



On the volatility of aromatic hydrocarbons in ionic liquids: Vapor-liquid equilibrium measurements and theoretical analysis

Emilio J. González ^a, José Palomar ^{b,*}, Pablo Navarro ^c, Marcos Larriba ^b, Julián García ^d, Francisco Rodríguez ^d

^a Departamento de Ingeniería Química Industrial y del medioambiente, Universidad Politécnica de Madrid, E-28006 Madrid, Spain

^b Sección de Ingeniería Química (Dpto. Química Física Aplicada), Universidad Autónoma de Madrid, E-28049 Madrid, Spain

^c CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro, Portugal

^d Department of Chemical Engineering, Complutense University of Madrid, E-28040 Madrid, Spain

ARTICLE INFO

Article history:

Received 27 September 2017

Received in revised form 17 November 2017

Accepted 21 November 2017

Available online 23 November 2017

Keywords:

Ionic liquids

Toluene

Aromatic hydrocarbons

VLE

HS-GC

COSMO-RS

ABSTRACT

The use of ionic liquids (ILs) as solvent in the liquid-liquid extraction of aromatic compounds is one of their most studied applications. Nevertheless, the recovery of the extracted hydrocarbons has been much less investigated, being a required task to complete the global separation process. Taking into account the negligible vapor pressure of the ILs, this step could be easily carried out by flash distillation, which requires the study of vapor-liquid equilibrium (VLE). In order to study this topic deeper, in this work a systematic analysis of the VLE and vapor-liquid-liquid equilibrium (VLLE) data for {aromatic hydrocarbon + IL} binary mixtures was carried out, from both an experimental and computational point of view. For that, new experimental VLE and VLLE data of 24 {toluene + IL} binary mixtures were measured at 323.15 K using a technique based on the static headspace gas chromatography (HS-GC), providing relevant information on the toluene retained in the liquid depending on the cation/anion structure of the IL in the mixture. Furthermore, the quantum chemical Conductor-like Screening Model for Real Solvents (COSMO-RS) method was applied to better understand the structure-property relationship determining the phase behavior of {aromatic hydrocarbon + IL} binary systems. First, the suitability of COSMO-RS to predict VLE and VLLE data of {toluene + IL} binary mixtures was evaluated by comparison to 225 experimental data at 323.15 K, including 24 different ILs over the whole composition range. Valuable conclusions were achieved respect to the molecular model of IL needed to adequately predict VLE and VLLE data of the {aromatic hydrocarbon + IL} binary mixtures. Once the computational approach was stated, COSMO-RS methodology was used to analyze the influence of the intermolecular interactions between the toluene and the IL component on the phase behavior of their mixtures. As a result, COSMO-RS was demonstrated as a useful tool for the rational design of ILs with optimized properties for the separation of aromatic + aliphatic hydrocarbon binary mixtures, considering both liquid-liquid extraction and solvent regeneration steps.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

To date, the use of ionic liquids (ILs) as solvents in the liquid-liquid extraction of aromatic hydrocarbons is one of the most studied applications in the field of the separation processes, as evidenced by the large number of references that can be found in the literature. Most of the works are based on the experimental determination of liquid-liquid equilibrium (LLE) data for {aliphatic + aromatic + IL} ternary systems, after which the ability of the ILs to extract aromatic hydrocarbons is evaluated through the selectivity and solute distribution ratio values [1–20]. In most cases, experimental LLE data are also correlated using thermodynamic models, mainly the NRTL equation. Usually, the aromatic compounds studied are benzene, toluene, ethylbenzene and

xylene isomers [3,5,6,11,15–18] while the aliphatic hydrocarbons include linear alkanes (such as hexane, heptane, and octane), and cycloalkanes (such as cyclohexane and cyclooctane) [11,18]. Regarding hydrocarbon mixtures, the most common is that composed of heptane and toluene, which has been widely considered as model to study this kind of systems [1,2,4,7,9,12–14,19,20]. Concerning the ILs applied as extraction solvents, those based on the imidazolium and pyridinium cationic families have been broadly explored, mainly in combination with bis(trifluoromethylsulfonyl)imide (NTf₂⁻) [5,6,8,9,11,15] although other anions including borate [12], phosphate [16] alkylsulfate [1,2,20], sulfonate [19], nitrate [10], or cyano [3,7,13] have been recently proposed. Many of these studies were focused on evaluating the effect of the cation substituents on the LLE. In particular, the initial goal was to analyze the impact of the alkyl chain length [2,8,9,10–15,20] on the phase equilibrium behavior; nevertheless, recent studies have also addressed the effect of including functional groups as hydroxyl-, benzyl-,

* Corresponding author.

