Selective Extraction of 1-Hexene Against n-Hexane in Ionic Liquids with or without Silver Salt

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S *Supporting Information*

ABSTRACT: This paper presents an extensive study on the feasibility of ionic liquids (ILs) for the extractive separation of a 1-hexene/n-hexane mixture. Seventeen ILs were tested at 313 K. The extraction selectivities of 1-hexene to n-hexane were in the range 1.5–3.0. The chemical structures of anion and cation in ILs greatly affected the extraction, and the functional groups, such as carbon–carbon double bond, nitrile, ester, and amide, in the ILs led to higher selectivities. The increase of alkyl chain length in cation led to the increase of extraction capacity of 1-hexene. To increase the distribution of 1-hexene in IL phase, silver salt was added to the ILs. It was found that ILs containing silver salt had a high distribution of 1-hexene, as well as high selectivity of 1-hexene against n-hexane. The extraction efficiency increased with the concentration of silver salt in ILs. When the initial feed concentration of 1-hexene was smaller, the selectivity of 1-hexene to n-hexane was higher. A simple mathematical model has been developed to describe the total 1-hexene content in the reaction media under study, on the basis of the formation of complexes between silver and 1-hexene with different stoichiometry. This work proves that the ILs can act as effective extractants in 1-hexene/n-hexane separation.

1. INTRODUCTION

Separation of olefin and paraffin mixtures is one of the most energy-intensive and difficult chemical separations in petrochemical industry due to the very small relative volatilities and close molecular sizes between the olefin and paraffin molecules, and the difference of structure and property between them is weakened with the increase of the carbon number of alkyl chain. Among them, 1-hexene is the co-monomer of linear polyethylene resin, which is the ideal material for the production of packaging film and agricultural covering film.[1] However, the mixture of olefin and paraffin is always found in the process of 1-hexene production.[2,3] Thus, the separation of 1-hexene and n-hexane is really an essential and difficult work.

Typically, the separations of olefin/paraffin mixtures, including 1-hexene/n-hexane mixture, are achieved by cryogenic distillation, which is an energy-intensive and costly process. More than 100 distillation trays and a high reflux ratio are required to achieve polymer-grade products, and the process must be operated at low temperatures and high pressures.[4] Up to now, several other methods, including extractive distillation,[5,6] physical and chemical absorption/extraction,[7–9] adsorption[10–18] and membrane separation,[19–24] were developed. Among these methods, absorption/extraction seems to be the most promising and economical process for olefin/paraffin separation. However, there are a number of disadvantages associated with the traditional volatile absorption/extraction solvents related to the low selectivity for olefin/paraffin separation, solvent losses, stability of the transition metal, and maximum temperature conditions that can be used. Therefore, solvents with high olefin capacity, selectivity, and resistance to contaminants and mild process conditions are still desired.

There is a growing interest in ionic liquids (ILs) due to their unique properties, such as negligible vapor pressure, high thermal and chemical stability, and the feasibility of structure and function tunability. Obviously, ILs have an intrinsic advantage over traditional volatile organic solvents due to the extremely low volatilities and good thermal stabilities, which enable a relatively easy recovery without any loss under appropriate conditions, and without contaminants in the product. Moreover, the physicochemical properties of ILs can also be finely tuned by combining the different cations and anions, or attaching the specific groups to synthesize the functionalized ILs to elevate separation efficiency. All of these unique properties made ILs being applied in many fields, especially in the extraction and absorption separation field.[25–29] ILs have been widely used for the olefin/paraffin separation. Mokrushina et al.[30] used more than 20 ionic liquids as the entrainers in extractive distillation for propene/propane separation. Lei et al.[31,32] used ionic liquids for 1-hexene/n-hexane separation. The selectivity of olefin to paraffin, which was calculated on the basis of activity coefficients at infinite dilution, showed that majority of ILs have the potential to replace conventional entrainers applied for the separation of olefin/paraffin, and the selectivity of 1-hexene to n-hexane reached 3.2 with [Bmim][SCN].[33–35] All the results indicated that the ILs had a high potential for the separation of any low-boiling alkane/alkene mixture. Thus, the IL is expected to become a powerful tool for olefin/paraffin separation. However, the influence of structure of ILs for the olefin/paraffin

Scheme 1. Synthetic Routes of Single-, and Dual-Functionalized Ionic Liquids with NTf$_2^-$ Anion
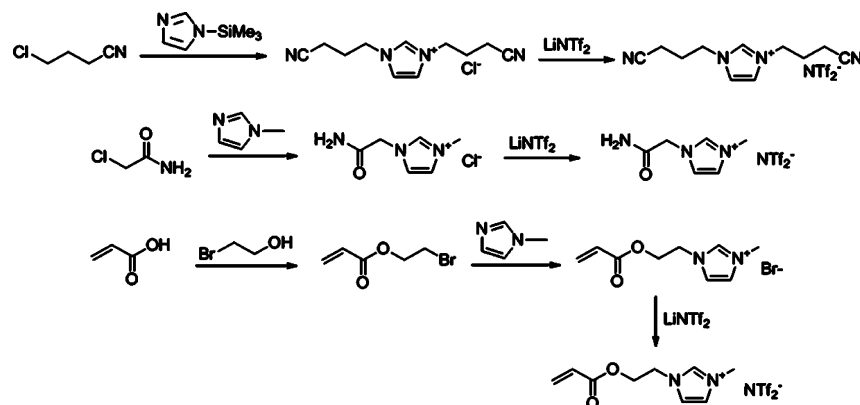
separation has not been extensively explored. Meanwhile, because the silver ion has an ability to bind specifically and reversibly with olefin, and forms a stable bond of π complexes by metal−olefin complex, silver ion or other complexation agents were added into ILs to enhance the capacity and selectivity for olefin. Ortiz et al.[36−38] used [Bmim]BF$_4$ containing silver salts for the separation of propene/propane and cycloolefins/cyclohexane, the selectivity coefficient reached 13 at a pressure of 1 bar for C$_3$H$_6$/C$_3$H$_8$, and the selectivity with [Bmpy][BF$_4$] containing silver salts reached 14.4 for C$_3$H$_6$/C$_3$H$_8$. Galán et al.[39] reported C$_2$H$_4$/C$_2$H$_6$ selectivities for various ILs containing silver salts at different temperatures, and the selectivity in ILs containing silver salt was almost 50 times higher than that in standard ILs at a pressure of 1 bar. All of them found that the ILs containing silver salt had an excellent effect to separate the olefin/paraffin mixture. Moreover, the stabilization of the metal cation was enhanced in ILs compared with organic solvent, and the ILs-Ag medium could be reused many times without any loss of absorption capability.[37,40] Therefore, it has a certain significance to study the 1-hexene and n-hexane separation with ILs containing silver salt.

