Vapor-liquid equilibria for n-heptane +(benzene, toluene, p-xylene, or ethylbenzene)+{[4empy][Tf2N] (0.3)+[emim][DCA] (0.7)} binary ionic liquid mixture

Abstract

Ionic liquids (ILs) have been extensively used as solvents in the liquid-liquid extraction of aromatics from aromatic/aliphatic mixtures. However, scarce studies have been done in order to experimentally evaluate the recovery of the hydrocarbons from the IL in extract-type streams. In this work, we have determined the vapor-liquid equilibria (VLE) for n-heptane + (benzene, toluene, p-xylene, or ethylbenzene) + {1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf2N])(0.3) + 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]) (0.7)}. This IL mixture was selected as a result of its high extractive performance. The VLE have been measured using a headspace-gas chromatography (HS-GC) technique at several temperatures (323.2 K, 343.2 K, and 363.2 K) and over the whole composition range in the miscibility region of the systems. The Non-Random Two Liquids (NRTL) model has been applied to fit the VLE data. The n-heptane/aromatic relative volatilities have been calculated to assess the recovery of n-heptane from the four aromatics of the aromatic fraction and the IL-mixture. Results show that the IL mixture induces a high selective n-heptane/aromatic separation over the whole range of compositions in all systems and at all temperatures set in this work.

1. Introduction

The use of alternative solvents instead of organic compounds is an interesting challenge for the research community, linking technological and environmental purposes. Room temperature ionic liquids (ILs) are compounds that combine the advantages of the handling of the liquids and the good performance of the salts in modifying the thermodynamic behavior. As a consequence, a high number of studies have been carried out focusing on the use of ILs as solvents.

The aromatic extraction from aromatic/aliphatic mixtures is one of the most prolific uses of ILs as solvents due to the high extractive properties shown by ILs. Lastly, the use of binary mixtures of ionic liquids has led to achieve IL-based solvents with high aromatic/aliphatic selectivities, high aromatic distribution ratios, adequate densities, and low viscosities. The {[4empy][Tf2N] +[emim][DCA]} binary IL mixture with [emim][DCA] mole fraction of 0.7 shows higher aromatic/aliphatic selectivities and aromatic distribution ratios than those of sulfolane, being compa- rable their densities and viscosities. In addition to this, its maximum operation temperature (MOT), 413 K, assures a high thermal range of application at industrial scale.

However, the studies focused in the recovery of the hydrocarbons from the IL-based solvent are scarce nowadays to establish the feasibility of the aromatic extraction using ILs. For that reason in our last work we have studied the recovery of the hydrocarbons in several extract-type streams with the {[4empy][Tf2N] +[emim][DCA]} mixture as a function of IL mixture composition. The best aliphatic/aromatic relative volatilities were found at the highest mole fraction of [emim][DCA]. Hence, the {[4empy][Tf2N] (0.3) +[emim][DCA] (0.7)} IL mixture seems to be a potential solvent to extract aromatics taking into account extractive and physical properties, thermal stability, and the recovery of hydrocarbons.
Here the VLE for \(n\)-heptane+(benzene, toluene, \(p\)-xylene, or ethylbenzene)+\{[4empy][Tf2N] (0.3)+[emim][DCA] (0.7)\} have been determined over the whole composition range and at 323.2 K, 343.2 K, and 363.2 K by using a headspace-gas chromatography (HS-GC) technique. Although the best aliphatic/aromatic relative volatilities were achieved using pure [emim][DCA], the most adequate composition of the mixture taking into account the extraction and recovery processes is \{[4empy][Tf2N] (0.3)+[emim][DCA] (0.7)\}. This work is aimed in confirming the selective recovery of the aliphatics from aromatics over the whole range of composition and also modeling the VLE data to the Non-Random Two Liquids (NRTL) model.