E-mail address: pepe.palomar@uam.es (J. Palomar).

or allyl-, in order to design functionalized ILs for selective separation of aromatic and aliphatic hydrocarbons [5–7]. Furthermore, the current trend is towards studying more complex mixtures such as quaternary systems or synthetic gasoline models [21–24] as well as using binary mixtures of ILs as solvent [23–25].

In general, the results obtained are quite promising, but they also indicate that the extraction capacity of the ILs as solvents is strongly affected by their ionic structure. Due to their high aromatic character, imidazolium- and pyridinium-based ILs have been the most studied ILs in the extraction of aromatics. In general, the typical substituents of these cations consist of alkyl groups, although new functional groups such as benzyl, vinyl or hydroxyethyl are being incorporated, which opens new opportunities [5,6]. For instance, Ebraimi et al. [6] concluded that the addition of a hydroxyethyl group to imidazolium cation significantly enhances the performance of the ionic liquid in terms of selectivity. An increase in the length of the alkyl chains in imidazolium or pyridinium based-ILs caused a rise in the aromatic distribution ratios but the opposite effect was observed in the values of aromatic/aliphatic selectivities [8–14].

The anion structure also has a significant effect on the extraction properties of ILs in the separation of aromatic hydrocarbons from aliphatic phase. High values of aromatic distribution ratios were obtained employing ILs formed by the NTf_2 , BF_4 , FAP, and FeCl_4 anions [9,12,16,18], whereas quite large aromatic/aliphatic selectivities were observed for ILs composed of hexafluorophosphate (PF_6), tris(pentafluoroethyl)trifluorophosphate (FAP), hydrogen sulfate (HSO_4), tricyanomethanide (TCM), dicyanamide (DCA), tetrathiocyanatocobaltate ($\text{Co}(\text{SCN})_4$) or thiocyanate (SCN) anions [2,4,5,15–20,22].

Despite the significant work made in this field to date, the above mentioned works are specifically focused on the liquid-liquid extraction process, leaving aside the recovery of the hydrocarbons from the IL-rich phase (extract). Since ILs have negligible vapor pressures, the selective separation of the extracted hydrocarbons from the IL is considered easily performed by evaporation [26]. However, the vapor-liquid-liquid phase behavior of hydrocarbon + IL mixture may mainly determine the capital investment and operating costs [27,28]. Therefore, new information – both experimental and theoretical – concerning the vapor liquid equilibrium (VLE) and the vapor-liquid-liquid equilibrium (VLLE) of the {aliphatic + aromatic + IL} systems is of a great interest, in order to improve our understanding of this field.

Although enough information on VLE for systems involving ILs can be found in the literature [4,29–48] these works mainly report experimental data for ionic liquid mixed with polar solvents such as alcohols or water. The number of experimental VLE data concerning mixtures containing hydrocarbons and ILs has substantially increased in recent years but it remains scarce [4,39–48]. As it is known, this information data can be obtained using dynamic or static methods. In general, the experimental VLE determination of totally miscible mixtures is usually conducted by isobaric and dynamic methods. Nevertheless, since ILs are quite viscous and their mixtures with hydrocarbons are rarely miscible over the whole composition range – what could complicate the mixing process – the use of a static and isothermal determination is a good option. In the particular case of the aromatic recovery from ILs, this is not the miscibility but it is the high concentration of the IL that implies a clear benefit of static techniques instead of dynamic ones. Accordingly, a static and isothermal method based on the headspace – gas chromatography (HS-GC) technique [49] was used in this work to obtain the experimental VLE data for systems containing hydrocarbons and ILs. This technique also requires a smaller quantity of sample than dynamic methods, which accelerates the equilibrium and drastically reduces the chemicals consumption. This latter is very important taking into account the high current price of the ILs. In the last years, we have published several works concerning the experimental determination of VLE data for systems containing *n*-heptane, toluene and ILs [4,43–48] using this technique in a satisfactory way. These works report

