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Investigation on the feasibility of separation process for extracting benzene from hexane/heptane by ionic liquids

Yong-Bin Ri*, Jin-Gun Rim, Gyong-Sim Yu, Song-Min Kim & Jong-Guk Won
Faculty of Chemistry, Kim Il Sung University, Pyongyang, DPR Korea
*E-mail: yb.ri0614@ryongnamsan.edu.kp

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UNIFAC-Lei model has been employed for the prediction of liquid-liquid equilibrium (LLE) of ternary systems of (benzene +hexane/heptane + ionic liquids IL) for the screening of ILs which can be used as potential solvents in the extraction process of benzene from stream of hydrocarbons. The capability of UNIFAC-Lei model to predict the LLE of ternary systems is evaluated, and it is shown that UNIFAC-Lei model allowed the fast appropriate descriptions of the LLE experimental data for the systems studied in this work. The conceptual extraction process for the separation of benzene and heptane/hexane using an IL is simulated via Aspen PlusV11.0. The results showed that [EMIM][NTf$_2$] was the best solvent for separating benzene from aliphatic hydrocarbons and the content of benzene in the extract can be achieved 83.3 wt% for the mixture with hexane and 94.7 wt% for the mixture with heptane from the feed containing 20 wt% of benzene, respectively.

Keywords: Extraction, Ionic liquid, LLE, Simulation, UNIFAC-Lei

Introduction

The separation of aromatic and aliphatic compounds presented in the refinery with naphtha cuts is an important problem because the gasoline requires the more aromatic compound than aliphatic compound to achieve a higher octane number. It is also challenging since these hydrocarbons have close boiling points and several systems of aromatic and aliphatic compounds form azeotropes[1-4]. Traditionally, volatile organic compounds (VOCs) such as sulfolane, dimethylsufoxide, N-methyl pyrrolidone, methyl carbonate, etc.[5] have been used for the separation of aromatic and aliphatic compounds, but they have harmful effects on the environment. Thus, replacement of VOCs in the separation of aromatic and aliphatic hydrocarbons by the effective and environmentally benign solvents is crucial for sustainable development[6-9].

ILs have been increasingly investigated as the promising solvents in these separation technologies for their unique properties such as negligible vapour pressure, high thermal and chemical stability, and good solvating ability[10-15]. Such applications require accurate knowledge of the physical properties of mixtures with ILs. In this respect, the estimation of LLE behaviour especially in the presence of ILs is an important stage because it can supply the concrete parameters to resolve the conceptual process design of IL-based extraction[16-19]. So, thermodynamic modelling of LLE data is essential for the design, optimization and operation of these processes.

Many publications have concerned LLE data for ternary systems of aromatic and aliphatic compounds containing ILs[1-4, 20-24] . Letcher and Deenadayalu[25] measured LLE data for three ternary systems of (benzene + alkanes + [Moim][Cl]), where the alkanes were heptane, dodecane and hexadecane. Alberto *et al.* [26] determined the LLE data for systems involving hexane, benzene, and [C$_n$mim][NTf$_2$] and reported that [Emim][NTf$_2$] with the shortest alkyl chain was the most suitable solvent to carry out the targeted separation. Garcia et al.[27] measured the ternary LLE data for hexane and benzene with [Bmim][MeSO$_4$] and discussed that higher selectivity values than that of the sulfolane system would lead to fewer stages and better purity when the IL is used as a solvent. They used the NRTL and UNIQUAC model for the correlation of these experimental data, which obtained from direct measurement of LLE data. In fact, though an increasing amount of experimental LLE data for the separation of mixtures with ILs as solvents is becoming available, experimental measurements for all these systems are impracticable because there are the huge number of possible combinations of ILs and hydrocarbons.

