g/L), quinoline (20.07 g/L), indole (12; 24; 36; 48 g/L), and acenaphthene (140.0 g/L); extraction temperature: 303.15 K; extraction time: 60 min)

Figure 5. EE and D of indole from model wash oil at different volume ratio (initial concentration :(initial concentration of model wash oil: naphthalene (120.1 g/L), quinoline (20.07 g/L), indole (12.05 g/L), and acenaphthene (140.0 g/L); extraction temperature: 303.15 K; extraction time: 60 min)

Figure 6. EE and D of indole from model wash oil at different extraction temperature (initial concentration: naphthalene (120.1 g/L), quinoline (20.07 g/L), indole (12.05 g/L), and acenaphthene (140.0 g/L); volume ratio: 1:1; extraction time: 60 min)

Figure 7. EE and D of indole from model wash oil at different extraction time (initial concentration: naphthalene (120.1 g/L), quinoline (20.07 g/L), indole (12.05 g/L), and acenaphthene (140.0 g/L); volume ratio: 1:1; extraction temperature: 303.15 K)

Figure 8. FT-IR spectra of $BmimBF_4$, Indole, and ILs layer

Figure 9. Structure of the stable indole-$BmimBF_4$ complex

Figure 10. Indole extraction efficiency and $BmimBF_4$ recycle efficiencies versus regeneration cycles

Figure 11. FT-IR spectra of recycled $BmimBF_4$ and standard $BmimBF_4$

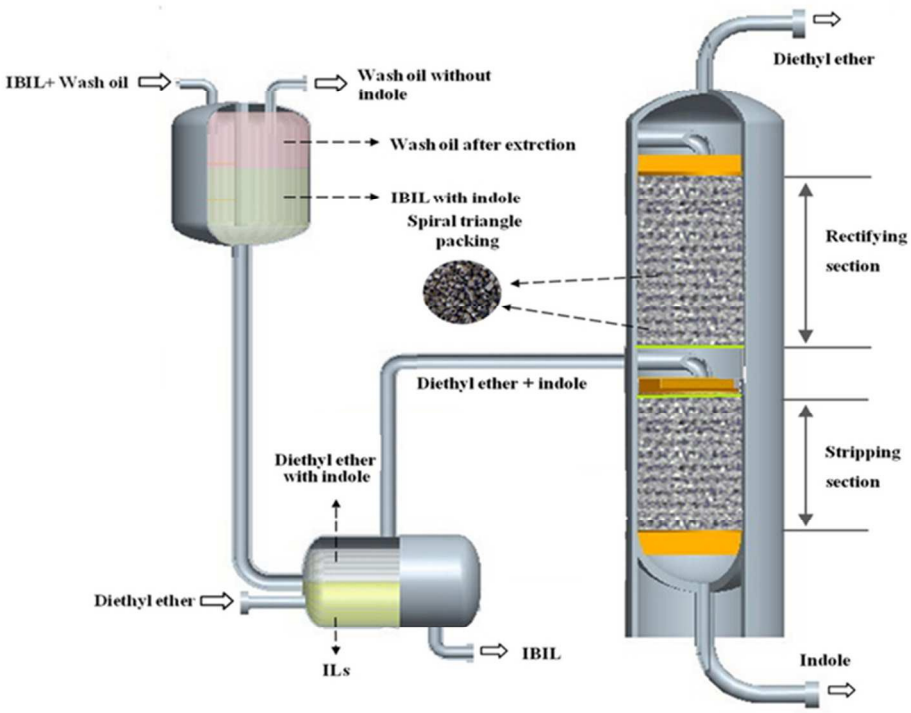
Figure 12. Flowsheet of the separation of indole from model wash oil.
B1. Extraction column, B2.Back-extraction column, B3. Flash separator, B4. Heater, B5. ILs tank. DE: diethyl ether; IL: ionic liquid

