

Liquid-Liquid Extraction of Toluene from Heptane Using [EMIM][NTF2] Ionic Liquid: Experimental and Extensive Thermodynamics Study

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ABSTRACT: The performance of the ionic liquid (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][NTF2]) as a green, non-aqueous and hydrophobic solvent and sulfolane as a conventional solvent for liquid-liquid extraction of toluene from its mixture with heptane was investigated. The LLE phase behavior was predicted with the help of the UNIFAC as a predictive thermodynamic model. The interfacial tension of the studied systems was measured to investigate the effect of the dissolved toluene concentration on interfacial tension. It was revealed that the average selectivity of the systems with IL (316.752) is much higher than the systems containing sulfolane (18.661) under similar experimental conditions. For low mass fractions of toluene less than 0.4, the performance of the IL is better, whereas, for high toluene mass fractions more than 0.4, sulfolane exhibits superior performance.

KEYWORDS: Separation; Toluene; Heptane; Ionic liquid; UNIFAC; Interfacial tension.

INTRODUCTION

The separation of aromatic hydrocarbons from aliphatic ones is the most important process in oil refineries because of their use in the production of valuable petrochemical products. This separation is a severe challenge due to the high demand for aromatic hydrocarbons in chemical and petrochemical industries and also growing legal constraints on the amount of aromatic in gasoline and other fuels [1,2,31].

Since these hydrocarbons have close boiling points and, in some cases, they may form an azeotrope; they cannot be separated through simple distillation. In the high weight-fraction ranges of aromatic in hydrocarbon mixtures, azeotrope distillation and extracted distillation are routinely applied. For low aromatic contents, the distillation process is not suitable and economical [2,3].

Conventional solvents used for the separation of aromatic hydrocarbons from aliphatic hydrocarbons are polar compounds such as sulfolane, normal methyl pyrrolidone, benzyl alcohol, ethylene glycols, and propylene carbonate. These solvents are mainly toxic, flammable, volatile, and hardly recyclable, and they also require additional distillation steps to perform the separation of the solvent from the extract and raffinate phases [2,4]. So solvent purification drives up additional costs and energy consumption. Therefore, the need to propose an alternative solvent with excellent environmental compatibility and a useful separation capability is felt.

Recently, ionic liquids have been introduced as a new green substitute for the conventional solvents in liquid-liquid extractions [1,2,5]. Ionic liquids are melting

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salt, containing organic and bulky-asymmetric cations and organic/inorganic anions. These ions have dissipated charges and low lattice energy that decrease their melting point and cause these compounds to be liquid at room temperature. Solvent recovery is simple thanks to their negligible vapor pressure at ambient conditions. Thus, ionic liquid purification can be carried out easily through a simple flash distillation or stripper [1,2,5,6]. Since ionic liquids' solubility in the hydrocarbon-rich phase is trivial, raffinate phase purification is done without much difficulty [4]; in this way, ionic liquids are considered as "green solvent". These compounds are also called "designer solvents" since there is a wide range of cations and anions for the synthesis of ionic liquids. In other words, certain cations or anions can be exploited in the process, depending on the ionic liquid function. So the number of ionic liquid solvents is much higher than conventional ones [7].

For example, circular functional groups can be anchored on ionic liquid cations to boost the aromatic solubility in ionic liquids [2,8]. Other unique features of ionic liquids are non-volatility, high heat stability, relatively high polarity, and nonflammable, nontoxic nature [9,11].

Garcia et al. took advantage of ionic liquids 1-alkyl-2,3-dimethyl imidazolium bis(trifluoromethylsulfonyl)imide ([*x*dmim][TF₂N]), where *x* refers to ethyl(e), propyl(p) or butyl(b) to separate toluene + heptane system at 313.2 K and atmospheric pressure. They concluded that the solubility of heptane was reduced in the IL because of the methyl group in the 1-alkyl-3-methylimidazolium cations. But this matter is not affected by the solubility of toluene in the IL. Moreover, [edmim][TF₂N] and [pdmim][TF₂N] ILs exhibit a higher distribution ratio of toluene and a higher separation factor than those of sulfolane [11]. *Ebrahimi et al.* investigated the effect of the addition of hydroxyl groups to the imidazolium cations on aromatic/aliphatic hydrocarbon separation at 313.2 K and atmospheric pressure. Their results indicated that the addition of hydroxyl groups to the imidazolium cations significantly enhances the performance of the ionic liquid in terms of selectivity [2].

In this work, we used the ionic liquid (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][NTF₂]) as a green solvent and sulfolane as a conventional solvent for the liquid-liquid extraction

of toluene from its mixture with heptane and compared their performance. The LLE data for the (heptane + toluene + [EMIM][NTF₂]) and (heptane + toluene + sulfolane) ternary systems at 298.15 K and atmospheric pressure were measured via H-NMR spectroscopy. Heptane and toluene distribution coefficient and selectivity were measured with the help of the LLE data. To validate the LLE data, the Othmer-Tobias equation was applied. The Flory-Huggins model was coupled with the Hansen solubility parameter to compare sulfolane and [EMIM][NTF₂] performance in the separation of toluene from its mixture with heptane. The recyclability of the solvent for its reuse in the liquid-liquid extraction was analyzed by using a rotary evaporator. To assess the effect of the concentration of the dissolved toluene in the solvent-rich phase on the interfacial tension of two phases (raffinate and extract), the interfacial tensions of the studied systems were measured in different concentrations of toluene in the feed. The LLE data were predicted, adopting the UNIFAC group contribution model as a predictive thermodynamic model.