2. Experimental

2.1 Chemicals

[emim][DCA] and [4empy][Tf2N] were purchased from Iolitec GmbH. They were used here without further purifications, with the mass fraction purities listed in Table 1. The water and halide contents for [emim][DCA] were less than 937 ppm and 2%, respectively, whereas in the case of [4empy][Tf2N] were below than 89 ppm and 0.1%, respectively. In order to maintain their identity, ILs were kept in their original vessels under a dry atmosphere into a moisture-controlled desiccator and were manipulated under a dry and inert atmosphere of nitrogen into a glove box. The structure of both ILs is presented in Fig. 1. The densities for both ILs were determined by an Anton Paar DMA-5000 at 293.2 K in order to compare their values with those just published as can be found in Table 2. The [emim][DCA] shows a density that is agreement with those reported by Freire et al., França et al., Seki et al., and Larriba et al., whereas the [4empy][Tf2N] has a density also in agreement with that published by Liu et al.. Moreover, all hydrocarbons tested here were acquired from Sigma-Aldrich with purities higher than 99.5 wt. % as can be also seen in Table 1.

2.2 VLE procedure and analysis

The isothermal VLE data was obtained using the HS-GC technique, recently applied to determine VLE for mixtures containing an aliphatic, an aromatic, and an IL. The details of the method were widely described in our previous work; hence, here we only comment the essential information to understand the background of the technique.

The equipment used was an Agilent Headspace 7697 A injector coupled to an Agilent GC 7890 A, the latter equipped with a flame ionization detector. The feed mixtures were prepared by mass using a Mettler Toledo XS205 balance with a precision of \(\pm10^{-5}\) g. The sample vials were filled with a controlled volume of 1.0 mL, being the headspace volume 19.0 mL. As commented before, the equilibrium temperatures were 323.2 K, 343.2 K, and 363.2 K, whereas an equilibration time of 2 h and a 100 rpm agitation were also needed to reach the equilibrium.

The partial pressures \(P_i\) developed by the hydrocarbons in the pseudobinary and pseudoternary mixtures with \{[4empy][Tf2N] (0.3)+[emim][DCA] (0.7)\} binary IL mixture were calculated using the relationship between the peak areas developed by the hydrocarbons with the IL mixture \(A_i\) and the peak areas developed by each hydrocarbon alone in the same conditions \(A_i^0\):

\[
P_i = \frac{P_i^0 A_i^0}{A_i}\]  

(1)
where $P_i^0$ refers to the vapor pressure of each pure hydrocarbon from literature. The vapor phase compositions were directly determined by the GC analysis. In the case of quaternary systems, the response factor method was used to correct the compositions. Finally, the liquid phase compositions ($x_i$) were calculated correcting the feed compositions ($z_i$) with the hydrocarbon amount that goes to the vapor phase:

$$
x_i = \frac{x_i F - (P_i N_G / RT)}{\sum_j (x_j F - (P_j N_G / RT))}
$$

where $F$ denotes the molar amount of the feed, $V_G$ is the headspace volume of the vial, and $R$ is the ideal gas law constant.

3. Results and discussion

The VLE were measured for all systems at 323.2 K, 343.2 K, and 363.2 K over the whole range of composition. The $x$-$P$ data obtained for the hydrocarbon+[{4empy}[Tf$_2$N] (0.3)+[emim][DCA] (0.7)] systems are displayed in Tables S1 and S2 in the Supplementary Information, whereas the $x$-$y$-$P$ data corresponded to n-heptane + (toluene, benzene, p-xylene, or ethylbenzene)+[{4empy}[Tf$_2$N] (0.3)+[emim][DCA] (0.7)] are listed in Tables S3 to S6 in the Supplementary Information, based on solvent-free compositions ($x'$). Finally, the $x$-$y$-$P$ data for n-heptane+(benzene, p-xylene, or ethylbenzene) systems are collected in Table S7 (Supplementary Information) in order to validate the suitability of the method for these systems and to be used as benchmark. The VLE data for the n-heptane +toluene mixture were just published in our previous work concerning the VLE for n-heptane þ toluene+[emim][DCA].