In this work, we described the investigation on the selective extraction of 1-hexene against n-hexane using ILs as the extractants. The imidazolium-based ILs have been studied widely, and the properties data were comprehensive. Therefore, 17 imidazolium-based ILs with different anions and different lengths of alkyl side chains in the cations were utilized. Especially, several functionalized ILs with unsaturated functional groups, such as carbon−carbon double bond, nitrile, ester, amide, and dual-functional ILs, were prepared (their structures are shown in the Supporting Information, Table S1), and their separation performances were investigated. The effects of the molecular size of anion, the length of alkyl side chain in cation and the structure of functional group on the extraction were evaluated. Furthermore, the silver ion was added into ILs to enhance the 1-hexene and n-hexane separation, and the total concentrations of the hydrocarbon components in the ionic liquids containing different concentration of silver salt at different initial feed compositions were presented.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Reagents. Ionic liquids (chemical names shown in the Supporting Information, Table S1), [C$_4$mim]OAc, [C$_4$mim]PF$_6$, [C$_4$mim]TfO, [C$_4$mim]BF$_4$, [C$_2$mim]TfO, [C$_2$mim]N(CN)$_2$, [C$_2$mim]NTf$_2$, [C$_3$mim]-

NTf$_2$, [C$_4$mim]NTf$_2$, [C$_5$mim]NTf$_2$, [C$_6$mim]NTf$_2$, [Amim]-NTf$_2$, and [CPmim]NTf$_2$ were obtained from Green Chemistry and Catalysis, LICP, CAS (China). All of the ILs were dried under vacuum at 323−343 K for 24 h to remove volatile impurities before use. The water mass fractions of ILs were determined by Karl Fischer titration, and the values are shown in the Supporting Information, Table S1. 1-Hexene, 2-chloroacetamide, 1-methylimidazole, acrylic acid, 2-bromoethanol, and 4-chlorobutyronitrile were purchased from Aladdin Reagent Co., Ltd. (China). n-Hexane was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). 1-(Trimethylsilyl)imidazole was obtained from Shanghai Kangtuo Chemical Co., Ltd. (China). Diethyl ether, dichloromethane, and cyclohexane (analytical grade) were all commercially obtained and used without further purification. The silver salt, AgNTf$_2$, was prepared by the reaction of Ag$_2$CO$_3$ with HNTf$_2$. The properties of the reagents are shown in the Supporting Information, Table S2.

2.2. Preparation of Single-, and Dual-Functionalized ILs. Amino acid-functionalized IL, 1-ethyl-3-methylimidazolium L-α-aminopropionic acid salt ([C$_2$mim]Ala), was synthesized according to the procedure reported by Fukumoto et al.[41] Other functionalized ILs were synthesized according to the procedure reported by Harlow et al.,[42−44] and the procedure is shown in Scheme 1.

Nitrile-functionalized ILs, 1, 3-Dibutyronitrile-imidazolium bis((trifluoromethyl)sulfonyl)imide ([(CP)$_2$im]NTf$_2$). 1-(Trimethylsilyl)imidazole was added drop-by-drop to the 4-chlorobutyronitrile (Cl(CH$_2$)$_3$CN) at 353.15 K under stirring for 24 h, and the resulting white solid was washed with diethyl ether. The product was dried in vacuum at 353.15 K for 24 h, and [(CP)$_2$im]Cl was obtained. Then, equimolar [(CP)$_2$im]Cl with lithium trifluoromethane−sulfonimide aqueous solution was mixed and stirred at room temperature for 10 h to form [(CP)$_2$im]NTf$_2$. The product [(CP)$_2$im]NTf$_2$ was extracted from aqueous solution with dichloromethane. Finally, [(CP)$_2$im]NTf$_2$ was dried under vacuum to remove water and dichloromethane.

Amido-functionalized ILs, 1-Nethylacetamido-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, ([CONmim]-NTf$_2$). 1-Methylimidazole was added drop-by-drop to the solution of 2-chloroacetamide in dry acetonitrile at 353.15 K under stirring for 24 h, the resulting white solid was washed with dichloromethane, and [CONmim]Cl was obtained. Then, equimolar [CONmim]Cl with lithium trifluoromethane−sulfonimide aqueous solution was mixed and stirred at room

Table 1. Phase Equilibrium Data of 1-Hexene (1)/n-Hexane (2)−ILs (3) Biphasic Systems and the Distribution Data of 1-Hexene and n-Hexane in Those Biphasic Systems at 313 K[a]

no.	IL	organic-rich phase			ionic liquid-rich phase			D_1	$S_{1,2}$	water (wt %)
		x_1	x_2	x_3	x_1	x_2	x_3			
					ILs with Different Anions					
1	[C$_4$mim]NTf$_2$	0.500	0.500	0	0.082	0.045	0.873	0.164	1.82	0.04
2	[C$_4$mim]TfO	0.506	0.494	0	0.038	0.019	0.943	0.075	1.95	0.11
3	[C$_4$mim]PF$_6$	0.508	0.492	0	0.021	0.008	0.971	0.041	2.54	0.06
4	[C$_4$mim]BF$_4$	0.506	0.494	0	0.016	0.006	0.978	0.032	2.60	0.09
5	[C$_2$mim]NTf$_2$	0.501	0.498	0.001	0.044	0.020	0.936	0.088	2.19	0.02
6	[C$_2$mim]TfO	0.504	0.495	0.001	0.016	0.007	0.977	0.032	2.24	0.04
7	[C$_2$mim]N(CN)$_2$	0.508	0.492	0	0.008	0.003	0.989	0.016	2.58	0.07
8	[C$_2$mim]Ala	0.507	0.491	0.002	0.009	0.005	0.986	0.018	1.74	0.98
9	[C$_4$mim]OAc	0.503	0.497	0	0.032	0.017	0.951	0.064	1.86	0.64
					ILs with Different Side Alkyl Chain Length or Functional Group in Cation					
10	[C$_6$mim]NTf$_2$	0.497	0.503	0	0.132	0.087	0.781	0.266	1.54	0.04
11	[C$_5$mim]NTf$_2$	0.497	0.499	0.004	0.111	0.072	0.817	0.223	1.55	0.05
12	[C$_3$mim]NTf$_2$	0.500	0.499	0.001	0.055	0.028	0.917	0.110	1.96	0.04
13	[CPmim]NTf$_2$	0.504	0.496	0	0.022	0.011	0.967	0.044	1.98	0.06
14	[Amim]NTf$_2$	0.504	0.493	0.003	0.048	0.023	0.929	0.095	2.04	0.04
15	[(CP)$_2$im]NTf$_2$	0.504	0.493	0.003	0.018	0.008	0.974	0.036	2.22	0.08
16	[AcOxC$_2$mim]NTf$_2$	0.508	0.489	0.003	0.024	0.010	0.966	0.047	2.30	0.10
17	[CONmim]NTf$_2$	0.506	0.489	0.005	0.006	0.002	0.992	0.012	2.93	0.10
18	sulfolane	0.497	0.498	0.0053	0.019	0.009	0.969	0.038	2.12	