In recent years, significant surveys have been carried out on the analysis and prediction of LLE data for ternary IL-based systems by the two main predictive approaches such as UNIFAC-Lei[28,29] and COSMO-RS model[30]. UNIFAC-Lei is generally selected over COSMO-RS due to its greater accuracy, if the necessary binary group interaction parameters exist for every pair of functional groups in the mixture, since it is a semiempirical approach where the parameters are already derived from experimental data[28]. Lei *et al.*[29] studied the UNIFAC-Lei model for IL-based systems and offered the new group interaction parameters into the current UNIFAC-Lei parameter matrix. It is sufficient to study the LLE of benzene and heptane/hexane containing many ILs and evaluate the availability of the IL-based extraction process for the separation. However, to our knowledge, the study on the systematic methodology about the IL-based extraction process using UNIFAC-Lei model has not been reported.

This work presents the phase behaviour prediction and extraction process simulation with ILs to separate benzene and heptane/hexane mixtures. The main purpose of the first part of this work is to examine the practicability of the UNIFAC-Lei model for the extraction of benzene and heptane/hexane mixtures as study object. In the second part of this work, this model is associated with the conceptual process design for the separation of benzene and heptane/hexane mixtures.

Experimental Section

UNIFAC Model

For liquid mixtures, UNIFAC model computes the activity coefficient of liquid mixtures in terms of constants which reflects the size and surface area of individual functional groups present in the mixture[31]. The activity coefficient can be calculated according to Eq. (1).

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad \ldots(1)$$

where γ_i^C represents the combinatorial contribution to the activity coefficient due to differences in the sizes and shapes of the groups, and $\ln\gamma_i^R$ represents the residual contribution from energetic interactions. The part $\ln\gamma_i^C$ contains the group parameters R_k and Q_k, and the values show the shape and size for the individual groups consisting of mixture. The part $\ln\gamma_i^R$ is a function of binary interaction parameters between groups, and the group interaction parameter ψ_{nm} is expressed as follows:

$$\psi_{nm} = \exp\left[-\left(a_{nm} / T\right)\right] \quad \ldots(2)$$

where, T is the absolute temperature, a_{nm} is the temperature-independent parameter for each pair of functional groups j and k, and $a_{nm} \neq a_{mn}$.

UNIFAC-Lei Model for IL-Based Systems

ILs have to be decomposed to functional group when using the UNIFAC-Lei model, in which three division methods can be used to predict the phase behaviour of IL-based systems. In the first division method, the IL is divided into one cation and one anion groups[32, 33], which approach does not reflect the influence of structural variation of substituents on the cation or anion on the separation performance. In the second division method, the IL is divided into cation core, anion and several CH_2 and CH_3 groups[34,35], which approach requires a large number of experimental data used to correlate the group interaction parameters. In the third method, the skeleton of cation and anion is treated as a whole, and the alkyl chain is divided into separate CH_2 and CH_3 groups[28, 29], which approach can be well reflected the electrical neutral groups of ILs. The approach using the third division method is called UNIFAC-Lei model and fragmentations of ILs are listed in Table 1. ILs [EMIM][NTf_2], [BMIM][NTf_2], [OMIM][NTf_2], [DMIM][NTf_2], [BMPY][NTf_2], [OMIM][Cl], and [HMIM][BF_4] have been constructed from the new [MIM][NTf_2], [MPY][NTf_2], [MIM][Cl], and [MIM][BF_4] groups combined with the established CH_2 and CH_3 groups already used in the UNIFAC-Lei model. The parameter R_k and Q_k for the groups investigated in this work can be found in the literature[28], as listed in Table 2. The group interaction parameters (a_{mn}anda_{nm}) between each pair of functional groups in their mixture with benzene and heptane/hexane and ILs are listed in Table 3 (Ref.28) The simulation procedure is given in the Supplementary Document.

Extraction Process Simulation

With the aim of separating the benzene from hexane/heptane by means of the best IL as an

Table 1 — Group division of ILs

ILs	Group division
[EMIM][NTf_2]	[MIM][NTf_2] + CH_2 + CH_3
[BMIM][NTf_2]	[MIM][NTf_2] + 3CH_2 + CH_3
[OMIM][NTf_2]	[MIM][NTf_2] + 7CH_2 + CH_3
[DMIM][NTf_2]	[MIM][NTf_2] + 9CH_2 + CH_3
[BMPY][NTf_2]	[MPY][NTf_2] + 9CH_2 + CH_3
[OMIM][Cl]	[MIM][Cl] + 7CH_2 + CH_3
[HMIM][BF_4]	[MIM][BF_4] + 5CH_2 + CH_3