Table 1. Chemicals used in extraction process

Compound	CAS NO	Purity	manufacturer
methylbenzene	108-88-3	>99.5% w	Beijing Chemical Reagent Co., Ltd
naphthalene	91-20-3	AR	Sinopharm Chemical Reagent Co., Ltd
quinoline	91-22-5	>98.0% w	Sinopharm Chemical Reagent Co., Ltd
acenaphthene	83-32-9	>98.0% w	J&K Chemical Reagent Co., Ltd
indole	120-72-9	CP	Shanghai Chemical Reagent Co., Ltd
$BmimBF_4$	174501-65-6	>98.0% w	Linzhoukeneng material Co., Ltd
$BmimPF_6$	174501-64-5	>98.0% w	Linzhoukeneng material Co., Ltd
BmimCl	79917-90-1	>98.0% w	Linzhoukeneng material Co., Ltd

Table 2. The simulation results of the experimental process by Aspen Plus

Stream ID	Mass flow / $Kg \cdot h^{-1}$			
	$BmimBF_4$	Methylbenzene	Indole	DE
1	0	480	6	0
2	600	0	0	0
3	0.869	478.30	0.5825	0
4	599.13	1.698	5.417	0
5	0	0	0	300
6	598.97	0.006204	0.2945	1.227
7	0.1549	1.692	5.123	298.77
8	3.94E-08	1.347941	2.83E-09	298.77
9	0.1549	0.3439	5.123	0.003868
stream ID	Mass fraction			
	$BmimBF_4$	Methylbenzene	Indole	DE
1	0	0.0123	0.9877	0
2	1	0	0	0
3	0.0018	0.9970	0.0012	0
4	0.9883	0.0028	0.0089	0
5	0	0	0	1
6	0.9975	0	0.0005	0.0020
7	0.0005	0.0055	0.0168	0.9772
8	0	0.0045	0	0.9955
9	0.0275	0.0611	0.9106	0.0007



The concept process of the separation of indole from model wash oil (IBIL: Imidazolium-based ionic liquid)

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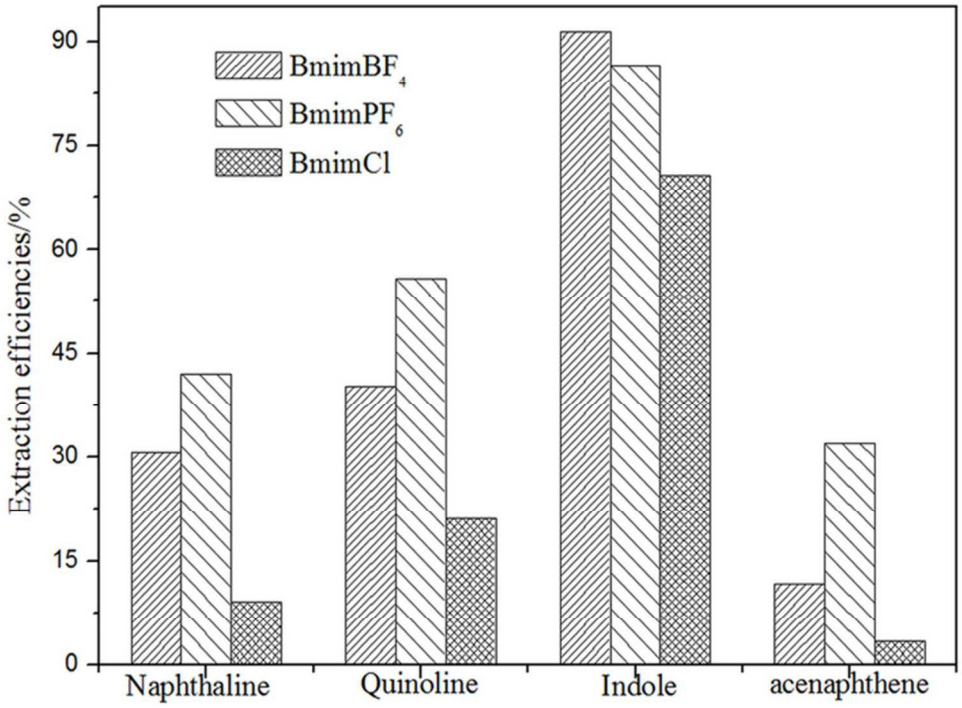