In other words, the present study is a comprehensive research on the liquid-liquid extraction of the studied system, in such a way it contains all the separation parameters. Such an in-depth study of the liquid-liquid extraction of the toluene + heptane system is not mentioned anywhere [26,27,30].

EXPERIMENTAL SECTION

Chemicals

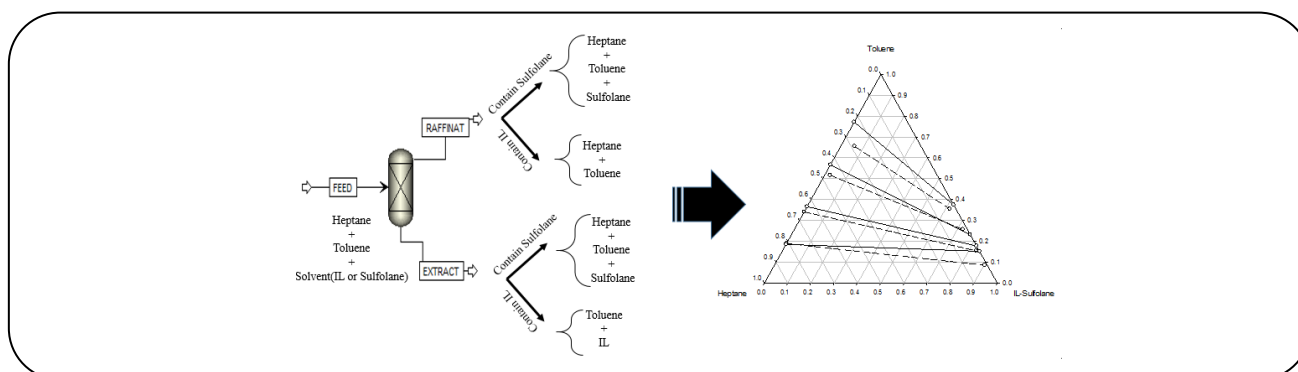
The specifications of the materials are detailed in Table 1.

Extraction processes

LLE experiments for the (heptane + toluene + [EMIM][NTF₂]) and (heptane + toluene + sulfolane) ternary systems were conducted at 298.15 K and atmospheric pressure. To obtain LLE data, 4 samples containing heptane and toluene with different concentrations of toluene (20, 40, 60, and 80% wt toluene) were prepared. Since toluene and heptane were volatile, the samples were prepared in glass cells with screw caps and septum. Then by adding the solvent to the feed, the system was rapidly divided into two phases (solvent-rich phase i.e extract and raffinate). In order to improve mass

Table 1: Specifications of the chemicals used.

Chemical name	Company	CAS-number	Purity
Toluene	Merck	108-88-3	>99%
Heptane	Merck	142-82-5	>99%
Sulfolane	Kimia Exir	126-33-0	>99%
[EMIM][NTF ₂]	Kimia Exir	174899-82-2	>98%

Fig. 1: The schematic of the extraction process of the heptane + toluene system via [EMIM][NTF₂] and sulfolane.

transfer between two phases, each sample was stirred for five h at 800 rpm using (Wisestir, MSH-20D-stirring-timer-heater, Germany). To achieve complete phase separation, each sample was placed in the incubator for 24 h at 298.15 K (Cooling incubator, CIT53, Germany).

Phase analysis

Mass fractions of compounds in the two insoluble phases for the studied system were evaluated using H-NMR spectroscopy. To this aim, 3 ml samples from each phase were taken out with the help of a very small and high-precision syringe, the lower phase sample is taken from the bottom of the container, and the upper phase sample is taken from the highest part, and their H-NMR spectra were obtained, making use of (BRUKER500 ultrashield, CDCl₃, 298.15 K). H-NMR spectrum of the (heptane + toluene + [EMIM][NTF₂]) and (heptane + toluene + sulfolane) ternary systems were illustrated in A1. H-NMR spectra processing was done with the aid of the MESTRENOVA software.

In H-NMR, each proton has a specific peak that distinguishes it from other protons. To obtain the mass fraction of components in each phase, the reference peak for each compound was selected. The selected peaks should not overlap with each other. In H-NMR, the peak area is proportional to the number of hydrogen

atoms/molecules that form it and the concentration of the compounds in the mixture. To measure the mass fraction of the compounds, each selected peak area was divided into the number of protons that form it. This process is called normalization and we called this value i.e N_i a normalize. The mass fractions of the components were calculated by dividing each normalization into the summation of normalizes as follows:

$$N_i = \frac{A_i}{m_i} \quad (1)$$

$$w_i = \frac{N_i}{\sum_i N_i} \quad (2)$$

In Equations (1) and (2) A_i , m_i , N_i , and w_i are peak area, the number of hydrogen, normalized amount, and mass fraction, respectively [28].