Table 2 — Parameters of R_k and Q_k

Group	R_k	Q_k
CH_3[a]	0.9011	0.8480
CH_2[a]	0.6744	0.5400
ACH[a]	0.5313	0.4000
[MIM][NTf_2]	8.3145	7.3920
[MPY][NTf_2]	6.7248	5.5793
[MIM][Cl]	5.7073	4.9741
[MIM][BF_4]	6.5669	4.0050

Table 3 — Group interaction parameters for the UNIFAC-Lei model[28]

m	n	a_{mn}	a_{nm}
CH_2	[MIM][NTf_2]	400.89	145.80
CH_2	[MPY][NTf_2]	327.30	301.96
CH_2	[MIM][Cl]	2093.97	1129.0
CH_2	[MIM][BF_4]	1108.51	588.74
ACH	[MIM][NTf_2]	602.87	-163.26
ACH	[MPY][NTf_2]	998.04	-131.54
ACH	[MIM][Cl]	418.17	526.13
ACH	[MIM][BF_4]	1494.39	85.64

extraction solvent, a simulation of the process was carried out by using the Aspen PlusV11.0 software. Liquid extractor was the operation unit selected, and it was isothermal at 298.15 K and 101.32 kPa. The feed simulated had 80 wt% of hexane/heptane and a 100 kg h^{-1} mass flow due to the fact that naphtha cracker feeds contain 10 – 25 wt % aromatic compounds. Solvent mass flow was varied in order to get a solvent-to-feed ratio (IL/F) ranging from 0.5 to 4.0. Then the mass flow for each component was computed for different equilibrium stages (NS) ranging from 2 to 6. Finally, the processes were optimized by sensitivity analysis as a function of IL/F and NS.

Results and Discussion

IL Solvent Screening

In order to select a suitable IL solvent to perform the extraction of benzene from hexane, or heptane, the selectivity (S) was estimated by using UNIFAC-Lei model. The selectivity is widely used to evaluate the feasibility of utilizing the IL in the liquid extraction, which is defined by the following expression:

$$S = \frac{x_1^I x_2^{II}}{x_1^{II} x_2^I} \qquad \ldots(3)$$

where x is the molar fraction, the superscripts I and II refer to the aliphatic hydrocarbon-rich (hexane or heptane) and solvent-rich (IL) phases, respectively, and the subscripts 1 and 2 refer to the inert (hexane or heptane) and the solute (benzene), respectively. The values of selectivity for 14 ternary systems of hexane/heptane + benzene + IL ([EMIM][NTf_2], [BMIM][NTf_2], [OMIM][NTf_2], [DMIM][NTf_2], [BMPY][NTf_2], [OMIM][Cl], and [HMIM][BF_4]) were calculated by the LLE data predicted using UNIFAC-Lei model on identifying the general relationship between molecular structure of ILs and hydrocarbons, as shown in Fig. 1. It can be indicated that UNIFAC-Lei model is the proper approach with a good agreement between the estimated and experimental selectivity values for the ternary systems, in which the experimental selectivity values were obtained from previous works[7, 25, 26, 36]. For ternary systems of hexane + benzene + IL, the estimated selectivity values decrease in the order of [EMIM][NTf_2]> [BMIM][NTf_2] > [OMIM][NTf_2] > [DMIM][NTf_2] when using homogolous ILs with the same anion [NTf_2]. This trend agreed with the experimental results. Also, the selectivity value for IL [EMIM][NTf_2] is higher than that of other ILs [BMPY][NTf_2], [OMIM][Cl] and [HMIM][BF_4]. The same behaviour mentioned above was observed for ternary systems of heptane + benzene + IL.