The distribution coefficients of naphthalene, quinoline, indole, and acenaphthene for different IBILs. (initial concentration of model wash oil: naphthalene (120.1 g/L), quinoline (20.07 g/L), indole (12.05 g/L), and acenaphthene (140.0 g/L); extraction temperature: 303.15 K; extraction time: 60 min; volume ratio of ILs-to-model wash oil: 1:1)
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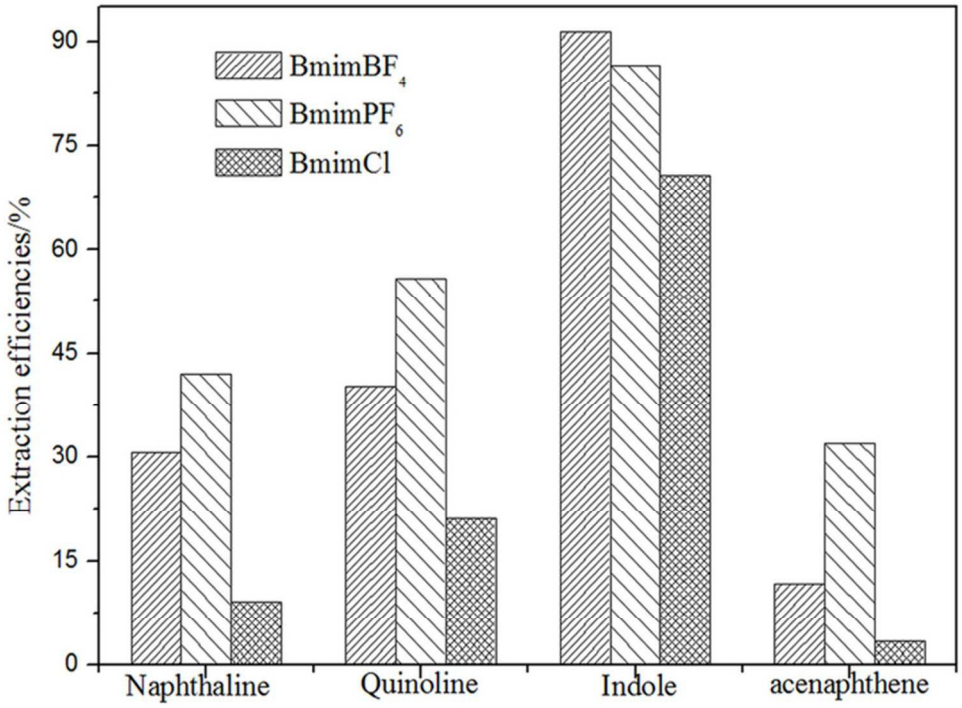

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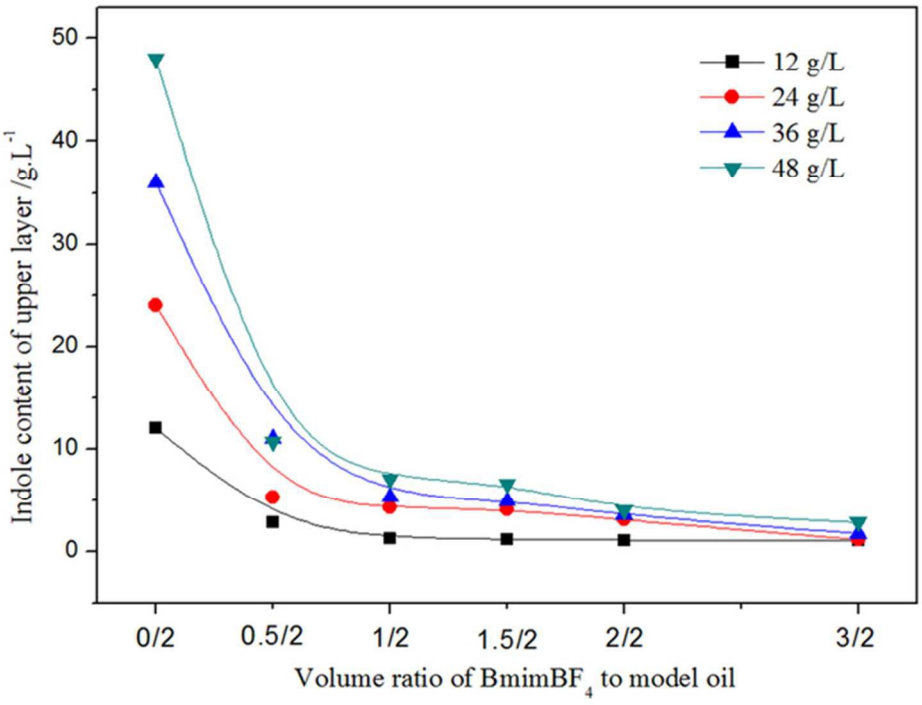