Solvent recovery

Solvent recovery for its reuse in liquid-liquid extraction was carried out by utilizing a rotary evaporator (BUCHI Heating Bath B-490). Therefore, the lower phase that contained toluene, solvent, and some amount of heptane was separated, and afterward, solvent recovery was done using a rotary evaporator. Then, the H-NMR

spectra of the recovered solvent were taken, which are reported in A2.

Interfacial tension

To investigate the effect of toluene dissolved concentration in solvent rich phase on the interfacial tension of two phases (raffinate and extract), we obtained five sets of interfacial tension data for each concentration of toluene in the feed of the studied system and reported the average value of them. Interfacial tension measurements were carried out at 298 K and atmospheric pressure by the plate method using (Sigma 700 Tensiometer, Germany, 298.15K). The platinum plate was thoroughly cleaned and flame-dried before each measurement. Measurements of the interfacial tension of pure water at 298 K were used to calibrate the tensiometer and check the cleanliness of the glassware. A vessel containing the liquid sample is raised until the plate touches the surface of the two phases (extract and raffinate). The liquid is drawn up in a meniscus on the solid surface and creates a force due to surface tension. The force is measured by the microbalance, and from this, the interfacial tensions are calculated [29].

RESULTS AND DISCUSSION

In order to separate toluene from heptane, the selected ionic liquid ought to have properties close to sulfolane as a conventional solvent used for the separation process in the studied system. In this work, the ionic liquid (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM][NTF₂]) has been chosen with properties similar to sulfolane. Also, from the thermodynamic point of view, the solubility diagram of toluene in the selected ionic liquid has been plotted based on the Flory-Huggins model (Fig. 2). The Hansen solubility parameters for the components of the studied system are given in A3 [13-15].

As shown in Fig. 2, the Gibbs free energy of {[EMIM][NTF₂] (1) + toluene (2)} binary system is negative for the toluene mass fractions lower than 0.7 which indicates good solubility of toluene in the selected ionic liquid.

Experimental LLE data.

The experimental LLE data for ternary systems {heptane (1) + toluene (2) + [EMIM][NTF₂] (3)} and {heptane (1) + toluene (2) + sulfolane (3)} at 298.15 K and atmospheric pressure are given in Table 2 and the ternary diagrams for the studied systems have been plotted in Fig. 3.

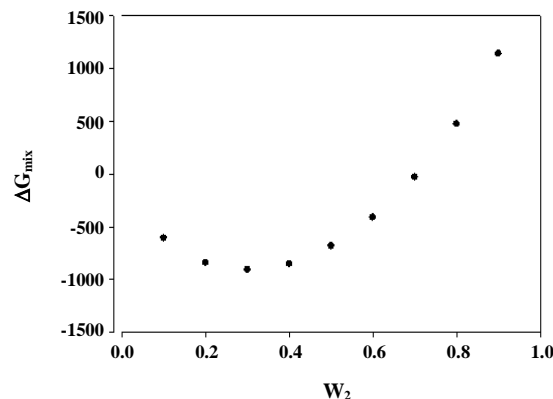


Fig. 2: Toluene miscibility based on the Flory-Huggins model for binary system {[EMIM][NTF₂] (1) + Toluene (2)} at 298.15K.

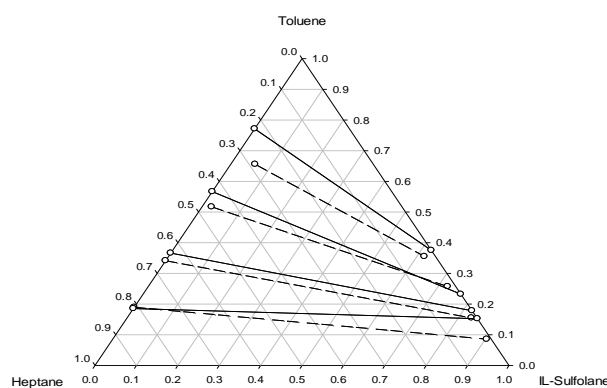


Fig. 3: Ternary diagrams of studied systems: (—) {Heptane (1) + Toluene (2) + [EMIM][NTF₂] (3)} and (---) {Heptane (1) + Toluene (2) + Sulfolane (3)} at 298.15 K and atmospheric pressure.

To verify experimental data, the results of the mass balance, as well as the UNIFAC model, were obtained and confirmed the experimental data, which are reported in A9.

According to the H-NMR analysis, no detectable signals for the ionic liquid have been observed in the heptane-rich phase, which reduces the number of extraction steps needed for solvent purification from the upper phase and brings down operational costs as well. While in the high mass fraction of toluene in {heptane (1) + toluene (2) + sulfolane (3)} system, there is some amount of sulfolane in the heptane-rich phase. Also, there are no detectable signals of heptane in the ionic liquid-rich-phase, which decreases extraction steps and facilitates solvent recovery and toluene separation from the lower phase.