[a]Volume ratio of IL, 1-hexene, and n-hexane is 2:1:1.

temperature for 10 h to form [CONmim]NTf$_2$. The product [CONmim]NTf$_2$ was extracted from aqueous solution with dichloromethane. Finally, [CONmim]NTf$_2$ was dried under vacuum to remove water and dichloromethane.

Acrylate-functionalized ILs, 1-Acryloyloxyethyl-3-methyl-imidazolium bis((trifluoromethyl)sulfonyl)imide, ([AcOxC$_2$mim]NTf$_2$). 2-Bromoethanol (1 equiv), 0.1 equiv of *p*-toluenesulfonic acid monohydrate (PTSA), and a few parts per million of 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (TEMPO) were dissolved in cyclohexane and stirred at 353.15 K for 1 h. A solution of 1.2 equiv of acrylic acid and cyclohexane was then added drop-by-drop to the latter mixture, stirring at 353.15 K for 12 h. After cooling, the preparation was washed three times with 10% NaOH aqueous solution. The organic solution was dried on MgSO$_4$, and evaporation under vacuum led to a pure 2-bromo-ethyl acrylate, which was reacted with 1-methylimidazole at 323.15 K over 24 h; the reaction mixture was stirred in diethyl ether, filtered on Büchner, and separated from the organic layer for [AcOxC$_2$mim]Br. Then, equimolar [AcOxC$_2$mim]Br with lithium trifluoromethane−sulfonimide aqueous solution ws mixed and stirred at room temperature for 10 h to form [AcOxC$_2$mim]NTf$_2$, and the product [AcOxC$_2$mim]NTf$_2$ was extracted from aqueous solution with dichloromethane. Finally, the [AcOxC$_2$mim]NTf$_2$ was dried under vacuum to remove water and dichloromethane.

The structures and purities of functionalized ILs were evaluated by ^{1}H NMR spectrum ((CD$_3$)$_2$SO, 500 Hz), which are shown as follows. [C$_2$mim]Ala: 9.99(s, 1H), 7.82(d, 2H), 4.25(q, 2H), 3.87(s, 3H), 2.85(d, 1H), 1.95(d, 2H), 1.39(t, 3H), 1.01(d, 3H). [(CP)$_2$im]NTf$_2$: 9.24(s, 1H), 7.82(d, 2H), 4.25(t, 4H), 2.59(t, 4H), 2.15(m, 4H). [CONmim]NTf$_2$: 9.18(s, 1H), 8.08(s, 1H), 7.71(d, 2H), 7.51(s, 1H), 5.00(s, 2H), 3.89(s, 3H). [AcOxC$_2$mim]NTf$_2$: 9.10(s, 1H), 7.74(s, 1H), 7.68(s, 1H), 6.33(dd, 1H), 6.15(dd, 1H), 6.00(dd, 1H), 4.20(t, 2H), 3.70(t, 2H), 2.50(s, 3H).

2.3. Extraction Equilibrium Experiments. The distribution of 1-hexene and n-hexane in liquid−liquid biphasic system was determined as follows: 3 mL of 1-hexene/n-hexane mixture (1:1, v/v) formed the organic phase. Equal volumes of the IL or IL/silver salt mixture were mixed in an Erlenmeyer flask. The flask was shaken at 313 ± 0.5 K for 8 h in a thermostatic rotary shaker with air bathing device under the speed of 200 rpm and then settled at the same temperature for 2 h. The shaking time was checked to be enough for extraction equilibrium. Samples were taken by buret without disturbing the phase boundary and diluted with the mixture of methanol and acetonitrile (1:4, v/v) for the high-pressure liquid chromatography (HPLC) analysis. In this experiment, the error limits of the volume and mass are estimated to be ±2.5% and ±0.14%, respectively, and the uncertainty of detection with HPLC analysis was ±2.7%. The extraction equilibrium experiments were repeated three times, and the relative uncertainties were usually within 6%, but they were almost 10% when the distribution coefficient of 1-hexene was below 0.04.

2.4. HPLC Analysis. The HPLC system consisted of a manual injector, a SunFire C18 column (5 μm, 4.6 × 250 mm), a Waters 515 HPLC pump, and a Waters 410 differential refraction detector. The mobile phase was a mixture of methanol/acetonitrile/ethylene diamine (20:80:0.2, v/v/v), with the flow rate of 0.4 mL/min. The temperature of column oven was set at 313.15 K. The retention time of the IL, 1-hexene, and n-hexane were 5.5, 10.5, and 12.5 min, respectively.

3. RESULTS AND DISCUSSION

Preliminary experiments were carried out and showed that the extraction equilibrium was almost achieved within 5 h with [C$_6$mim]PF$_6$, which has a high viscosity of 690 cP at 293.15 K,[45] and the viscosity of the other tested ILs in this study were all below 690 cP. Thus, the extraction time was set at 8 h in all experiments. The distribution coefficient data of 1-hexene and n-hexane in IL and 1-hexene/n-hexane biphasic system were

determined, and the results are presented in Table 1. The distribution coefficient of solute i (D_i) and the selectivity of solute i to solute j ($S_{i,j}$) were calculated using eqs 1 and 2:

$$D_i = x_i^{IL}/x_i^{org} \tag{1}$$

$$S_{i,j} = D_i/D_j \tag{2}$$

where x_i^{IL} and x_i^{org} stand for the molar fractions of solute in the IL phase and in the organic phase, respectively.