The indole content of upper layer for different initial phenols concentration under different volume ratio. (initial concentration of model wash oil: naphthalene (120.1 g/L), quinoline (20.07 g/L), indole (12; 24; 36; 48 g/L), and acenaphthene (140.0 g/L); extraction temperature: 303.15 K; extraction time: 60 min)
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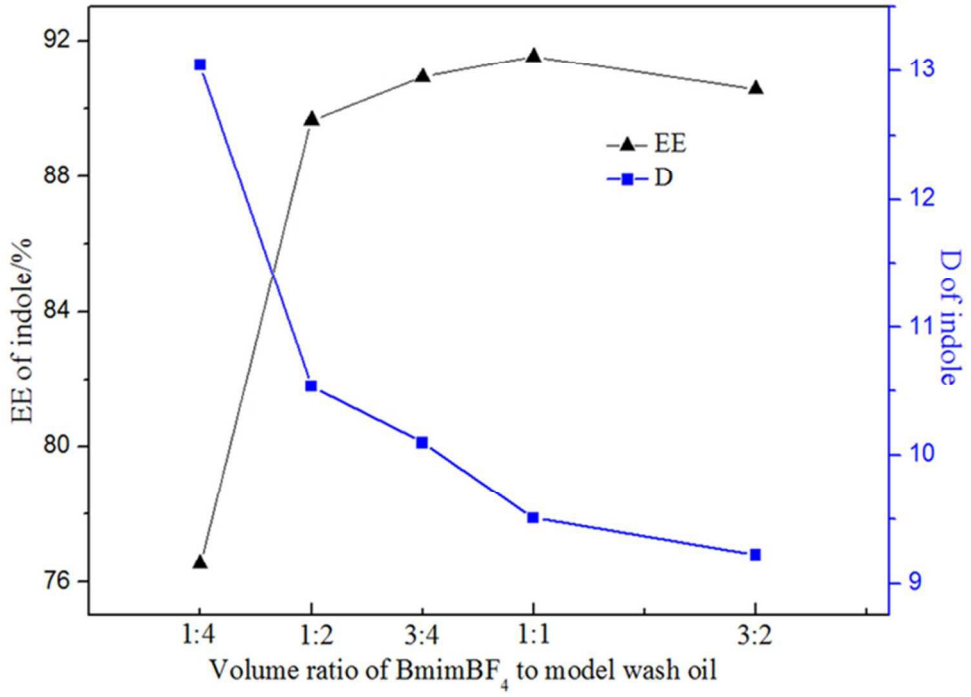