Table 2. Experimental LLE data in mass fraction for ternary systems of {Heptane (1) + Toluene (2) + [EMIM][NTF₂] (3)} and {Heptane (1) + Toluene (2) + Sulfolane (3)} at T=298.15 K and atmospheric pressure.

W_1^I	W_1^{II}	W_1^{Feed}	W_2^I	W_2^{II}	W_2^{Feed}	W_3^I	W_3^{II}	W_3^{Feed}
{Heptane (1) + Toluene (2) + [EMIM][NTF ₂](3)}								
0.8145	0.0	0.3603	0.1855	0.1525	0.0873	0	0.8475	0.5524
0.6338	0.0	0.2796	0.3662	0.1783	0.1844	0.0	0.8217	0.536
0.4333	0.0	0.2207	0.5667	0.2323	0.3215	0.0	0.7677	0.4577
0.2228	0.0	0.1256	0.7712	0.3748	0.5182	0.0	0.6252	0.3562
{Heptane (1) + Toluene (2) + Sulfolane (3)}								
0.8104	0.0108	0.3662	0.1896	0.0856	0.0999	0.0	0.9036	0.5339
0.6587	0.0129	0.2682	0.3413	0.1548	0.1731	0.0	0.8323	0.5587
0.4599	0.0194	0.1932	0.5168	0.2572	0.2970	0.0233	0.7234	0.5098
0.2852	0.0266	0.1157	0.6558	0.3553	0.4656	0.059	0.6181	0.4187

w is the mass fraction and subscripts *I* and *II* refer to upper and lower phase, respectively.

Standard uncertainty: $W=0.005$ and $T=2K$.

In contrast, some amount of heptane is detected in the sulfolane-rich phase of {heptane (1) + toluene (2) + sulfolane (3)} system that makes solvent recovery difficult.

Partial solubility of toluene in ionic liquid and sulfolane, partial solubility of heptane in sulfolane, and high solubility of toluene in heptane are evident in Fig. 3. In contrast, heptane is insoluble in ionic liquids. The two-phase region area of the system containing ionic liquid is larger than the system containing sulfolane, allowing for a wide area of working points. The negative slope of tie lines in the high mass fractions of toluene indicates the high solubility of toluene in heptane compared to ionic liquid and sulfolane. In this way, the tie line slope decreases by decreasing the amount of toluene. It is worth noting that the solubility of toluene in the ionic liquid and sulfolane is higher than that of heptane. Therefore, the toluene distribution ratio goes down by raising the toluene mass fraction in the feed, which in turn increases the amount of solvent required for separation. Also, at high mass fractions of toluene, the slope of tie lines for the systems with the ionic liquid is more negative than the systems with sulfolane, indicating the good performance of sulfolane for toluene separation in comparison with ionic liquid. Conversely, at lower mass fractions of toluene, the slope of tie lines for the systems with the ionic liquid is more favorable than those with sulfolane, implying the good performance of the ionic liquid for toluene extraction.

To verify the reliability of the experimental LLE data, the Othmer-Tobias correlation, which is a general equation between the two-phase components, has been applied [5,12,32]:

$$\ln \left(\frac{1 - w_3^{II}}{w_3^{II}} \right) = a + b \ln \left(\frac{1 - w_1^{II}}{w_1^{II}} \right) \quad (3)$$

Where W_3^{II} is the mass fraction of ionic liquid or sulfolane in the lower phase (ionic liquid/sulfolane rich phase), w_1^I is heptane mass fraction in the upper phase (heptane-rich phase), a and b are constants of the Othmer-Tobias correlation. The Othmer-Tobias parameters are given in Table 3. The values obtained for the regression coefficient (R^2) in Table 3 and Fig. A4 are close to 1, which confirms the accuracy of the experimental results. The Othmer-Tobias diagrams for the studied systems are reported in Fig. A4.

Distribution ratio and selectivity.

The efficiency of the ionic liquid and sulfolane in the liquid-liquid extraction of toluene from heptane is evaluated via the distribution ratio (β_i) and selectivity (S) parameter, as shown below:

$$\beta_i = \frac{w_i^I}{w_i^{II}} \quad (4)$$

$$S_{2,1} = \frac{\beta_2}{\beta_1} = \frac{w_2^I/w_2^{II}}{w_1^I/w_1^{II}} \quad (5)$$

Table 3: Othmer-Tobias equation parameters for both ternary systems.

system	a	b	R ²
{Heptane (1) + Toluene (2) + [EMIM][NTF ₂] (3)}	-1.1771	0.4438	0.9282
{Heptane (1) + Toluene (2) + Sulfolane (3)}	-1.1286	0.7455	0.9973

In the above equations, w is the mass fraction, subscripts *I* and *II* refer to upper and lower phases, and superscripts 1 and 2 refer to heptane and toluene, respectively.