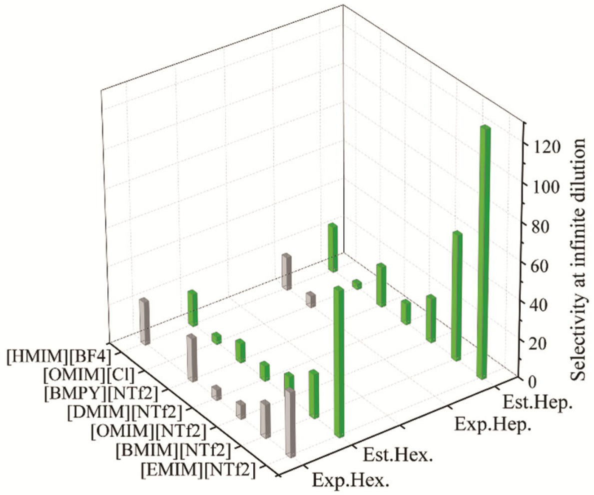

Fig. 1 — Selectivity of hexane/heptane to benzene at infinite dilution for the ILs at T = 298.15K. The gray square pillars indicate the experimental values from references[7, 25, 26, 36], and the green square pillars indicate the predicted values from UNIFAC-Lei model in this work

Other properties of ILs are also important for the perspective of industrial process design. These include viscosity, chemical stability, toxicity, flammability, ease of recovery, recyclability and cost. Although an optimum solute distribution ratio, which can minimize the amount of IL solvent required to perform a given extraction, is achieved for ILs with longer alkyl chains, their greater viscosity may discourage the pumping, mixing, and agitation operations. ILs with [Cl] anions are not appropriate for the continuous process because they are solid at the room temperature. In the perspective of environment protection, ILs with [BF_4] anion are excluded in the screening range for the selection of a suitable IL solvent because some HF dissociated from them can cause the corrosion and environmental pollution[37]. Thus, the use of [EMIM][NTf_2] is the best selection for hexane/heptane and benzene separation by IL-based extraction. The IL screening results are corresponding to a previous work concluded that [EMIM][NTf_2] was a reliable alternative to volatile organic solvents such as sulfolane or other ILs in the liquid-liquid extraction processes for the separation of aromatic and aliphatic hydrocarbons.

Feasibility Analysis for Conceptual Process Design

The LLE behaviour plays an important role in the conceptual process design of the liquid extraction. To investigate the feasibility of IL-based extraction process, the LLE behaviours of mixtures of hexane/heptane with [EMIM][NTf_2] were compared with those of [BMIM][NTf_2]at T = 298.3K, as plotted in Fig. 2. For systems of hexane/heptane + benzene + [EMIM][NTf_2], the LLE experimental data put with the predicted LLE data into triangle diagrams in order to validate the accuracy of the UNIFAC-Lei model. In two cases, the values of the root mean square deviation of the composition are 0.216 and 0.163, respectively. As can be observed, the miscible region in the case of hexane + benzene + [EMIM][NTf_2] presents lower than that of hexane + benzene +

