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Chapter

Extraction of Aromatic Compounds from Their Mixtures with Alkanes: From Ternary to Quaternary (or Higher) Systems

Ángeles Domínguez, Begoña González, Patricia F. Requejo and Sandra Corderí

Abstract

Ionic liquids have been proposed as separation agents for liquid extraction of aromatic compounds from their mixtures with alkanes, with the aim of improving the separation process and replacing conventional organic solvents. A significant number of experimental liquid-liquid equilibrium data for ternary system alkane + aromatic compound + ionic liquid can be found in literature; however there are few data for quaternary or higher systems involving more than one aliphatic compound, several aromatic compounds or a mixture of ionic liquids as separation agent. These data are also necessary because molecular interactions between the compounds in the mixture can modify the affinity of the solvent for the aromatic compound of interest. In this chapter we review the published data involving more than three components, and we present new liquid-liquid equilibrium data for the quaternary systems heptane + cyclohexane + toluene + 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide and heptane + cyclohexane + toluene + 1-hexyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide.

Keywords: ionic liquids, aromatic compounds, liquid extraction

1. Introduction

Aromatic compounds, such as benzene, toluene, ethylbenzene and xylenes (BTEX), are raw materials for the production of polymers, resins paints and other products of industrial interest. They are mainly obtained from catalytic reforming and cracking processes in oil refineries, as a mixture of aromatic and aliphatic hydrocarbons. Aromatic content depends on the process characteristics, and it can range between 20 and 65 wt% for reformate gasoline and between 50 and more than 90% for pyrolysis gasoline [1].

The separation of aromatic from aliphatic compounds is difficult because they usually have close boiling points and many of their mixtures show azeotropic behaviour. One of the most used processes to separate these aromatic compounds is liquid-liquid extraction, due to the fact that it can be used for a wide range of aromatic concentration in the mixture. Sulfolane, among other solvents, is widely used in these processes because of its high selectivity (S) for aromatics although it is
generally used when aromatic content is high. After the extraction process, further separation units are needed to recover sulfolane from raffinate and extract phases.

The increasing concern for the environment has induced the search of new solvents that reduce pollution and energy costs, making the extraction process more environmentally friendly. One of the alternatives proposed is the use of ionic liquids (ILs) as solvents for the extraction of aromatic compounds, and consequently a large number of papers reporting liquid-liquid equilibria (LLE) data of ternary system aliphatic + aromatic + IL can be found in the literature. From experimental data, selectivity and distribution coefficients ($\beta$) can be calculated and used to evaluate the capability of the solvent since high selectivity together with high distribution coefficients are suitable. Canales and Brennecke [1] compared ILs and conventional solvents for the extraction of aromatic from aliphatic compounds, finding that ILs are potentially alternatives to currently used solvents.

Even though the information obtained from ternary systems is crucial, we cannot be certain that selectivity and distribution coefficients obtained from ternary systems will remain unchanged when more components, aromatics or aliphatic are present in the mixture. Because of this, selectivity and solute distribution coefficients should be determined for complex mixtures, in order to obtain more actual data.

Some papers related to quaternary or higher systems using sulfolane to extract aromatics from aliphatic compounds can be found in the literature [2–8], while similar information using ILs as extractant agents is scarce, taking into account the huge number of ILs that can be used [9–22]. It also should be noted that mixtures of ILs or organic solvent + IL can be selected as separation agents [23], greatly increasing the number of systems that should be studied.

In this chapter, a literature review on the results obtained using ILs for the extraction of aromatic compounds in systems with more than three components is performed. Furthermore new liquid-liquid equilibrium experimental data for the quaternary systems heptane + cyclohexane + toluene + 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, [EMim][NTf$_2$], and heptane + cyclohexane + toluene + 1-hexyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, [HMim][NTf$_2$], are presented.

2. Literature review

2.1 Quaternary systems with two aliphatic compounds

Up to now, a quite wide range of papers dealing with liquid-liquid equilibrium data of hydrocarbon + aromatic + IL ternary systems can be found in literature. These studies are essential to determine the capability of ILs to extract aromatic compounds; however, many other compounds are present in refinery streams, and these compounds can modify the extraction process.

With the aim of analysing the influence of more than one aliphatic compound on the extraction of aromatics, liquid-liquid equilibrium data of several quaternary systems have been published [9–14].