The distribution ratio signifies the amount of extraction solvent required. With the distribution ratio increasing, the solvent required as well as the column diameter decrease, and in turn, the operational costs fall. The selectivity indicates the solvent extraction efficiency and ease of extraction. The higher the selectivity, the lower the number of equilibrium stages required for extraction and the amount of solvent in the extraction phase, which subsequently facilitates solvent recovery. Therefore, an ideal extraction solvent needs to have a higher distribution ratio and selectivity. The heptane and toluene distribution ratio and selectivity are presented as a function of toluene mass fraction in the upper phase of the studied ternary mixtures at 298.15 K and atmospheric pressure, respectively (Fig.4). The calculated values of distribution ratio and selectivity for the studied systems are reported in A5. The heptane distribution ratio and selectivity are respectively equal to zero and infinite in the ionic liquid-rich phase; nonetheless, for better comparison between the ionic liquid and sulfolane efficiencies, a minimum value of 0.001 has been applied for heptane in the ionic liquid-rich phase.

According to Fig.4.a, the heptane distribution ratio of the systems with sulfolane is higher than that with the ionic liquid in the whole range of toluene mass fractions and goes up with increasing the aromatic content in the upper phase. On the other hand, heptane is more soluble in sulfolane than ionic liquid. This is mainly because of the expansion of carbon chains, leading to a large steric hindrance to the solubility of alkanes in ionic liquids [1].

As can be seen in Fig.4.b, for the toluene mass fractions lower than 0.4, the toluene distribution ratio of the systems containing ionic liquid is higher than systems containing sulfolane, whereas when it comes to the toluene mass fractions of over 0.4, this content is higher for systems with sulfolane. In contrast, at lower mass fractions of aromatic,

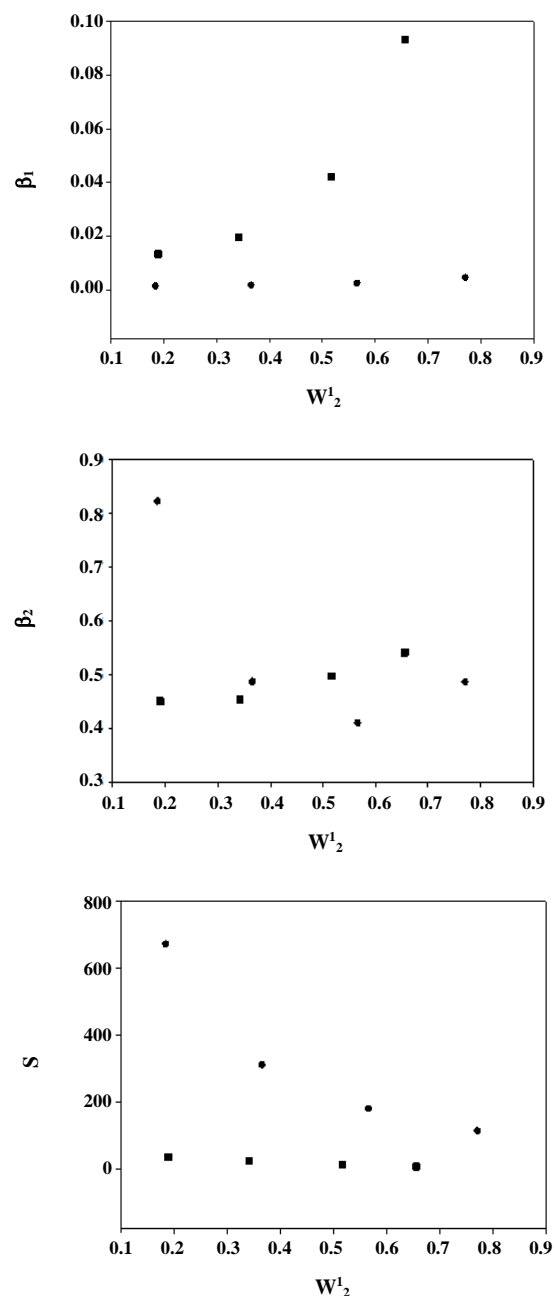


Fig. 4: a) Heptane distribution ratio, b) Toluene distribution ratio and c) Selectivity as a function of toluene mass fraction in upper phase for the ternary systems at 298.15 K and atmospheric pressure: (●) {Heptane (1)+Toluene (2) + [EMIM][NTF₂](3)}, (■) {Heptane (1) + Toluene (2) + Sulfolane (3)}.

toluene is more soluble in ionic liquid, but toluene solubility in sulfolane can be improved at higher mass fractions of aromatic. Imidazole cation skeleton and sulfolane, featuring circular structures, enhance aromatic-ionic liquid and aromatic-sulfolane interactions. The solubility of toluene is low in the ionic liquid because there is a ring in the structure of the toluene molecule and this ring has a steric hindrance. Furthermore, the presence of the mobile electron cloud in the upper and lower part of the aromatic ring produces a strong electrostatic field that multiplies the aromatic-ionic liquid interaction [1,2,8].