As shown in Table 1, the selectivity coefficients of most ILs for 1-hexene/n-hexane separation are between 1.5 and 3.0, showing that ILs exhibits obvious effect for 1-hexene/n-hexane separation under the studied conditions, and from the result, we can find that the distribution coefficient of 1-hexene in ILs with NTf_2^- as anion is greater than the others; it even reaches 0.27 for [C_6mim]NTf_2.

Also, the separation of 1-hexene/n-hexane in sulfolane was detected in this work, and the result is shown in Table 1, as well. It can be found that, in most ILs, there were larger distributions of 1-hexene than that in sulfolane, and half of ILs had greater selectivities of 1-hexene to n-hexane than in sulfolane, as well.

The selectivity coefficients of 1-hexene/n-hexane in [C_4mim]NTf_2, [C_4mim]OAc, [C_2mim]NTf_2, and [C_2mim]-TfO were similar with the results calculated on the basis of activity coefficients at infinite dilution in some ILs, which were 1.8 in [C_4mim]NTf_2,[35] 2.1 in [C_4mim]OAc, and so on,[46−48] but they were smaller than those that were obtained using the COSMO-RS model, which were larger than 2.5.[31]

3.1. Influence of the Anion. As shown in Figure 1, ILs with different properties of anions had significant effect on the
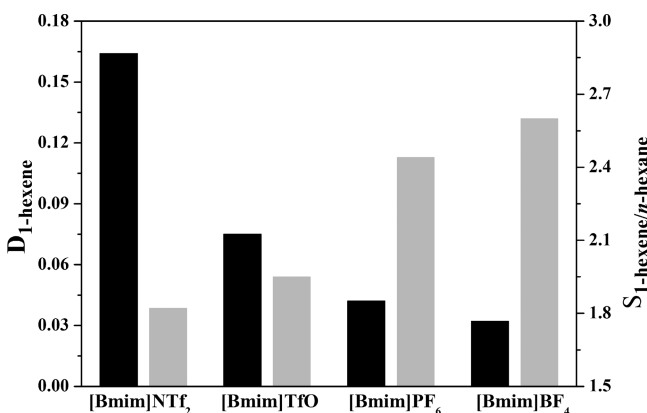
Figure 1. Effect of molecular weight and polarity of anion in [C_4mim]-based ILs on the distribution data of 1-hexene and n-hexane in IL-1-hexene/n-hexane biphasic systems at 313 K. Volume ratio of IL, 1-hexene, and n-hexane is 2:1:1. Black: the distribution coefficient of 1-hexene in biphasic systems. Gray: the selectivity of 1-hexene to n-hexane in biphasic systems.

distribution of 1-hexene in the biphasic systems. When the cation was the same ([C_4mim]$^+$, entries 1, 2, 3, and 4 in Table 1), the distribution coefficient of 1-hexene in the biphasic system followed the order: [C_4mim]NTf_2 > [C_4mim]TfO > [C_4mim]PF$_6$ > [C_4mim]BF$_4$. On the one hand, it is contributed to the molecular weight of anion. It is well-known that the van der Waals interaction between ILs and 1-hexene or n-hexane increases with the increase of the molecular weight of IL, which causes an increase of the distribution of 1-hexene and n-hexane in ILs. The molecular weights of different anions follow the

order BF_4^- < PF_6^- < TfO^- < NTf_2^-, which is in agreement with the order of the distribution coefficient of 1-hexene in the biphasic system. On the other hand, the polarity of the anion significantly influences the distribution of 1-hexene in ILs with the same cation. The polarity of [C_4mim]$^+$-based ILs follows the order [C_4mim]BF$_4$ > [C_4mim]PF$_6$ > [C_4mim]TfO > [C_4mim]NTf_2.[49] Since both 1-hexene and n-hexane are nonpolar molecules, the [C_4mim]NTf_2 with less polarity has the strongest affinity with two hydrocarbons, which is favorable for the distribution of 1-hexene in the IL phase. However, [C_4mim]BF$_4$ has the largest polarity compared with other ILs, so the distribution coefficient of 1-hexene in the biphasic system is relatively lower.

At the same time, it was found that the IL system that had a larger distribution of 1-hexene had the relatively lower selectivity for 1-hexene against n-hexane, as shown in Figure 1. The order of selectivity of 1-hexene to n-hexane with the [C_4mim]-based ILs was [C_4mim]BF$_4$ > [C_4mim]PF$_6$ > [C_4mim]TfO > [C_4mim]NTf_2, which agrees with the experimental results calculated on the basis of activity coefficients at infinite dilution in the same ILs[50] but was different from the predicted data using the COSMO-RS model.[31,32] According to the Prausnitz and Anderson's solution thermodynamic theory,[51] the contributions of physical force to the selectivity of olefin/paraffin separation included the polar effect, dispersion effect, and inductive effect of the entrainer, and the polarity of entrainer had a greater influence than the sum of the others on the selectivity for 1-hexene/n-hexane separation. Therefore, the higher selectivity was found with the higher polarity of IL. As mentioned, the polarity of [C_4mim]-based ILs follows the order [C_4mim]BF$_4$ > [C_4mim]PF$_6$ > [C_4mim]TfO > [C_4mim]NTf_2; therefore, the selectivity of 1-hexene to n-hexane has the same order. Furthermore, the hydrogen-bond interaction between the extractant and the H on the unsaturated double bond (HC=CH···X, where X = NH_3, OH_2, FH, and so on)[52] will affect the separation of 1-hexene/n-hexane. In all of the ILs, anion BF_4^- has the highest electron cloud density on the F atom and has the strongest hydrogen-bond interaction with the H on the unsaturated double bond. Thus, [C_4mim]BF$_4$ has the highest separation selectivity for 1-hexene/n-hexane. However the electron-attracting group S=O in the anion NTf_2^- and TfO^- leads to relatively lower electron density on the F atom and reduces the hydrogen-bond interaction, and makes a lower selectivity for 1-hexene/n-hexane.

As shown in Table 1, the functional groups in anions also have significant effects on the separation of 1-hexene and n-hexane. The CN group functional IL [C_2mim]N(CN)$_2$ has a relatively higher selectivity for 1-hexene/n-hexane compared with that of [C_2mim]NTf_2 and [C_2mim]TfO (entries 5, 6, and 7 in Table 1), and the selectivity coefficient reaches 2.58, but the distribution of 1-hexene in biphasic system falls slightly. It was in compliance with the result of propene/propane separation with ILs.[30] The increase of selectivity is probably due to the specific π−π interaction between the CN group and the unsaturated double bond of 1-hexene and the polarity of IL is high with CN group. However, the CN- is a strong hydrophilic group and markedly enhances the hydrophilicity of IL, which does not favor the distribution of 1-hexene into ILs phase. Besides, when Ala$^-$ is utilized as an anion, both the distribution coefficient and the selectivity decreased compared with that of [C_2mim]NTf_2 and [C_2mim]TfO (entries 5, 6, and 8 in Table 1).