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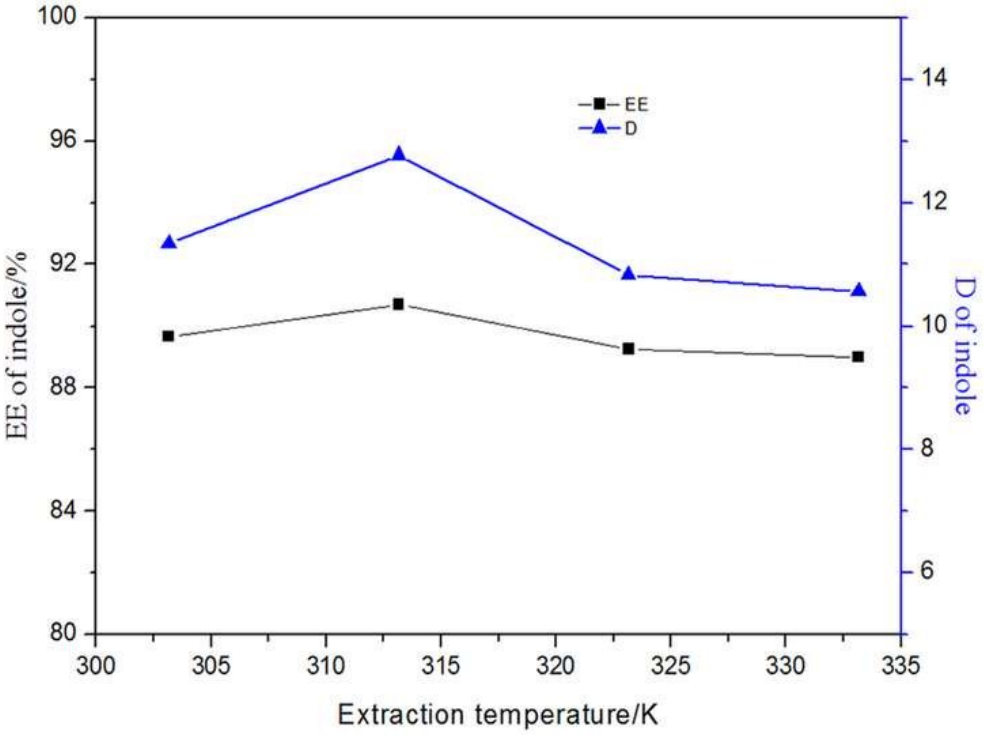

EE and D of indole from model wash oil at different extraction temperature. (initial concentration: naphthalene (120.1 g/L), quinoline (20.07 g/L), indole (12.05 g/L), and acenaphthene (140.0 g/L); volume ratio: 1:1; extraction time: 60 min)
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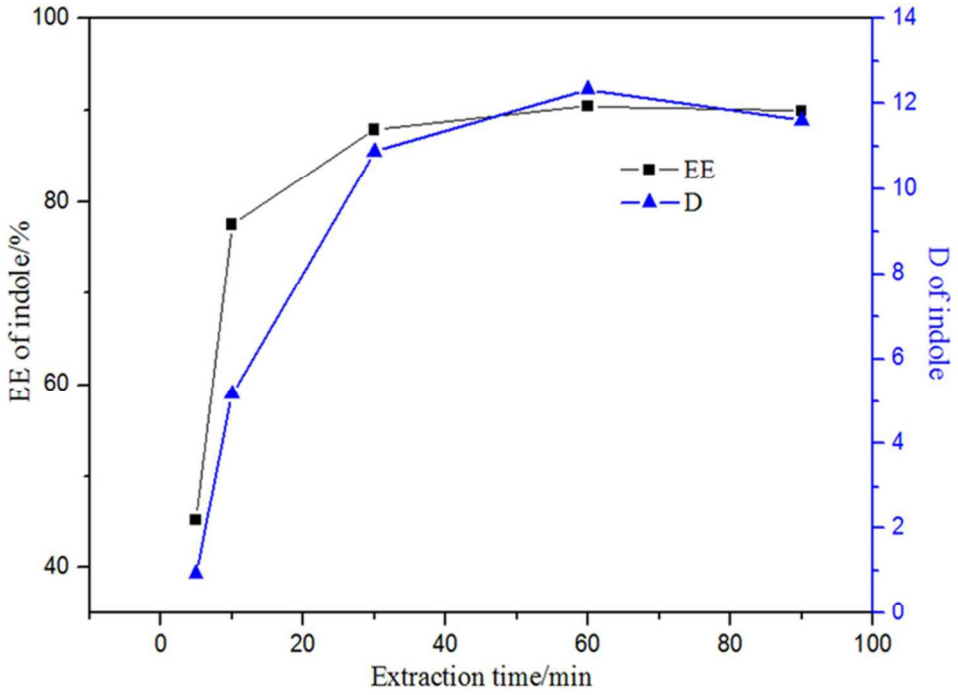