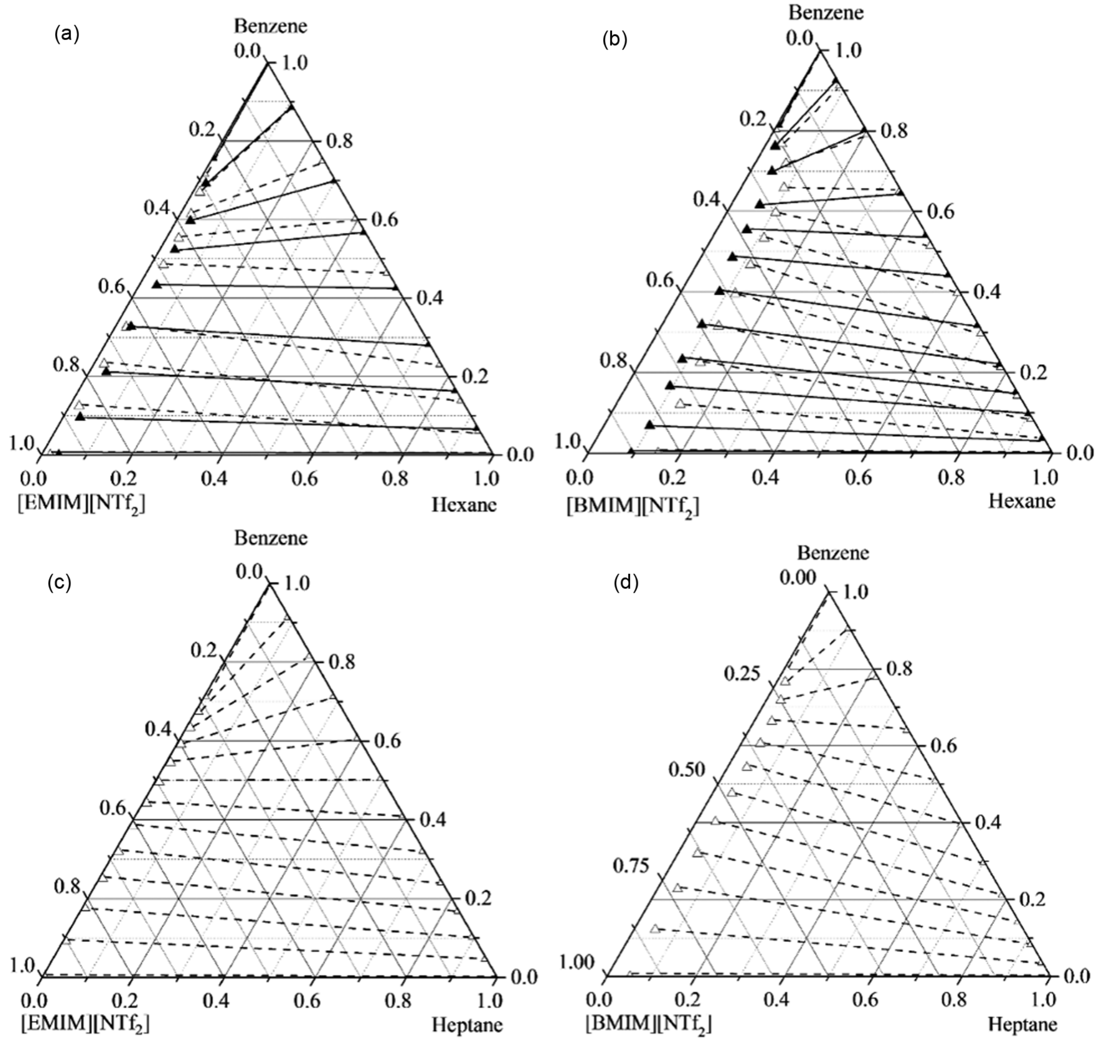

Fig. 2 — LLE of the ternary systems: (a) hexane + benzene + [EMIM][NTf_2]; (b) hexane + benzene + [BMIM][NTf_2]; (c) heptane + benzene + [EMIM][NTf_2]; and (d) heptane + benzene + [BMIM][NTf_2] at T=298.15K. Solid lines and full triangles indicate experimental tie-lines and points in (a) and (b), and dashed lines and empty triangles indicate predicted data using UNIFAC-Lei model

[BMIM][NTf$_2$]. The cases of mixtures with heptane present the same trend, that is, the miscible region when using [EMIM][NTf$_2$] is lower than that of [BMIM][NTf$_2$]. On the other hand, for mixtures hexane or heptane and benzene with the same IL solvent, the case of hexane has larger miscible region than the case of heptane. The more aliphatic hydrocarbon such as hexane and heptane enter the extract phase of the IL if the miscible region is large, and hence the extraction effect of benzene can decrease. If some IL is present in the raffinate phase from the extractor containing aliphatic hydrocarbons, the IL must be removed in the raffinate. The presence of IL in the raffinate will be unacceptable in an industrial plant because the IL can cause contamination of other processes. An interesting fact observable from Fig. 2 is that the IL and aliphatic hydrocarbon are completely immiscible in all cases. So, the separation unit to recover the IL solvent presented in the raffinate stream of the extractor can be excluded, since very few of IL can enter the raffinate of aliphatic hydrocarbon. According to the above interpretation, the conceptual process for the separation of hexane/heptane and benzene using the IL solvent can be composed of an extractor and a Flash Tank, as shown in Fig. 3. Table 4 shows the comparison between extraction simulation results in cases of hexane or heptane and benzene with [EMIM][NTf$_2$] or [BMIM][NTf$_2$] as a solvent in the extractor. In all cases, purities of aliphatic hydrocarbon were higher than 99.0 wt% and ILs with the purity less than 0.08 wt% enter the raffinate phases. For the separation of hexane and benzene, the purity of benzene can be achieved 85.5 wt % and 59.3 wt% in the Flash Tank when using [EMIM][NTf$_2$] and [BMIM][NTf$_2$] as solvents, respectively. For the separation of heptane and benzene, the purity of benzene can be achieved 94.5 wt% and 66.2 wt% in the same way, respectively. The amounts of benzene extracted from hexane/heptane in the case of [BMIM][NTf$_2$] were less than those of hexane/heptane + benzene + [EMIM][NTf$_2$]. These results are corresponding to the interpretation on the miscible region in the extract phase of triangle diagrams of hexane/heptane + benzene + [EMIM][NTf$_2$]/[BMIM][NTf$_2$] mentioned above.