3.2. Influence of the Alkyl-Side Chain of the Imidazolium Cation. The cations of ILs also have an effect on the separation according to the data shown in Table 1.

Mokrushin et al.[30] found that the side alkyl chain lengths in cations have great influence on the separation of olefin/paraffin. Therefore, in order to analyze the effect of the side alkyl chain lengths in cations, different 1-alkyl-3-methylimidazolium salts of the general type [Rmim]NTf$_2$ (R = ethyl, propyl, butyl, pentyl, and hexyl) were selected to separate 1-hexene and n-hexane (entries 1, 5, 10, 11, and 12 in Table 1). The experimental results are shown in Figure 2. With the increase in the length of
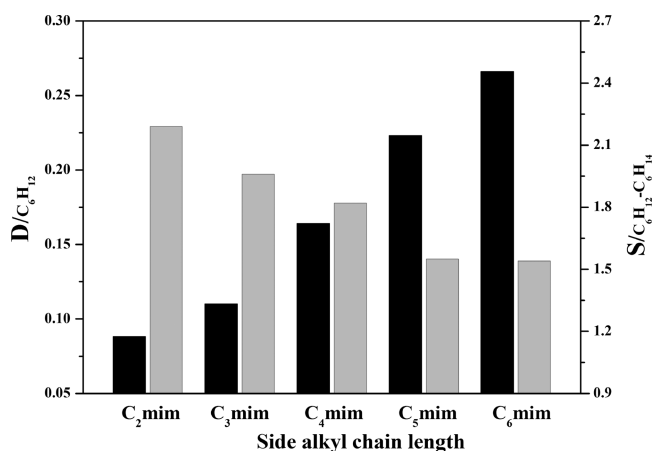

Figure 2. Dependence of the distribution coefficients of 1-hexene and the selectivity of 1-hexene to n-hexane on the length of the alkyl side chain of the imidazolium cation at 313 K. The volume ratio of IL, 1-hexene, and n-hexane is 2:1:1. Black: the distribution coefficient of 1-hexene in biphasic systems. Gray: the selectivity of 1-hexene to n-hexane in biphasic systems.

alkyl side chain, the distribution coefficient of 1-hexene in biphasic system increases remarkably from 0.088 to 0.266, and the selectivity of 1-hexene to n-hexane decreases slightly. This phenomenon is in consistent with the propene/propane[30] and 1-hexene/n-hexane separation results[35] and the predicted result using COSMO-RS model.[32] It results from the fact that when the side alkyl chain length of a cation increases, the van der Waals interaction between IL and 1-hexene/n-hexane increases, which improves the distribution of 1-hexene in the IL phase. Thus, it is helpful to increase the extraction capacity of ILs by increasing the alkyl chain length. However, the steric shielding effect with the long alkyl chain length of cations will inhibit the π−π interaction between imidazole center and C=C double bond and lead to a lower selectivity.

As mentioned, the ILs with a nitrile functional group had a high selectivity for 1-hexene/n-hexane, thus, several NTf$_2$-based ILs with unsaturated functional groups, such as carbon−carbon double bond, nitrile, ester, amide, were prepared (their structures are shown in Supporting Information, Table S1) and used as extractants. The experimental results show that the functional ILs have a larger effect on the selectivity of 1-hexene/n-hexane (entries 13, 14, 16, and 17 in Table 1). The selectivity coefficient of [Amim]NTf$_2$ for 1-hexene/n-hexane is larger than that of [C$_3$mim]NTf$_2$, enhanced from 1.96 to 2.04, because of the functional effect of carbon−carbon double bond. When the single nitrile, amide, or ester group is introduced into cation, the selectivity for 1-hexene/n-hexane is enhanced obviously, especially, the amide functional IL [CONmim]NTf$_2$

reaches a selectivity coefficient of almost 3. It is probably due to the specific interaction between the functional group of ILs and the unsaturated double bond of 1-hexene. Also, the strong hydrophilic functional group would markedly enhance the polarity of IL, so that the selectivity of 1-hexene to n-hexane enhances according to the Prausnitz and Anderson's solution thermodynamic theory. Thus, a 1,3-dual functionalized IL with two nitrile groups, [(CP)$_2$im]NTf$_2$, was synthesized to further improve the selectivity for 1-hexene against n-hexane. As shown in Table 1 (entry 15), the selectivity coefficient increases from 1.98 with single-functionalized IL [CPmim]NTf$_2$ to 2.22 with the 1,3-dual functionalized IL [(CP)$_2$im]NTf$_2$. The experimental results indicated that the functional groups had positive effect on 1-hexene/n-hexane separation selectivity. Nevertheless, the distribution coefficients of 1-hexene in these biphasic systems decreased simultaneously.

3.3. Influence of Silver Salt on Extraction. To improve the capacity of extraction for 1-hexene, a complexation agent (Ag$^+$) was added to the ILs. Because the viscosity of IL increased when the silver ion was added in it, and this may present mass-transfer and pumping difficulties, we added silver ion to [C$_4$mim]NTf$_2$, which has the lower viscosity and higher solubility of 1-hexene, and the separation performance was studied. All the experimental results showed that ILs containing silver ion (AgNTf$_2$) have much higher capacity for 1-hexene than n-hexane at 313 K, due to a chemical interaction between the 1-hexene and silver ion.