The relative volatilities ($a_{12}$) of n-heptane (1) from aromatics (2) were calculated to evaluate the IL mixture effect on the hydrocarbon separation as:

$$
a_{12} = \frac{K_1}{K_2} = \frac{y_1/x_1}{y_2/x_2}
$$

where $K$ is the K-value for each hydrocarbon. The values of $a_{12}$ are listed in Tables S3 to S7 in the Supplementary Information.

The VLE data of all systems including the IL mixture were modeled using Non-Random Two Liquids (NRTL) thermodynamic model. The low deviations between the experimental VLE data and those calculated by NRTL in previous works dealing with hydrocarbons and ILs suggested the use of this thermodynamic model. The objective function (OF) used in the NRTL model was defined as follows:

$$
0F = \sum_{i=1}^N \sum_{j=1}^1 \left| x_{i,calc} - x_{i,exp} \right| + \sum_{i=1}^1 \sum_{j=1}^N \left| P_{i,calc} - P_{i,exp} \right|
$$

where $a$, which was fixed to 300, denotes the weighting coefficient of mole fraction deviations to balance the difference of magnitude between $x$ and $P_i$ and $N$ is the number of VLE points. The Solver tool of Microsoft Excel spreadsheet software was employed to adjust all systems.

The parameters obtained from all adjustments are included in Table 2, jointly with the deviations of the liquid mole fractions, $Dx$,and the equilibrium pressures, $DP$, determined as follows:

$$
\Delta x = \frac{\sum_{i=1}^1 \left| x_{i,calc} - x_{i,exp} \right|}{N}
$$

$$
\Delta P = \frac{\sum_{i=1}^1 \left| P_{i,calc} - P_{i,exp} \right|}{N}
$$

The goodness of the NRTL adjustments can be seen through the low liquid mole fraction and pressure deviations collected in Table 3 or by a graphical comparison between the experimental
values and the adjustments to NRTL in Figs. 2 to 6 and S1 to S8 in the Supporting Information.

3.1 Hydrocarbon + {[4empy][Tf2N] (0.3) + [emim][DCA] (0.7)} Systems

The VLE data of (n-heptane, toluene, benzene, p-xylene, or ethylbenzene) t {[4empy][Tf2N] (0.3) t [emim][DCA] (0.7)} as a function of temperature are shown in Fig. 2. As can be seen, the pressure increases as the mole fraction of the hydrocarbons does until the pressure is equal to those of the pure hydrocarbons. This zone in which the pressure is a function of the mole fraction corresponds to the VLE. The other composition gap with a constant value for the pressure represents a vapor-liquid-liquid equilibrium (VLLE) region, in which x1 represent the overall liquid mole fraction. Thus, the composition at which the two zones converge is the maximum hydrocarbon solubility in the IL mixture. As a result, the compositions for the hydrocarbon in the two liquid phases in the VLLE experiments are their solubility in the IL mixture for the IL-rich phase and that regarding to pure hydrocarbon. The maximum solubilities of the hydrocarbons as a function of temperature are collected in Table S2 according to the experimental VLE data obtained in this work.

As expected, the range of compositions of the VLE was higher for the aromatics than for the n-heptane because of the stronger interaction between the aromatics and ILs and, thus, their higher miscibility in the IL mixture. The temperature hardly affected the hydrocarbon solubility in the IL mixture in the range from 323.2 K to 363.2 K.

Focusing only on the aromatic + {[4empy][Tf2N] (0.3) + [emim][DCA] (0.7)} systems, the benzene composition gap in the VLE region was quite higher than that of toluene, whereas the lowest gaps were for the p-xylene and ethylbenzene. Therefore, low values of molecular weight for the aromatic imply high solubility of the aromatic in the IL mixture. This trend was in agreement with our previous work about the liquid-liquid equilibrium in aromatic + {[4empy][Tf2N] (0.3) + [emim][DCA] (0.7)} systems at 313.2 K [10].

3.2. n-Heptane+aromatic+ {[4empy][TfN] (0.3)+ [emim][DCA](0.7)} systems

The VLE data obtained for the pseudoternary mixtures of n-heptane + aromatic + {[4empy][Tf2N] (0.3) + [emim][DCA] (0.7)} are graphically presented in Figs. 3 to 6 at the equilibrium temperature of 323.2 K and as a function of the IL mole fraction in the liquid phase.