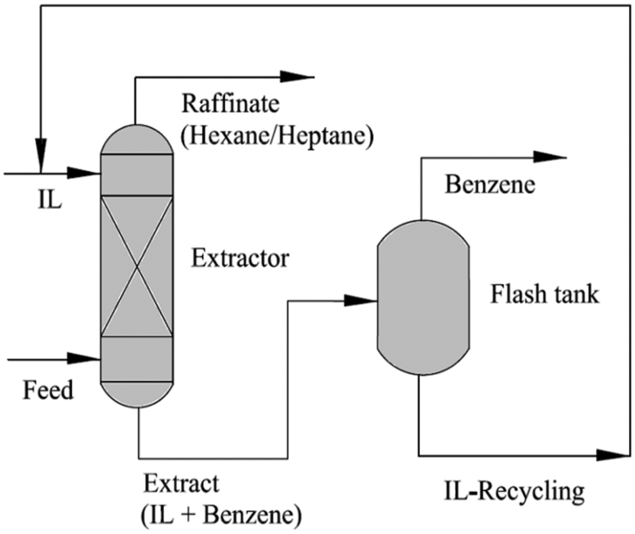

Fig. 3 — Scheme of Liquid – Liquid extraction using an IL solvent for the separation of hexane/heptane and benzene

Column operating results

Fig. 4 shows the change of purity of hexane/heptane in the raffinate stream according to the process parameters, IL/F and NS. As shown in Fig. 4, the purity of hexane/heptane in the raffinate stream dramatically increased when IL/F increased in cases of the same NS. On the other hand, the purity of hexane/heptane in the raffinate stream plotted a gentle slope at the increasing trend when NS increased in cases of the same IL/F. It can be concluded that the effect of the amount of IL solvent on the purity of hexane/heptane is more significant than that of NS. For the separation of hexane and benzene, the purity of hexane maintained at 99 wt% when NS was higher than 5 and IL/F was more than 3.5. For the separation of heptane and benzene, the purity of heptane maintained at 99 wt% when NS was higher than 5 and IL/F was more than 2.5. Then, the regeneration of IL solvent using the flask tank was investigated. The purity of IL solvent and the energy requirement in the

Table 4 — Compositions (wt%) of the raffinate and extract stream in the extractor for separating benzene from hexane/heptane using [EMIM][NTf$_2$] or [BMIM][NTf$_2$] as a solvent

Feed streams		raffinate stream			extract stream		
Feed	IL	Aliphatic	benzene	IL	Aliphatic	benzene	IL
hexane + benzene	[EMIM][NTf$_2$]	99.05	0.87	0.08	0.9	5.3	93.75
	[BMIM][NTf$_2$]	99.23	0.7	0.07	3.47	5.05	91.5
heptane + benzene	[EMIM][NTf$_2$]	99.51	0.47	0.02	0.31	5.31	94.3
	[BMIM][NTf$_2$]	99.72	0.25	0.03	2.69	5.28	92.03