The effect of the silver ion concentration on the 1-hexene/n-hexane extraction was investigated, and the results are shown in Figure 3. It is shown that the IL with a higher concentration of
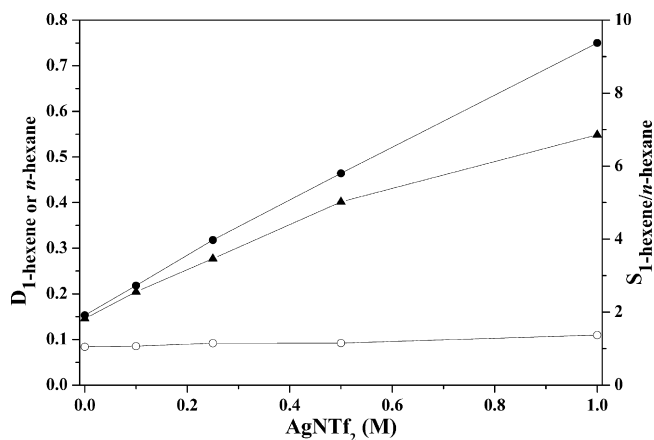

Figure 3. Influence of silver salt concentration in [C$_4$mim]NTf$_2$-Ag on the distribution coefficient of 1-hexene and selectivity of 1-hexene to n-hexane at 313 K. Volume ratio of [C$_4$mim]NTf$_2$-Ag, 1-hexene, and n-hexane is 2:1:1. (●) the distribution coefficient of 1-hexene in biphasic systems; (○) the distribution coefficient of n-hexane in biphasic systems; (▲) the selectivity of 1-hexene to n-hexane in biphasic systems.

silver ion has a larger distribution coefficient of 1-hexene, which is attributed to the fact that more interaction sites are available for 1-hexene with the increase of the concentration of silver ion. The distribution coefficient of 1-hexene reached 0.317 in [C$_4$mim]NTf$_2$-Ag [0.25 M], which was twice as large as in [C$_4$mim]NTf$_2$. The distribution coefficient of n-hexane changed slightly with the increase of the concentration of silver ion, however, which meant that there was only a physical interaction between n-hexane and ILs containing silver salt

(Figure 3). Furthermore, a salting out effect was not observed, because the presence of the salt did not decrease the solubility of *n*-hexane in IL phase. Thus, both the distribution coefficients of 1-hexene and selectivity coefficients of 1-hexene to *n*-hexane increased when the concentration of silver salt AgNTf$_2$ in the IL increased.

The liquid−liquid equilibrium experiments for the ternary systems (1-hexene/*n*-hexane/IL or 1-hexene/*n*-hexane/IL containing silver salt [0.25 M]) were carried out with different initial feed compositions, in which the concentration of 1-hexene was in the range 5−95% (v/v). The experimental data are shown in the Supporting Information, Table S3. These experiments were performed following the same procedure described in extraction equilibrium experiments above. It can be found that when the silver ion concentration is 0.25 mol/L, the lower the content of 1-hexene in the feed composition, the higher the selectivity obtained for 1-hexene/*n*-hexane. It was because the chemical complexation played a more significantly role on the distribution of two aliphatic hydrocarbons compared with the physical solubility effects, and the total concentration of 1-hexene in IL phase was much greater than that of *n*-hexane and got the higher selectivity. However, when the content of 1-hexene in the feed was higher, the silver sites became saturated via interaction with 1-hexene; thus, the distribution of 1-hexene and *n*-hexane in IL containing silver salt was dominated by physical solubility effect, and higher 1-hexene content resulted only in increased physical absorption. At the volume fraction of 1-hexene over 0.8 in feed, the selectivity started to level out.

Figure 4 shows the total concentrations of 1-hexene or *n*-hexane in [C$_4$mim]NTf$_2$-Ag or [C$_4$mim]NTf$_2$ with the mole

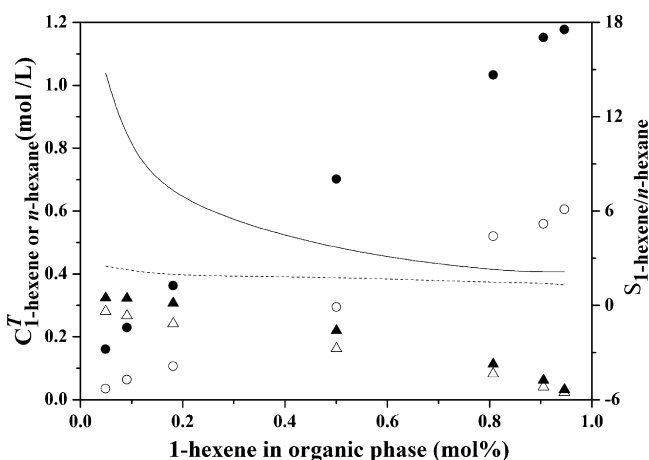**Figure 4.** Total concentrations of 1-hexene and *n*-hexane in [C$_4$mim]NTf$_2$ with or without AgNTf$_2$ with the mole ratio of 1-hexene and *n*-hexane in organic phase. Initial feed composition of 1-hexene and *n*-hexane between 5% and 95%; volume ratio of biphase is 1:1. (●) 1-hexene in [C$_4$mim]NTf$_2$-Ag [0.25 M]; (○) 1-hexene in [C$_4$mim]NTf$_2$; (▲) *n*-hexane in [C$_4$mim]NTf$_2$-Ag [0.25 M]; (△) *n*-hexane in [C$_4$mim]NTf$_2$. Solid: the selectivity of 1-hexene to *n*-hexane in [C$_4$mim]NTf$_2$-Ag [0.25 M]. Dash: the selectivity of 1-hexene to *n*-hexane in [C$_4$mim]NTf$_2$.

ratio of 1-hexene and *n*-hexane in organic phase at equilibrium. As expected, in both cases, the total concentrations of two aliphatic hydrocarbons changed linearly with the mole ratio of 1-hexene and *n*-hexane in organic phase, especially of the 1-hexene. The total concentration of 1-hexene in IL containing

silver salt was much larger than that of *n*-hexane, and the total concentration of *n*-hexane almost kept constant in IL containing silver salt compared with free-based IL at the same mole ratio, which confirmed again that there was only physical interaction in *n*-hexane and IL containing silver salt system, and it would be correct to assume that the solubility of *n*-hexane in the IL containing silver salt was the same as in the silver-free IL.

With the experimental data, the phase diagrams for 1-hexene + *n*-hexane + [C$_4$mim]NTf$_2$ and 1-hexene + *n*-hexane + Ag-[C$_4$mim]NTf$_2$ are shown in Figure 5. We can see that the miscible range is larger with the IL containing silver than the IL without silver. The solubility of 1-hexene was larger in the IL containing silver, but the content of *n*-hexane in IL phase almost kept constant.