As it is clear from Fig.4.c, in the whole range of toluene mass fractions in the upper phase, the selectivity for systems with ionic liquid is much more than for systems with sulfolane under similar conditions, implying the better performance of ionic liquid than sulfolane in the separation of the heptane + toluene system. A comparison with literature data has also been carried out, suggesting that the values of selectivity in the present work are much higher than those reported in the literature [26,27]. Because the main reason is that there is no heptane in the ionic liquid-rich phase of the studied system, while some amount of heptane in the ionic liquid-rich phase has been reported in other pieces of research. The results are reported in A6.

Solvent recovery.

With a view to solvent recovery for reusing it in liquid-liquid extraction, the rotary evaporator is employed. According to H-NMR analysis, no detectable signals for toluene and heptane have been observed in the solvent-rich phase for the [EMIM][NTF₂] ionic liquid and sulfolane solvent. The H-NMR spectrums of the recovered solvents are given in A2.

THERMODYNAMIC STUDY

Study of the interactions between the components by the Flory-Huggins model.

To the best of our knowledge, for the first time in the present study, we took advantage of the Flory-Huggins (FH) thermodynamic model to investigate the solubility power of the solvents in liquid-liquid extraction systems. In fact, with the intention of examining toluene interaction with the ionic liquid and sulfolane without the availability of experimental data and predicting the solubility of toluene in the studied solvents, the FH model was applied. The FH parameter (χ_{ij}) for two binary systems is

evaluated, as shown in Eqs. (6-7) and are given in Table 4 [16,17]. The component solubility parameters are reported in A3.

$$\chi_{12} = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (6)$$

$$V_1 = \frac{M W}{\rho} \quad (7)$$

δ_i is the solubility parameter of component i and V_1 refer to the solvent molar volume.

For $\chi_{ij} > 0.5$, the interactions between dissimilar molecules are higher than those between similar molecules, and the solvent is called “bad solvent” because the solute cannot be dissolved in it.

For $\chi_{ij} < 0.5$, the interactions between similar molecules are higher than those between dissimilar molecules, and the solvent is called “good solvent” for the reason that the solute can be dissolved in it.

In Table 4, the FH parameter (χ_{ij}) for the toluene-ionic liquid ([EMIM][NTF₂]) binary system is 0.2 indicating a high attraction between the ionic liquid and toluene, so [EMIM][NTF₂] is a good solvent for toluene. Contrarily, the FH parameter (χ_{ij}) for the toluene-sulfolane binary system is 3.1, indicating that sulfolane is a bad solvent for toluene.

To investigate the solubility in two binary systems, the Gibbs free energy diagram as a function of toluene mass fraction is depicted in Fig.5.

From Fig. 5 the Gibbs free energy is negative for [EMIM][NTF₂] (1) + toluene (2) and positive for sulfolane (1) + toluene (2) binary systems when the toluene mass fraction is lower than 0.7, which implies better solubility of toluene in [EMIM][NTF₂] than in sulfolane. With the toluene mass fraction increased over 0.7, the toluene solubility in sulfolane rises, but its solubility in [EMIM][NTF₂] declines. Therefore, for low mass fractions of toluene, [EMIM][NTF₂] has better performance than sulfolane, whereas, for the higher content of toluene, sulfolane is a better solvent. These results confirm the toluene distribution ratio results.

Thermodynamic modeling by the UNIFAC model.

Most of the thermodynamic models exploited to model the liquid-liquid equilibrium are correlative models like the NRTL and the UNIQUAC. In this study,

Table 4: The Flory-Huggins parameter for two binary systems.

Binary system	χ_{ij}
Toluene - [EMIM][NTF ₂]	0.2
Toluene - Sulfolane	3.1

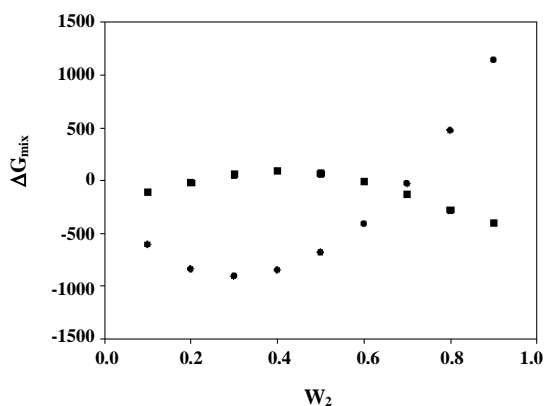


Fig. 5: The Gibbs free energy changes diagram as a function of toluene mass fraction at 298.15 K: (●) { [EMIM][NTF₂] (1) + Toluene (2) }, (■) { Sulfolane (1) + Toluene (2) }.

we use the UNIFAC thermodynamic model as a predictive model to estimate LLE data without the availability of experimental data. The molecular van der Waals volume, molecular van der Waals surface area, interaction parameter, and mass fraction are given in A7 [18-21]. The deviation between experimental and model data is calculated by the root to mean square deviation, RMSD as defined below:

$$RMSD = \left\{ \frac{\sum_i \sum_l \sum_m (w_{ilm}^{exp} - w_{ilm}^{calc})^2}{6m} \right\}^{\frac{1}{2}} \quad (8)$$

Where w represents the mass fraction and the subscripts i, l , and m refer to the number of components, phase, and tie lines, respectively. The calculated error for the studied systems is 0.0593 and 0.1297 for the systems containing ionic liquid and sulfolane, respectively.