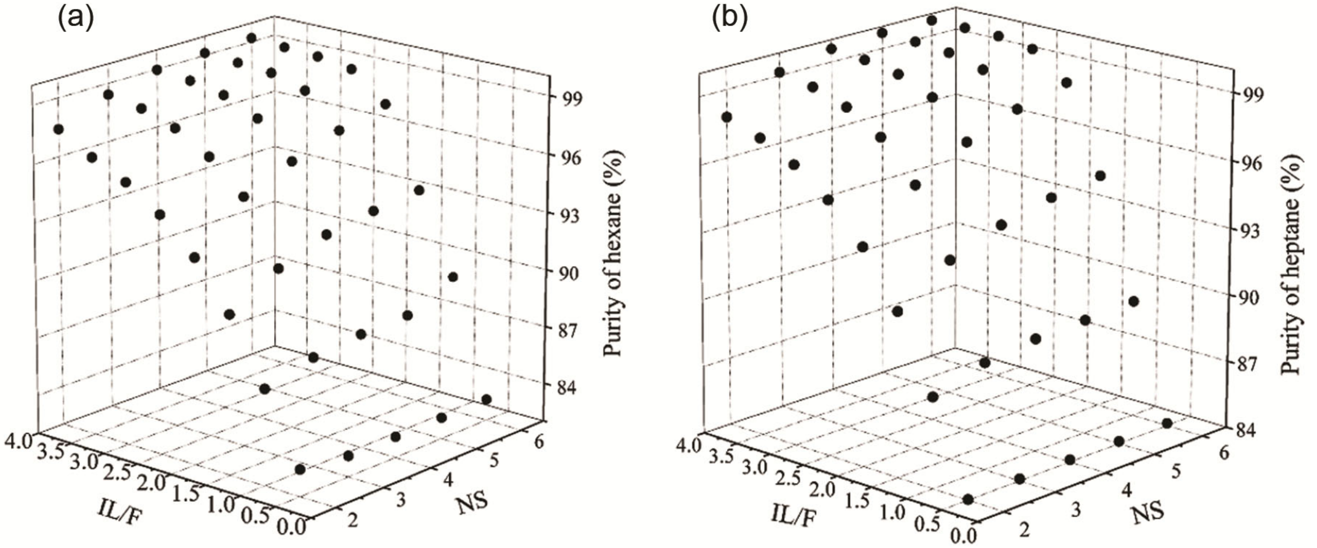

Fig. 4 — Purity of hexane/heptane in raffinate stream as a function of IL/F and NS: (a) for the mixture with hexane and (b) for the mixture with heptane

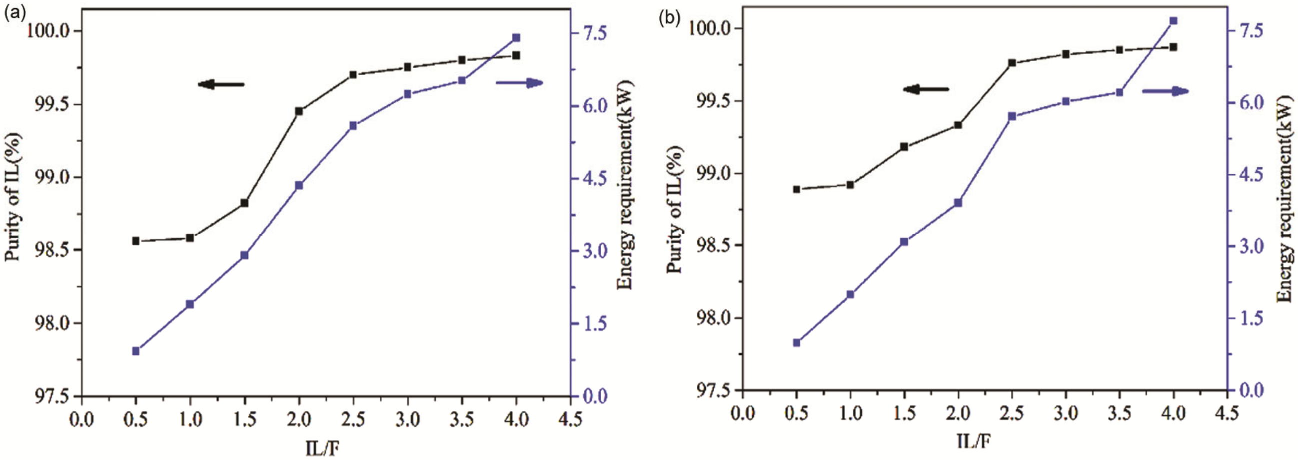

Fig. 5 — Variation of purity of the removed IL and energy requirement in the Flash Tank when increasing IL/F: (a) for the mixture of benzene and hexane; (b) for the mixture of benzene and heptane