To successfully describe the absorption process of 1-hexene with physical and chemical effects, an equilibrium model was developed.[7,53] The 1-hexene reacts with the silver ion forming π-complexes in the silver-[C$_4$mim]NTf$_2$ mixture, and it is described by the following reaction:

$$Ag^+ + C_6H_{12} \leftrightarrow Ag^+(C_6H_{12}) \quad \text{primary complexation}$$
(3)
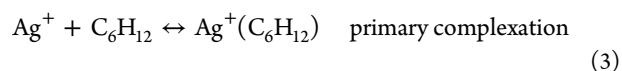
When 1-hexene concentration is high or the silver load is high, the secondary and tertiary complex species might be formed through consecutive reactions of the primary complex with another molecule of 1-hexene or silver ion, but Wentink et al.[53] found that in C6-olefin isomer 1-hexene also produces 1:2 complexes with silver ion, and Sunderrajan et al.[54] characterized the complexation of 1-hexene with silver using infrared spectroscopy and showed that there was no indication that the tertiary complex was formed between 1-hexene and silver ion. Ortiz et al.[37] applied an equilibrium model without tertiary complex to correlate the solubility of propylene in IL containing silver salt with a satisfying fitting result. Therefore, an assumption of without tertiary complex is made in this model.

$$Ag^+(C_6H_{12}) + C_6H_{12} \leftrightarrow Ag^+(C_6H_{12})_2$$

$$\text{secondary complexation}$$
(4)
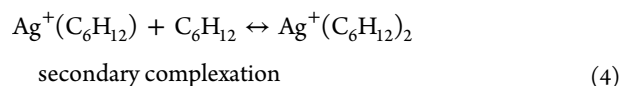
The equilibrium constants are defined as

$$K_{Eq1} = \frac{[Ag^+(C_6H_{12})]}{[Ag^+][C_6H_{12}]}$$
(5a)

$$K_{Eq2} = \frac{[Ag^+(C_6H_{12})_2]}{[Ag^+(C_6H_{12})][C_6H_{12}]}$$
(5b)

The total concentration of 1-hexene is consisted of physical solubility and chemical complexation with silver ion:

$$[C_6H_{12}]^T = [C_6H_{12}] + [Ag^+(C_6H_{12})] + 2[Ag^+(C_6H_{12})_2]$$
(6)

Combining eqs 5 and 6 obtains

$$[C_6H_{12}]^T = [C_6H_{12}](1 + K_{Eq1}[Ag^+] + 2K_{Eq1}K_{Eq2}[Ag^+]$$

$$[C_6H_{12}])$$
(7)

The concentration of free silver ion can be found by the total concentration of the silver ion minus the silver concentrations in the primary and secondary complexes.
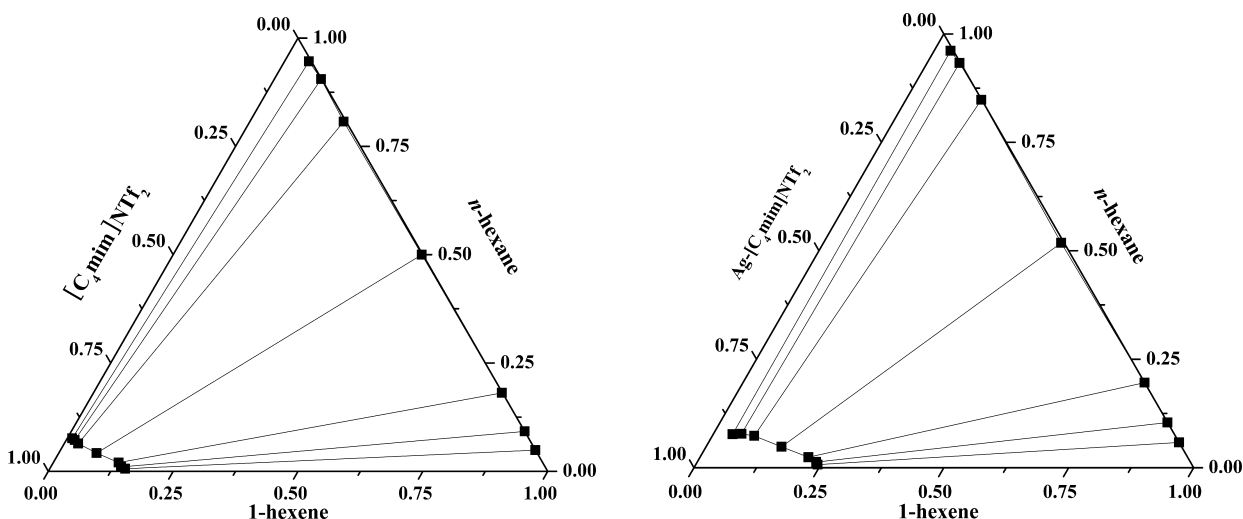
Figure 5. Tie lines for the ternary mixture of 1-hexene + n-hexane + $[C_4mim]NTf_2$ (left) and 1-hexene + n-hexane + Ag-$[C_4mim]NTf_2$ (right) at T = 313.15 K.

$$[Ag^+] = [Ag^+]^T - [Ag^+(C_6H_{12})] - [Ag^+(C_6H_{12})_2] \quad (8)$$

Combining eqs 5 and 8 obtains

$$[Ag^+] = \frac{[Ag^+]^T}{1 + K_{Eq1}[C_6H_{12}] + K_{Eq1}K_{Eq2}(C_6H_{12})^2} \quad (9)$$

Combining eqs 7 and 9 gives the total 1-hexene concentration as a function of the physically solubility of 1-hexene and concentration of the silver ion (eq 10), and the equilibrium constants can be determined by fitting with nonlinear least-squares method using the software Matlab R2009b.

$$[C_6H_{12}]^T = [C_6H_{12}]$$
$$\times \left(1 + \frac{K_{Eq1}[Ag^+]^T + 2K_{Eq1}K_{Eq2}[Ag^+]^T(C_6H_{12})}{1 + K_{Eq1}[C_6H_{12}] + K_{Eq1}K_{Eq2}(C_6H_{12})^2}\right)$$
$$(10)$$

Using the experimental data and Figure 4, the equilibrium constants for the primary and secondary complexation reactions were calculated, and the values were 2.78 and 35.24, respectively. The accuracy of the calculation results is presented in the parity graph shown in Figure 6; the correlation coefficient value R^2 is 0.9863, and the average absolute deviation is 9.1%. The equilibrium constants suggest that the formation of the secondary complex species is more favorable than the primary complex under similar operation conditions, which is consistent with the result of the experimental characterization of 1-hexene complexation with silver salt in solution.[54]