The VLE data for the same pseudoternary mixtures at 343.2 K and 363.2 K are graphically shown in Figs. S1 to S8 in the Supporting Information. The VLE data for the same systems without the IL mixture are also shown in Figs. 3 to 6 and in Figs. S1 to S8 in the Supporting Information in order to be used as benchmark. As can be seen, the experimental values for the n-heptane t aromatic systems are in agreement with those taken from the literature, validating the HS-GC technique for all the systems included in this work.

The x'-y diagrams (a) from Figs 3 to 6 and S1 to S8 in the Supporting Information show that the vapor mole fraction of n-heptane in equilibrium is considerably higher for the n-heptane + aromatic + {[4empy][Tf2N] (0.3) + [emim][DCA] (0.7)} systems than for the n-heptane + aromatic systems. This fact can be also seen in the x’,y-P diagrams (b) from the same figures, where the equilibrium lines of the vapor and liquid moves away one from the other as the IL mole fraction increases.

The VLE data comparison of n-heptane + benzene system with and without the IL mixture deserves to be highlighted as a result of the flipping phenomenon observed with {[4empy][Tf2N] + [emim][DCA]}. As can be noticed in Fig. 4 at 323.2 K and in Figs. S3 to S4 at the temperatures of
343.2 K and 363.2 K, the vapor pressure of benzene is higher than that of n-heptane in the n-heptane + benzene binary system. However, in the n-heptane + benzene + \{[\text{4empy}][\text{Tf2N}] + [\text{emim}][\text{DCA}]\} system, the more volatile compound is the n-heptane. Hence, the order of volatilities drastically changed in favor to the n-heptane as a result of the effect of \{[\text{4empy}][\text{Tf2N}] + [\text{emim}][\text{DCA}]\} in the equilibrium.

Taking into account the VLE data obtained in this work, it is possible to claim that the separation of n-heptane from the four aromatics in extract-type compositions is completely dependent on the molecular weight of the aromatic. The more selective n-heptane aromatic separation was observed in the case of the highest aromatic molecular weight (p-xylene, ethylbenzene). In order to facilitate this comparison, the n-heptane/aromatic relative volatilities from all pseudoternary systems included in this work are graphically represented in Fig. 7. As observed, an increase in the aromatic molecular weight implies an increase in the n-heptane/aromatic relative volatility. The temperature influence in the VLE is also discussed from Fig. 7 because its effect can be easily appreciated from the n-heptane/aromatic relative volatility. As can be seen, an increase in the temperature value causes a decrease in the n-heptane/aromatic relative volatility values in all systems.

4. Conclusions

In this work, the VLE for n-heptane + (toluene, benzene, p-xylene, or ethylbenzene) + \{[\text{4empy}][\text{Tf2N}] (0.3) + [\text{emim}][\text{DCA}] (0.7)\} pseudoternary systems have been determined at 323.2 K, 343.2 K, and 363.2 K over the whole range of compositions into the miscible region. In addition, the VLE of all pure hydrocarbons in the IL mixture has been studied over the whole range of compositions and at the selected temperatures. All VLE data obtained have been successfully fitted to the NRTL model. The main advance of this work has been the high n-heptane/aromatic relative volatility values obtained in the VLE determinations carried out. The n-heptane relative volatility from benzene and toluene has been up to 30 and 50 times higher in the pseudoternary system than in the corresponding binary systems, respectively. The maximum increase in the n-heptane/aromatic relative volatility for the p-xylene and ethylbenzene cases has been about 15 times. The lowest temperature, 323.2 K, has let to achieve the highest n-heptane/aromatic relative volatilities values. Finally, it is possible to claim that the \{[\text{4empy}][\text{Tf2N}] (0.3) + [\text{emim}][\text{DCA}] (0.7)\} mixture show an efficient behavior in

the n-heptane selective recovery from the aromatics in extract-type models. Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.fluid.2016.02.018.