Flash Tank which removed benzene were plotted against IL/F parameter, as shown in Fig. 5. The operating conditions of the Flash Tank were controlled to archive the target which the purity of benzene removed was 85wt% for mixture with hexane and 95wt% for mixture with heptane from reference to Section 3.2, respectively. In two cases, [EMIM][NTf$_2$] was recovered at the purity higher than 99.8 wt% when IL/F was fixed at the interval of 2.5 and 4.0. But the heat duty of Flash Tank required for recovering [EMIM][NTf$_2$] was dramatically increased at 4.0 of IL/F. Thus, the suitable control interval of IL/F is from 2.5 to 3.5 in the consideration of energy requirement and the high purity of [EMIM][NTf$_2$] for recycling to the extractor. The optimum operating parameters of the separation process for extracting benzene from hexane/heptane using [EMIM][NTf$_2$] as a suitable solvent are listed in Table 5. Likewise, the ability of the IL as a suitable solvent in liquid–liquid extraction processes for the separation of the mixture hexane/heptane + benzene was proved. In addition, it is not necessary to change the equipment and IL solvent for separating different aliphatic hydrocarbons and benzene, but the amount of IL must be controlled for the high extraction effect of benzene and low energy requirement.

Table 5 — Optimum operating parameters of the separation process for extracting benzene from hexane/heptane using [EMIM][NTf$_2$] as a suitable solvent

Parameter		Mixture	
		benzene + hexane	benzene + heptane
Extraction column			
NS		5	5
[EMIM][NTf$_2$], kg/h		350	250
Feed, kg/h		100	100
IL/F		3.5	2.5
Flow rate of raffinate, kg/h		77.34	79.57
Composition of raffinate, wt%	benzene	0.87	0.47
	hexane	99.05	
	heptane		99.51
	[EMIM][NTf$_2$]	0.08	0.02
Flash Tank			
Temperature, ℃		156.5	167.7
Pressure, bar		0.2	0.2
Vapour fraction		0.215	0.26
Heat duty, kW		4.45	4.03
Benzene stream, wt%	benzene	83.31	94.74
	hexane	16.69	
	heptane		5.26
	[EMIM][NTf$_2$]	0	0
IL-Recycling stream, wt%	benzene	0.86	0.8
	hexane	$3.1\ 10^{-5}$	
	heptane		$4.7\ 10^{-6}$
	[EMIM][NTf$_2$]	99.14	99.2
IL recovery, %		99.98	99.99

Conclusion

The separation of hexane/heptane and benzene by extraction with an IL is feasible, especially with [EMIM][NTf$_2$], as can be concluded from the predicted LLE data and the evaluation of extraction process. These data allowed the identification of theoretically appropriate operating conditions for a room-temperature countercurrent continuous extraction process. Such conditions were optimized by means of simulation techniques. Also, scaling up for industrial implementation seems feasible. Therefore, UNIFAC-Lei model is a useful predictive tool with great potential in both the screening of ILs and process design for specific extraction applications. Finally, [EMIM][NTf$_2$] was the best solvent for separating benzene from aliphatic hydrocarbons and the content of benzene in the extract can be achieved 83.3 wt% for the mixture with hexane and 94.7 wt% for the mixture with heptane from the feed containing 20 wt% of benzene, respectively.

Notation

[EMIM][NTf$_2$]	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[BMIM][NTf$_2$]	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[OMIM][NTf$_2$]	1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[DMIM][NTf$_2$]	1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[BMPY][NTf$_2$]	1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide
[OMIM][Cl]	1-octyl-3-methylimidazolium chloride
[HMIM][BF$_4$]	1-hexyl-3-methylimidazolium tetrafluoroborate

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