EE and D of indole from model wash oil at different extraction time (initial concentration: naphthalene (120.1 g/L), quinoline (20.07 g/L), indole (12.05 g/L), and acenaphthene (140.0 g/L); volume ratio: 1:1; extraction temperature: 303.15 K)
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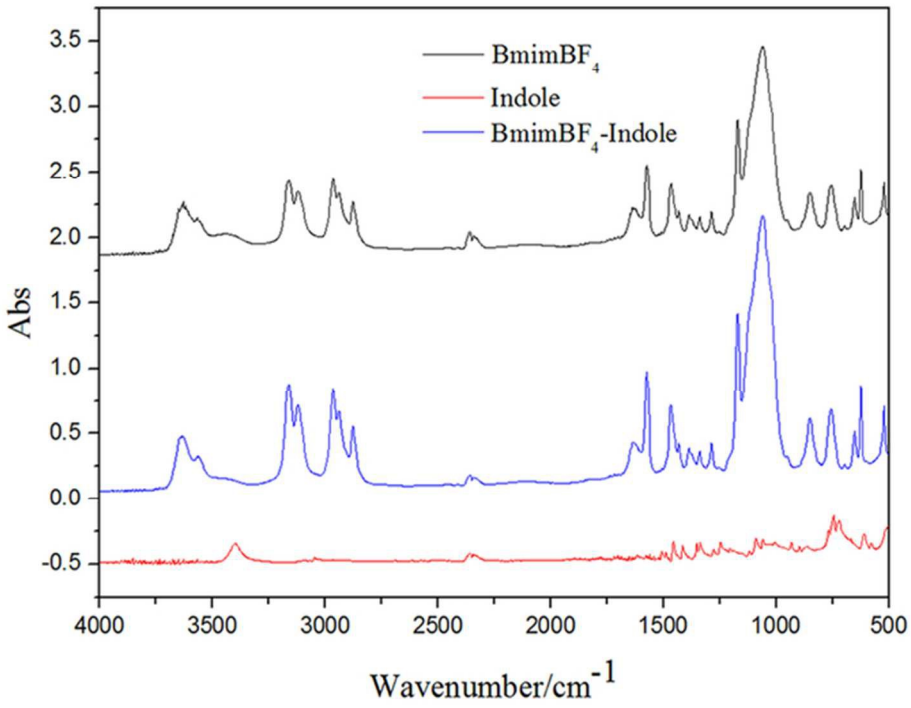

FT-IR spectra of BmimBF4, Indole, and ILs layer
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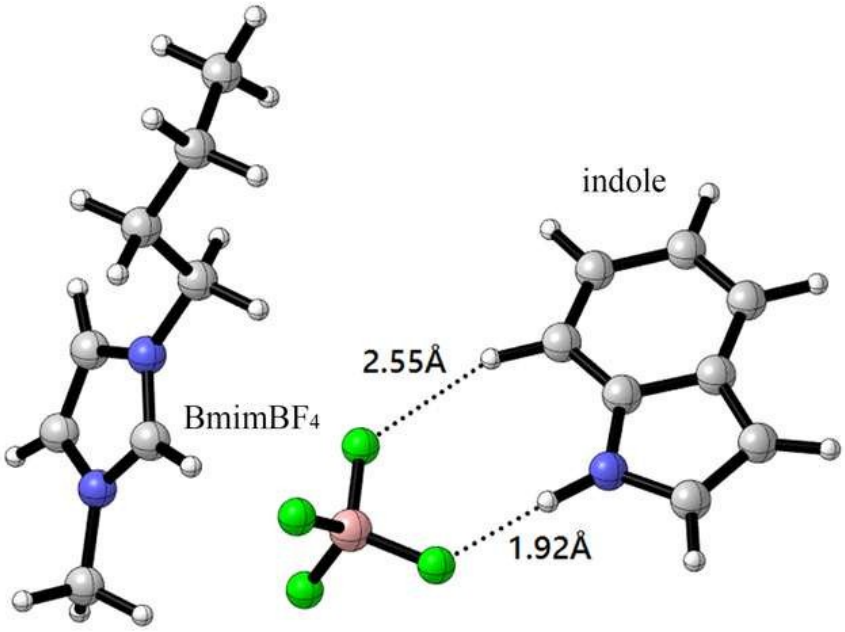