Investigation of interfacial tension and the effect of toluene concentration on the separation process

For the first time, in this study, we explored the effect of toluene concentration on interfacial surface tension and modeled the interfacial surface tension of heptane + toluene + [EMIM][NTF₂] and heptane + toluene + sulfolane systems.

Interfacial tension is defined as the change in Gibbs free energy per unit change in interfacial area for the two immiscible phases such as liquid-liquid or gas-liquid [22]. This property has a dramatic effect on mass transfer and heat transfer between the two phases in contact. So it is an essential parameter when it comes to designing fluid contactors, especially for the liquid-liquid extractor. Since the solute concentration alters along the height of the extractor column, which induces the change in the interfacial tension of the two immiscible phases, having accurate information about the relationship between the solute concentration and interfacial tension is critical for the best design of liquid-liquid extractor.

Small interfacial tension indicates a low capability of the dispersed phase to form a stable emulsion and decreases the size of dispersed phase droplets which increases the mass transfer area and extraction rate and may increase the dispersed phase hold-up. The low capacity of the system to form a stable emulsion also causes some difficulties in the separation of the two extracts and the raffinate phases after liquid-liquid extraction. It is worth mentioning that in the case of high interfacial tension, thanks to the high capability of the fluid to form a stable emulsion, the two liquid phases must be stirred severely to increase the mass transfer area. However, this feature accelerates the separation of the two extract and raffinate phases after the liquid-liquid extraction process.

Modeling the interfacial tension for the heptane + toluene + [EMIM][NTF₂] and heptane + toluene + sulfolane systems.

The ionic liquid can be considered as a molecule, by assuming strong electrostatic forces between its cations and anions; Shian and Prausnitz proposed a model for the prediction of the interfacial tension of nonelectrolyte solution based on thermodynamics concepts [24,25]. To calculate the interfacial tension for a nonelectrolyte solution, the following equation is used:

$$\sum_i (w_i^\alpha w_i^\beta)^{1/2} \exp \left(\frac{\sigma A_i^{int}}{RT} \right) = 1 \quad (9)$$

In the above equation σ , A_i^{int} , w , and superscripts α and β stand for interfacial tension, partial molar interfacial area, mass fraction, and upper and lower phase, respectively. The partial molar interfacial area of each component can be approximately equal to its average value,

Table 5: Experimental and calculated interfacial tension data ± 0.0001 for ternary systems at 298.15 K and atmospheric pressure.

Toluene + heptane + [EMIM][NTF ₂]			
Toluene mass fraction in feed (% wt)	Heptane mass fraction in feed(% wt)	The average value of experimental interfacial tension $\sigma(\frac{mN}{m})$	The calculated value for interfacial tension $\sigma(\frac{mN}{m})$
0.0873	0.3603	6.5114	6.6283
0.1844	0.2796	6.1316	5.0733
0.3215	0.2207	3.2770	3.7696
0.5182	0.1256	-	2.3075
Toluene + heptane + sulfolane			
Toluene mass fraction in feed (% wt)	Heptane mass fraction in feed(% wt)	Average value of experimental interfacial tension $\sigma(\frac{mN}{m})$	calculated value for interfacial tension $\sigma(\frac{mN}{m})$
0.0999	0.3662	5.5018	5.2396
0.1731	0.2682	3.1710	3.9322
0.2970	0.1932	2.3086	1.8377
0.4656	0.1157	-	0.9489

Standard uncertainty: $\sigma = 0.0001(\frac{mN}{m})$, $T=2K$, $w=0.005$.

i. e., $A_1^{int} = A_2^{int} = A_3^{int} = A_{ave}^{int} = constant$.

Accordingly, by dividing Eq. (9) to $\exp\left(\frac{\sigma A_i^{int}}{RT}\right)$, the following relationship is obtained to calculate the interfacial tension:

$$\sigma = \frac{-RT}{A_{av}^{int}} \ln \left(\sum_i (w_i^\alpha w_i^\beta)^{\frac{1}{2}} \right) - KRT \ln \left(\sum_i (w_i^\alpha w_i^\beta)^{\frac{1}{2}} \right) \quad (10)$$

In the above equation, K is a constant that equals $\frac{1}{A_{av}^{int}}$ (The derivation of this relation is summarized in A8). In this study, we obtained five sets of interfacial tension data for each concentration of toluene in the feed and used the average value of the data. The experimental interfacial tension data for the ternary systems are reported in Table 5.

The minimum value of interfacial tension measured by the device is $2 \frac{mN}{m}$, so for 80% concentration of toluene in the feed, because the interfacial tension is lower than $2 \frac{mN}{m}$, no value is reported.