Rquejo et al. [9–11] studied the extraction of benzene from its mixtures with octane and decane using tributylmethylammonium bis(trifluoromethylsulfonyl) imide, [N$_{4441}$][NTf$_2$]; 1-butyl-1-methylpyrrolidinium dicyanamide, [BMpyr] [DCA]; and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [BMpyr][NTf$_2$], and the results of the quaternary system were compared with those obtained for the ternary systems octane + benzene + IL and decane + benzene + IL.

Using [N$_{4441}$][NTf$_2$], the highest values of $\beta$ were obtained for the ternary system octane + benzene + [N$_{4441}$][NTf$_2$], while the $\beta$ values calculated for the
ternary system decane + benzene + [N4441][NTf₂] and for the quaternary system are similar. Selectivity values are quite similar for the ternary and quaternary systems; consequently the presence of two alkanes does not seem to affect them [9].

Solute distribution coefficient is similar for both ternary systems octane + benzene + [BMpyr][DCA] and decane + benzene + [BMpyr][DCA] and for the quaternary system octane + decane + benzene + [BMpyr][DCA], while the selectivity for the quaternary system is lower than for the ternary system with decane and higher than for the ternary system with octane [10].

A different influence was found comparing the ternary systems octane + benzene + [BMpyr][NTf₂] and decane + benzene + [BMpyr][NTf₂] with the quaternary system decane + octane (1) + benzene (2) + [BMpyr][NTf₂] [11]. In that case, both solute distribution coefficients and selectivity are lower for the quaternary system.

The extraction of toluene from its mixtures with heptane and cyclohexane, using ethyl-methylimidazolium-based ILs, was studied by Corderí et al. [12–14]. The selected anions were methylsulphate [MSO₄], acetate [OAc] and dicyanamide [N(CN)₂]. According to their results, solute distribution coefficient clearly follows the trend: 

\[ [\text{EMim}][\text{N(CN)}_2] > [\text{EMim}][\text{OAc}] > [\text{EMim}][\text{MSO}_4] \]

With regard to selectivity, higher values were obtained with [EMim][N(CN)₂]. Comparing quaternary systems with the respective ternary ones, the following results were obtained:

i. Solute distribution coefficients for the ternary systems with [EMim][MSO₄] are quite similar and higher than those obtained for the quaternary system at higher toluene composition in the hydrocarbon-rich phase. When the toluene concentration in the hydrocarbon-rich phase is lower than 0.2, similar values of \( \beta \) were obtained for the ternary and the quaternary systems.

ii. In the case of [EMim][OAc], \( \beta \) values for the quaternary system are slightly higher than those obtained for the ternary systems independent of the toluene concentration in the hydrocarbon-rich phase.

iii. Similar \( \beta \) values were obtained for the ternary and quaternary systems using [EMim][N(CN)₂].

iv. In all cases, selectivity values for the quaternary system are between the values of the ternary systems.

As it can be seen, both solute distribution coefficients and selectivity values can be influenced by the presence of another hydrocarbon in different ways. The lack of more experimental data does not allow us to take general conclusions about the influence of other aliphatic compounds present in the mixture; consequently more experimental data would be necessary.

2.2 Quaternary systems with IL mixtures as extraction agents

Among all the ILs that have been studied as separation agents, only a small number of them have shown simultaneously solute distribution coefficients and selectivity higher than sulfolane since, generally, high selectivities are related to low solute distribution coefficients and vice versa. On the other hand, most ILs present quite high viscosity, which make their use difficult in extraction processes. The proper selection of two ILs could lead to a separation agent, whose physical properties and extraction performance overcome those of sulfolane. Therefore, some pairs of ILs have been tested to extract aromatics, mainly benzene or toluene, from their mixtures with alkanes.
Sakal et al. [15] carried out the extraction of benzene from benzene + cyclohexane mixtures using 1,3-dimethylimidazolium dimethylphosphate, [MMim][DMP], and 1-methylimidazolium tetrafluoroborate, [Mim][BF₄], and the mixtures [Mim][BF₄] wt. 50% + [MMim][DMP] wt. 50% and [Mim][BF₄] wt. 25% + [MMim][DMP] wt. 75%. Both selectivity and solute distribution coefficient follow the same trend: [MMim][DMP] > [Mim][BF₄] wt. 25% + [MMim][DMP] wt. 75% > [Mim][BF₄] wt. 50% + [MMim][DMP] wt. 50%. Additionally, IL mixtures of 1-methylimidazolium perchlorate, [Mim][ClO₄] and [MMim][DMP], at the same mass ratios were also checked, finding that the addition of [Mim][BF₄] or [Mim][ClO₄] does not improve the extraction capacity of [MMim][DMP].