The experimental data were correlated using the nonrandom two liquid equation (NRTL),[55] the equation for a solution of m components is

$$\ln \gamma_i = \frac{\sum_{j=1}^m x_j \tau_{ji} G_{ji}}{\sum_{k=1}^m x_k G_{ki}} + \sum_{j=1}^m \frac{x_j G_{ji}}{\sum_{k=1}^m x_k G_{kj}}$$
$$\times \left(\tau_{ji} - \frac{\sum_{r=1}^m x_r \tau_{rj} G_{rj}}{\sum_{k=1}^m x_k G_{ki}}\right) \quad (11)$$
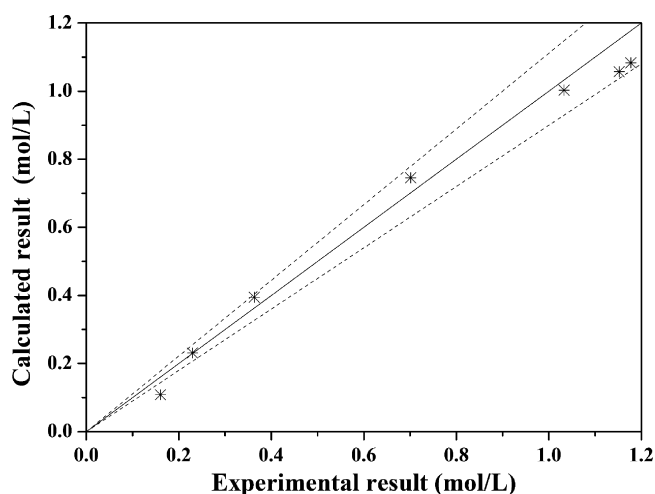
Where

Figure 6. Parity graph of 1-hexene for calculated and experimental equilibrium values in $[C_4mim]NTf_2$- $AgNTf_2$ [0.25 M].

$$G_{ji} = \exp(-\alpha_{ij}\tau_{ji}) \quad G_{Ii} = 1 \quad \tau_{ji} = a_{ij} + b_{ij}/T \quad \tau_{Ii} = 0$$

$$\alpha_{ij} = \alpha_{ji}$$

where x = the mole fraction, α_{ij} = the nonrandomness parameter, γ = the activity coefficient, τ = the interaction parameter, and i, j, k = the component indices.

The binary parameters of the NRTL equation (α_{ij}, a_{ij}, a_{ji}, b_{ij}/K, and b_{ji}/K) were determined via data regression using ASPEN Plus V7.0 and are shown in the Supporting Information, Table S4. Since the IL has no vapor pressure and its concentration in the organic phase is close to zero, the parameter regression is not asked to fulfill the equation for the equality of the fugacity for the IL. The experimental and correlated tie-lines in a triangular diagram are shown in Figure 7.

The root-mean-square deviation (rmsd) is defined as

$$rmsd = \left\{\sum_i \sum_j \sum_k (x_{ijk}^{exp} - x_{ijk}^{calc})^2/6n\right\}^{1/2}$$
$$(12)$$

where x is the mole fraction; the subscripts i, j, and k provide a designation for the component, phase, and the tie lines, respectively. The value n designates the number of tie lines.
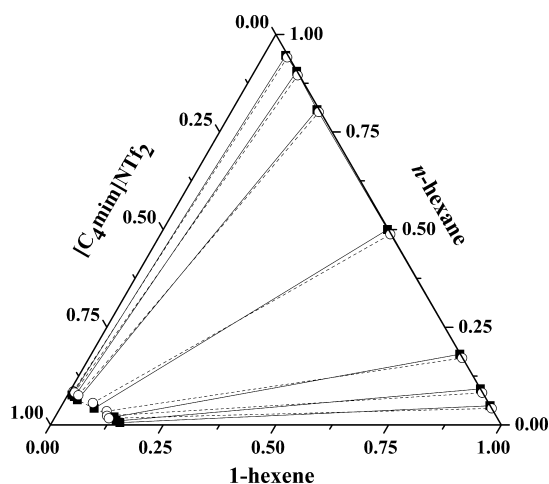
Figure 7. Tie lines for the ternary mixture of 1-hexene + *n*-hexane + [C₄mim]NTf₂ at *T* = 313.15 K. Experiments: ■, dashed lines; calculated: ○, solid lines.

The value of rmsd was 0.012 and provides the goodness of fit of the correlations, but it is slightly larger than the other system.[55,56]

4. CONCLUSIONS

The 1-hexene/*n*-hexane extraction separation by means of IL extractants was carried out. It showed that ILs had a significant effect for the separation of 1-hexene/*n*-hexane. All of the ILs dissolved 1-hexene preferably compared to *n*-hexane, and most of the selectivity of 1-hexene to *n*-hexane was above 2.0 under the experimental conditions. The distribution coefficient of 1-hexene in ILs with NTf₂⁻ as anion was greater than the others; it even reached 0.27 for [C₆mim]NTf₂. However, the distribution coefficients of 1-hexene in ILs were low, which might cause a large consumption of ILs in the extraction processes.

The studies showed that different anion and cation of IL had the effect on the extraction. The size, polarity, and functional group of anion had significant effect on the distribution of 1-hexene and *n*-hexane. Also, with the increase of the length of alkyl side chain on cation, the distribution of 1-hexene in biphasic system increased remarkably, the distribution of 1-hexene in [C₆mim]NTf₂ was three times that in [C₂mim]NTf₂. The cations with the functional groups, such as carbon−carbon double bond, nitrile, and amide, have enhanced the selectivity coefficient of 1-hexene to *n*-hexane, and the dual-functional IL had a higher selectivity than the single functional IL in 1-hexene/*n*-hexane extraction, but the distribution coefficients of 1-hexene in biphasic system decreased because of the high polarity of these groups.

Furthermore, ILs containing silver salt performed much better than standard ionic liquids in the selective extraction of 1-hexene/*n*-hexane. The higher silver ion concentration leads to a higher distribution of 1-hexene and selectivity of 1-hexene to *n*-hexane. The simple mathematical model that has been developed to describe the total 1-hexene concentration in IL containing silver salt showed that the formation of the secondary complex species was more favorable than the primary complex, this induced that the IL containing silver salt had a tremendous selectivity for 1-hexene against *n*-hexane, the selectivity coefficient even reached 15 when the

concentration of 1-hexene was 5% (v/v) in the initial feed at 313 K.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Chemicals and reagents used in this work, experimental liquid−liquid equilibrium data with different initial feed composition and the binary parameters and rmsd of the NRTL equation used to correlate the experimental data. This information is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ NOMENCLATURE

K_{Eq} = complexation equilibrium constant (l mol⁻¹)
x = molar concentration (mol %)

Superscript/Subscript

IL = ionic liquid phase
org = organic phase
1, 2 = reaction identification
Eq = equilibrium

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