VLE data using both pure ILs (tricyanomethanide-, or dicyanamide, or thiocyanate-, or bis(trifluoromethylsulfonyl)imide-based ILs), and IL/IL or IL/inorganic salt mixtures as mass agent. The obtained results show that: i) the presence of ILs results in a considerable enhancement of the relative volatility of *n*-heptane from toluene.; ii) the relative volatilities achieved using mixture of ILs as mass agent are intermediate between those achieved using pure ILs; iii) the use of IL/inorganic mixtures as entrainer does not get improve the high relative volatility of *n*-heptane from toluene achieved with pure ILs. Although this information is very useful, it is not enough to establish general conclusions for ILs in general, being necessary to evaluate a higher and more representative sample of ILs to get more knowledge about the phase behavior of these systems.

In the research on IL potential application, one main first stage is the selection of the cation-anion combination, which confers the required properties to the IL solvent. In this context, *a priori* computational methods capable of predicting thermodynamic data of IL-based systems may be of great utility. The quantum-chemical approach COSMO-RS has demonstrated to present a general suitability to describe thermodynamic properties in systems containing ILs [50], including gas-liquid (GLE) [51–54], vapor-liquid (VLE) [55–59], liquid-liquid (LLE) [60–65] and solid-liquid (SLE) [66–70] equilibrium data. In fact, COSMO-RS has been applied with success to predict the LLE [62,63,65,71–74] and VLE diagrams [27,75–77] involved in the separation of {aliphatic + aromatic} systems by using IL as extracting agents. Predictions from COSMO-based models have been recently applied to the conceptual design of the two main unit operations – liquid-liquid extraction and vacuum distillation – proposed to separate aromatic and aliphatic hydrocarbons with ILs [27,28,75]. These studies indicated the convenience of considering both separation stages when selecting the best IL as extracting solvent and, as consequence, the importance of the availability of LLE and VLE data. An additional advantage of the physically-founded COSMO-RS theory is that it provides a better understanding of the fluid system behavior from a molecular point of view. For example, excess enthalpy (H^E) predicted by COSMO-RS has been demonstrated a valuable thermodynamic property to analyze the mixture behavior of ILs with organic compounds. Relationships between H^E values and GLE, VLE, LLE and SLE data have been systematically established [51,52,65,66,67,73,78]. Since COSMO-RS method estimates the contribution of the intermolecular interactions between the components to the excess enthalpy of the mixture, this theoretical information can be consistently used to design ILs with desired properties for specific applications [51–53,65,79], i.e. ILs that minimize the energy expenses of solvent regeneration stage.

The main goal of this work is to perform a systematic study of the VLE of {aromatic hydrocarbon + IL} binary mixtures, to accomplish this relevant information required for the potential development of new separation process of {aromatic + aliphatic} hydrocarbon mixtures based on IL extracting solvents. For this purpose, firstly, new experimental VLE data for 24 {toluene + IL} binary mixtures were measured at 323.15 K by HS-GC. Although this work is mainly focused on the VLE region, experimental data were obtained in a wide composition range, including the saturation zone in which two liquid-phases (VLLE) are observed. Toluene was taken as a reference of aromatic hydrocarbon. The toluene – IL interaction is a simple but useful approach to understand the aromatic – IL interactions in the phase behavior. In fact, several works have used this simplified model to study the phase behavior – LLE and VLE – of this kind of mixtures [2,4,7,9,12–14, 43–47]. The ILs included in this work was selected – among those commonly proposed based on their favorable LLE data – to evaluate the effect of the ionic structure (cation, anion and substituents) on the VLE of {toluene + ionic liquid} mixtures [1–16]. For that, a total of 24 ILs were included, involving several pyridinium and imidazolium-based cations with borate- (BF_4), cyano- (SCN, DCA), imide- (NTf_2), sulfate- (ESO_4 , MSO_4 , HSO_4) and sulfonate- (MSO_3) based anions. Secondly, COSMO-RS simulations were carried out to complement the analysis of VLE phase behavior of {toluene + IL}. As preliminary step, COSMO-

Download English Version:

<https://daneshyari.com/en/article/7843222>

Download Persian Version:

<https://daneshyari.com/article/7843222>

[Daneshyari.com](https://daneshyari.com)