Potdar et al. [16] determined LLE data for the quaternary system hexane + benzene + 1-ethyl-3-methylimidazolium ethylsulphate, [EMim][ESO₄], + 1-ethyl-3-methylimidazolium methylsulphate, [EMim][MSO₄]. The comparison between β and S obtained using the mixture of ILs and each of them separately shows that the mixture of ILs has a lower extraction capacity. These worse results can be due to the fact that there is less free volume in a combination of these two ILs, hindering the solution of benzene in the ILs mixture.

The mixtures of N-butylpyridinium tetrafluoroborate, [Bpy][BF₄], with N-butylpyridinium bis(trifluoromethylsulfonyl)imide, [Bpy][NTf₂], and with 1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide, [4BMpy][NTf₂], were tested for the extraction of toluene from the mixture heptane-toluene. These ILs were selected because of the higher selectivity and the lower solute distribution coefficient showed by [Bpy][BF₄] and the opposite behaviour showed by [Bpy][NTf₂] and [4BMpy][NTf₂] [17–18]. In both cases, β and S values higher than those obtained using sulfolane were achieved with a [Bpy][BF₄] mole fraction of 0.7 in the mixture of ILs.

On the basis of the results obtained using 1-ethyl-3-methylimidazolium tricyanomethanide, [EMim][TCM], as well as 1-ethyl-3-methylimidazolium dicyanamide, [EMim][DCA], for the extraction of toluene from heptane, a mixture of [EMim][TCM] + [EMim][DCA] with a [EMim][TCM] mole fraction of 0.8 was selected to carry out the same extraction process [19]. Both solute distribution coefficient and selectivity are higher using this IL mixture than using sulfolane. Since selectivity values using the IL mixture were almost double than those using sulfolane, toluene extracted by the IL mixture would be significantly purer.

The capability of the binary mixture of 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide, [4EMpy][NTf₂], and 1-ethyl-3-methylimidazolium dicyanamide, [EMim][DCA], as solvent for the extraction of toluene from its mixtures with heptane or 2,3-dimethylpentane or cyclohexane was evaluated by Larriba et al. [20]. The IL [4EMpy][NTf₂] was selected because it showed solute distribution coefficients for toluene higher than sulfolane. On the other hand, toluene selectivity of [EMim][DCA] is substantially higher than that of sulfolane. The extraction of toluene from other alkanes (hexane, octane or nonane) was also performed [21]. According to the authors, selectivity values increase when n-alkane chain length increases, while toluene distribution coefficients follow the opposite trend. Taking into account the results, the IL mixture can be an alternative to sulfolane in the extraction of toluene from mixtures toluene-n-alkane with low concentration of toluene.

The same mixture of ILs was selected for the extraction of benzene or ethylbenzene or xylenes from heptane [22]. The mixture with a [4EMpy][NTf₂] molar fraction of 0.3 was chosen in all cases because of its density and viscosity similar to sulfolane and good extraction performance obtained in preliminary tests. As well as using a single IL, best results were obtained in the separation of benzene, whereas the lowest values of β and S were obtained in the separation of ethylbenzene. Compared to sulfolane, the mixture of ILs showed higher extractive properties in
the extraction of benzene and higher selectivity and slightly lower solute distribution coefficients for p-xylene/heptane separation.

As mentioned above, one of the main drawbacks of the use of ILs as extraction agents is their high viscosity that is difficult for the separation process. The selection of an appropriate solvent to mix with the IL could break the hydrogen bonds between the cation and the anion, lowering the viscosity but retaining the intrinsic properties of the IL. With the aim of lowering viscosity and decreasing costs, the mixtures of [EMim][OAc] + acetonitrile and [EMim][ESO₄] + acetonitrile were used to extract benzene from a benzene + hexane mixture [23]. It is worth noting that solute distribution coefficients are very low compared to the values obtained using a single IL; however, both hexane composition in extract phase and solvent composition in raffinate phase are practically zero. This fact would considerably simplify the solvent recovery.

2.3 Systems with more than four components

LLE data for systems with more than four components are very scarce. As a continuation of the extraction studies using a mixture of ILs, Larriba et al. [24] analysed the separation of BTEX fraction from a reformer gasoline model (n-hexane, n-heptane, n-octane). In that case, aromatic distribution coefficients using the IL mixture were significantly lower than using sulfolane, whereas selectivity values were higher. It is interesting to point out that in all pseudoternary system alkane + aromatic + IL mixture previously studied by the authors, they achieved better results using the mixture [4EMpy][NTf₂] + [EMim][DCA] than using sulfolane. In order to improve these results, [EMim][DCA] was replaced by [EMim][TCM], and a mixture of [4EMpy][NTf₂] + [EMim][TCM] with a [EMim][TCM] mole fraction of 0.6 was selected on the bases of extraction yield and thermophysical properties of the mixture [25]. The extraction results were used to perform the simulation of the extraction process including the extraction column and the recovery section of the solvent.