By plotting the experimental interfacial tension data against $-RT \ln \left(\sum_i (w_i^\alpha w_i^\beta)^{\frac{1}{2}} \right)$, the constant value K is

computed for each system. The average partial molar interfacial area for each system can also be obtained by using, $k = \frac{1}{A_{av}^{int}}$; this value is $666.6667 \times 10^{-9} m^2$ and $714.2857 \times 10^{-9} m^2$ for the systems containing the ionic liquid and sulfolane, respectively. Diagrams are plotted in Fig.6.

With the value of K and mass fraction data at hand, the calculated interfacial tension is acquired based on the model (reported in Table 5). Besides, the Root Mean Square Deviation (RMSD) between the experimental and model interfacial tension data is calculated. The RMSD values are 0.2943 and 0.5385 for the system containing the ionic liquid and sulfolane, respectively. On the other hand, this model has a better result for the system with the ionic liquid than that with sulfolane.

To investigate the solute concentration impact on the interfacial tension, the interfacial tension changes diagram as a function of toluene mass fraction in the feed is illustrated in Fig.6.

As can be seen in Fig. 6, the change in the concentration of toluene as solute and the main component of mass transfer in the liquid-liquid extraction has a marked effect on the interfacial tension of the systems in a way that by raising the toluene concentration in the feed, the interfacial tensions of the two studied systems drop. As the toluene concentration increases in the feed, the toluene mass transfer or the toluene solubility intensifies

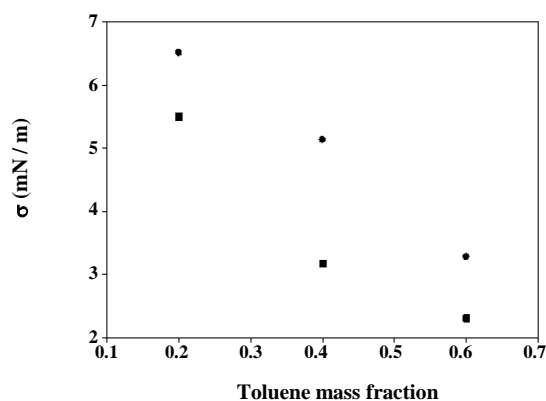


Fig. 6: The interfacial tension changes diagram as a function of toluene mass fraction in the feed at 298.15 K: (●) {Heptane (1) + Toluene (2) + [EMIM][NTF₂] (3)}, (■) {Heptane (1) + Toluene (2) + Sulfolane (3)}.

in the solvent-rich-phase, and the mutual solubility of phases increases, which thereby reduces the interfacial tension of the systems and expands the interfacial area. What is more, over the whole range of toluene mass fractions in the feed, the interfacial tension for the systems containing the ionic liquid is higher than those of sulfolane, indicating a lower interfacial area for the systems with the ionic liquid. This confirms the interfacial area results obtained from the model. The high interfacial tension of the systems containing ionic liquid accelerates the separation of the extract and raffinate phases after liquid-liquid extraction.

CONCLUSIONS

In this work, liquid-liquid extraction of the aromatic compounds from the aliphatic ones with the help of the [EMIM][NTF₂] ionic liquid and sulfolane were investigated. The experimental determination of the LLE data for the (heptane + toluene + [EMIM][NTF₂]) and (heptane + toluene + sulfolane) ternary systems were carried out at 298.15 K and atmospheric pressure. A high degree of quality of the experimental LLE data was ascertained by applying the Othmer-Tobias (OT) correlation.

According to the heptane distribution ratio, heptane is more soluble in sulfolane than the studied ionic liquid. This is mainly due to the extension of the carbon chains and their major steric hindrance, which prevents the solubility of alkane in the ionic liquid. Moreover, at any mass fraction of toluene in the upper phase, the selectivity of the systems containing IL is much higher than the systems with sulfolane under the same conditions. Toluene

distribution ratio and the Flory-Huggins model results demonstrate that the IL ([EMIM][NTF₂]) has better performance than sulfolane in the separation of toluene from heptane for the low mass fractions of toluene. Whereas, at higher values of the toluene mass fraction, sulfolane exhibits better performance. The UNIFAC model predicts the experimental LLE phase behavior of the studied systems satisfactorily. The interfacial surface tension data prove that the concentration of toluene as solute has a significant effect on the interfacial tension of the system as mentioned above in such a way that by increasing the toluene concentration in the feed, the interfacial tension of the two studied systems declines.

Nomenclature

N_i	Normalized amount of component i
T	Temperature
A_i	Peak area of component i
m_i	Number of hydrogen of component i
w_i	Mass fraction of component i
w_i^I	Mass fraction of component I in the upper phase
w_i^{II}	Mass fraction of component I in the lower phase
β_i	Distribution ratio of component i
S	Selectivity
x_{ij}	Flory-Huggins parameter of component i and j
δ_i	Solubility parameter of component i
V_1	Solvent molar volume
MW	Molecular weight
RMSD	Root mean square deviation
σ	Interfacial tension
A_i^{int}	Partial molar interfacial area
FH	Flory-Huggins
ΔG	Gibbs free energy
H-NMR	Hydrogen nuclear magnetic resonance
R^2	Regression coefficient
R	Gas constant
ρ	Density

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