Structure of the stable indole-BmimBF4 complex
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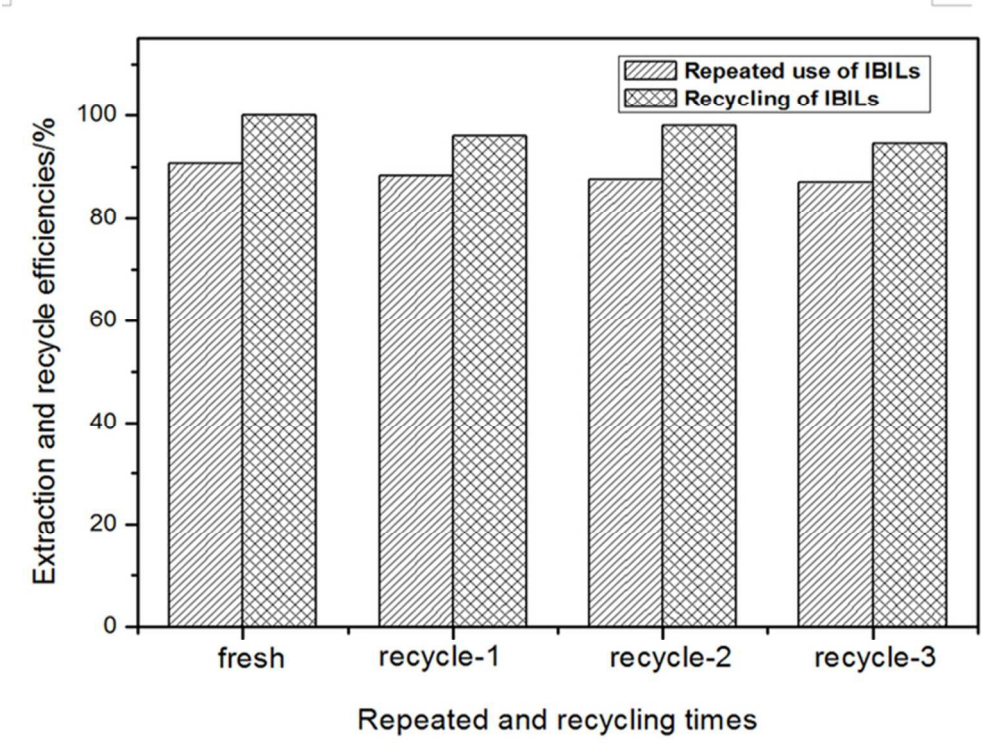
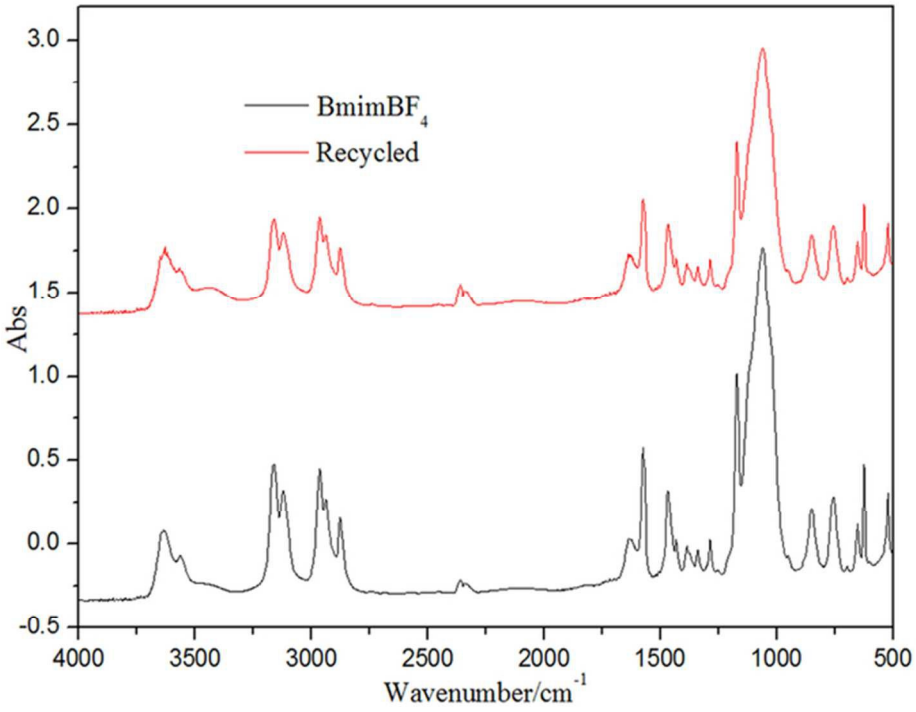
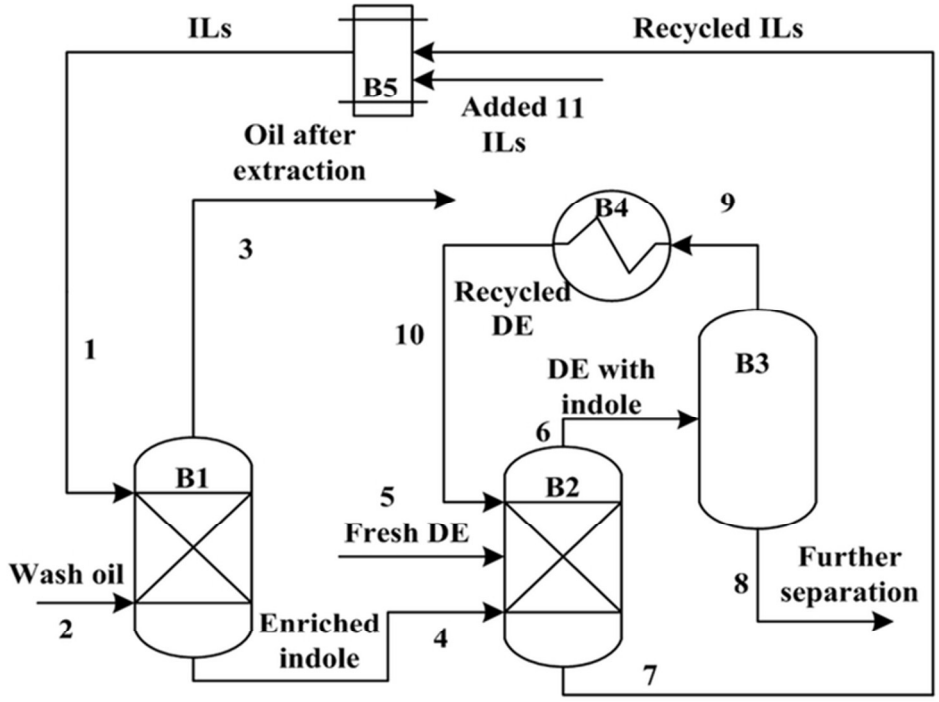


Indole extraction efficiency and BmimBF4 recycle efficiencies versus regeneration cycles
62x46mm (300 x 300 DPI)



FT-IR spectra of recycled BmimBF4 and standard BmimBF4
62x46mm (300 x 300 DPI)



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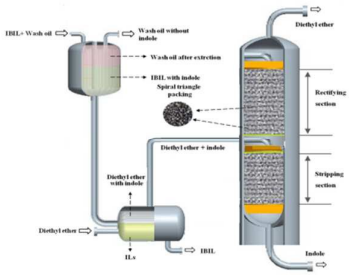
Type of Article:
Paper

Table of contents entry

An ionic liquid extraction process for the separation of indole from wash oil

TiantianJiao, Xulei Zhuang, Lihong Zhao, Chunshan Li*, Hongnan Chen, Suojiang Zhang *



1. Imidazolium-based ionic liquids (IBILs) were developed as the extraction medium to separate indole from wash oil.
2. The process is environmentally friendly and IBILs could be easily recycled。
3. The extraction conditions are very mildly.
4. A separation process was proposed based on the process simulation.