In order to study the extraction of BTEX fraction from naphtha reformate using 1-butyl-3-methylimidazolium hexafluorophosphate, [BMim][PF₆], Al-Rashed et al. [26] determined liquid-liquid equilibrium data for the system hexane + heptane + octane + benzene + toluene + o-xylene + [BMim][PF₆]. Comparing the aromatic extraction between this system and those systems with only one aromatic, they concluded that a combination of the three aromatic compounds affected negatively on the extractive capability of the IL. According to the authors, this can be because the aromatic compounds in one phase can strongly associate between them through π-π forces. Furthermore, the electrostatic association between the aromatic alkyl chains and alkanes present in the mixture also influences the extractive capability of the IL.

The gasoline or naphtha model was constituted by equal amounts of alkanes in all the above-mentioned studies.

3. Experimental part

In order to analyse the influence of the alkyl chain length of the IL cation on the extraction of toluene from its mixture with heptane and cyclohexane, liquid-liquid equilibrium data of the quaternary systems heptane + cyclohexane + toluene + 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, [EMim][NTf₂], and heptane + cyclohexane + toluene + 1-hexyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, [HMim][NTf₂], were determined. Experimental data were compared to the results obtained for the ternary systems heptane + toluene + [EMim][NTf₂], cyclohexane + toluene + [EMim][NTf₂], heptane + toluene + [HMim][NTf₂] and cyclohexane + toluene + [HMim][NTf₂] [27, 28].
3.1 Chemicals and experimental procedure

The ILs [EMim][NTf₂] and [HMim][NTf₂] were supplied by IoLiTec GmbH. They were subjected to vacuum and moderate temperature (P = 0.2 Pa, T = 343 K) for several days to eliminate water and volatile compounds that could be present. Cyclohexane, heptane and toluene were supplied by VWR Prolabo, and they were used without further purification. Mass purity of all chemicals was higher than 99%. In order to prevent water absorption, all chemicals were kept and manipulated under inert gas atmosphere.

Figure 1 shows a representation of the quaternary systems studied in this work where grey surfaces represent the miscible areas on the top and the base of the tetrahedron. Due to the very negligible miscibility of these ILs in the aliphatic mixture (checked by ¹H-NRM), no IL is present in the aliphatic hydrocarbon phase. For the determination of liquid-liquid equilibrium data, samples of a mixture of the four components were prepared by weight using a Mettler AXE-205 Delta Range balance. In order to select the composition of the initial samples, a sectional plane (SP), in which the mole fraction of the ionic liquid is constant, was selected as it can be seen in Figure 1. This sectional plane is perpendicular to the tie lines, and the compositions of the other three compounds involved in the initial quaternary mixtures were selected in such a way that they cover the sectional plane.

The samples were vigorously stirred by using a magnetic stirrer for 6 hours and left to settle down overnight. Afterwards, a sample of each phase was withdrawn with a syringe, and it was analysed by gas chromatography.

The compositions of cyclohexane, heptane and toluene were analysed with a Hewlett-Packard 5890 Series II gas chromatograph with a Hewlett-Packard 5971 mass selective detector and a Hewlett-Packard-5MS capillary column (60 m × 0.250 mm × 0.25 μm). Because of the IL negligible vapour pressure, they cannot be analysed by gas chromatography; consequently, their composition was calculated through a mass balance. An empty precolumn was used to avoid the IL that could not be retained by the liner to go into the chromatograph. The temperature programme has initial temperature of 343.15 K for 10.30 min, ramp of 15 K min⁻¹ and final temperature of 368.15 K for 4.30 min. The injector and detector were maintained at 553.15 K, and the helium carrier gas flow rate was kept constant at 1 mL min⁻¹ in the column. Two analyses of each sample were performed to obtain a mean value.

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Figure 1.
Schematic representation of the quaternary system and the sectional plane (SP).
In order to determine the error in the composition, quaternary mixtures with known composition were analysed by chromatography, and their obtained compositions were compared with those obtained by weight. The error in the compositions was estimated to be ±0.004.

3.2 Results and discussion

From experimental values, solute distribution coefficient, \( \beta \), and selectivity, \( S \), were calculated by the following equations:

\[
\beta = \frac{x_3^II}{x_3^I}
\]

\[
S = \frac{x_3^II x_1^II}{x_3^I x_1^I}
\]

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<th>IL-rich phase</th>
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Table 1. Experimental LLE data, solute distribution coefficients, \( \beta \), and selectivity, \( S \), for the quaternary system heptane (1) + cyclohexane (2) + toluene (3) + [EMim][NTf2] (4).
where \( x \) is the mole fraction; the superscripts \( I \) and \( II \) indicate the hydrocarbon-rich phase and the IL-rich phase, respectively; and the subscripts \( 1 + 2 \) refer to the mole fraction of heptane plus cyclohexane and \( 3 \) refers to toluene.

Tables 1 and 2 show the experimental data at 298.15 K, \( \beta \) and \( S \) for the system heptane + cyclohexane + toluene + [EMim][NTf₂] or [HMim][NTf₂], respectively.

As it can be seen from the tables, selectivity is higher using [EMim][NTf₂], while higher solute distribution coefficients were obtained using [HMim][NTf₂]. Since \( S > 1 \) in both cases, [HMim][NTf₂] would be the best choice due to \( \beta \) values higher than 1 which facilitate the extraction process, and less solvent and less separation stages would be necessary. Figures 2 and 3 show the tie lines for the pseudoternary system (heptane + cyclohexane) (1) + toluene (2) + IL (3). The higher \( \beta \) values obtained for the extraction using [HMim][NTf₂] are reflected in the positive slope of the tie lines for toluene molar fractions up to 0.45.

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<td>0.741</td>
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Table 2. Experimental LLE data, solute distribution coefficients, \( \beta \), and selectivity, \( S \), for the quaternary system heptane (1) + cyclohexane (2) + toluene (3) + [HMim][NTf₂] (4).
Selectivity and solute distribution coefficients for the quaternary system heptane + cyclohexane + toluene + [EMim][NTf$_2$] can be compared to the results obtained for the ternary systems heptane + toluene + [EMim][NTf$_2$] and cyclohexane + toluene + [EMim][NTf$_2$] [27]. β values are similar for the ternary and quaternary systems, while S for the ternary system heptane + toluene + [EMim][NTf$_2$] (between 3 and 24) and the quaternary system are similar and higher than the ternary system with cyclohexane (between 8 and 4).

Figure 2.
Tie lines for the quaternary systems heptane + cyclohexane + toluene + [EMim][NTf$_2$].

Figure 3.
Tie lines for the quaternary systems heptane + cyclohexane + toluene + [HMim][NTf$_2$].
Regarding the quaternary system heptane + cyclohexane + toluene + [HMim][NTf₂], the experimental data of the ternary systems heptane + toluene + [HMim][NTf₂] and cyclohexane + toluene + [HMim][NTf₂] can also be found in literature [28]. In that case, both $\beta$ and $S$ are higher for the quaternary system, which implies that, in some cases, the addition of another component can enhance the extraction of the aromatic compound.

Solute distribution coefficient and selectivity can be compared to those obtained using 1-ethyl-3-methylimidazolium methylsulphate, [EMim][MSO₄] [13]; 1-ethyl-3-methylimidazolium dicyanamide, [EMim][N(CN)₂] [14]; or 1-ethyl-3-methylimidazolium acetate ionic liquid, [EMim][OAc] [12]. Solute distribution coefficient follows the following trend:

\[ [HMim][HNTf₂] > [EMim][HNTf₂] > [EMim][N(CN)₂] > [EMim][OAc] > [EMim][MSO₄]. \]

$\beta$ values obtained with ionic liquids with NTf₂ anion are significantly higher, reaching values greater than one in the case of [HMim][HNTf₂]. Regarding the selectivity, the trend is

\[ [EMim][N(CN)₂] > [EMim][MSO₄] > [EMim][HNTf₂] > [EMim][OAc] > [HMim][HNTf₂]. \]

Since selectivity and solute distribution coefficient do not follow the same trend, the selection of the most adequate IL should be a compromise between these two factors affecting extraction process.

4. Conclusions

Single ILs, IL mixtures and also mixtures of an IL and an organic solvent have been used to extract aromatics from its mixtures with aliphatic compounds. The obtained results show that, in general, ILs can be considered to replace conventional solvents such as sulfolane. However, before this replacement and taking into account the different results obtained for systems with more than three components, the study of the extraction of aromatic compounds from real naphtha reformate or pyrolysation gasoline, including the solvent recovery process, must be carried out.

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