LLE data for the ionic liquid 3-methyl-N-butyl pyridinium dicyanamide with several aromatic and aliphatic hydrocarbons

Citation for published version (APA):

Hansmeier, A. R., Jongmans, M. T. G., Meindersma, G. W., & Haan, de, A. B. (2010). LLE data for the ionic liquid 3-methyl-N-butyl pyridinium dicyanamide with several aromatic and aliphatic hydrocarbons. *International Journal of Thermodynamics*, 42(4), 484-490. <https://doi.org/10.1016/j.jct.2009.11.001>, <https://doi.org/10.1016/j.ijnonlinmec.2007.01.008>

DOI:

[10.1016/j.jct.2009.11.001](https://doi.org/10.1016/j.jct.2009.11.001)

[10.1016/j.ijnonlinmec.2007.01.008](https://doi.org/10.1016/j.ijnonlinmec.2007.01.008)

Document status and date:

Published: 01/01/2010

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

LLE data for the ionic liquid 3-methyl-*N*-butyl pyridinium dicyanamide with several aromatic and aliphatic hydrocarbons

Antje R. Hansmeier*, Mark Jongmans, G. Wytze Meindersma, Andre B. de Haan

Chair of Process Systems Engineering (SPS), Technical University of Eindhoven, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

ARTICLE INFO

Article history:

Received 7 July 2009

Received in revised form 29 October 2009

Accepted 2 November 2009

Available online 10 November 2009

Keywords:

BTX separation

Extraction

Ionic liquids

ABSTRACT

(Liquid + liquid) equilibrium data for ternary systems of several aromatic and aliphatic hydrocarbons with the ionic liquid 3-methyl-*N*-butylpyridinium dicyanamide were determined at $T = 303.15$ K and 328.15 K and atmospheric pressure. As aromatics benzene, cumene and *p*-xylene have been chosen, as paraffins *n*-hexane and *n*-nonane were used. The experimental data were regressed and could be adequately correlated with the NRTL model. A logical order in the extraction capacity of 3-methyl-*N*-butylpyridinium dicyanamide for the different aromatics is obtained: benzene > *p*-xylene > cumene.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

The separation of aromatic and aliphatic hydrocarbons is complicated due to overlapping boiling points and azeotrope formation. Hence, the conventional processes for this type of separation are extraction or extractive distillation with polar, organic compounds. Industrially most common processes use solvents such as NFM (Uhde Morphyllane® process), Sulfolane® (UOP/Shell Sulfolane® Process), NMP, ethylene glycols, etc. [1].

Another class of solvents, which are considered promising to replace organic solvents in industrial processes [2], are ionic liquids (ILs). Ionic liquids are liquid salts consisting of large, mostly organic, cations and a great variety of anions. Their positive properties are a wide liquid temperature range (~ 300 K), low vapour pressure and the ability of tailoring. The latter provides the possibility to develop a special solvent for a specific application, e.g. separation of aromatic and aliphatic hydrocarbons.

The criteria, which a suitable ionic liquid for the separation of aromatic and aliphatic hydrocarbons must meet, are the same as for conventional solvents [3–5]. In general, this means high solubility for the aromatic hydrocarbons in the solvent combined with a high selectivity resulting from a low solubility of the aliphatic components.

In the open literature mostly imidazolium based ionic liquids combined with anions such as $[\text{TF}_2\text{N}]^-$, $[\text{CH}_3\text{SO}_4]^-$, and $[\text{BF}_4]^-$ are described as solvents for the extraction of aromatic hydrocarbons from aliphatic components [6–13]. For the extraction of toluene from *n*-

heptane it was recently shown that anions such as $[\text{DCA}]^-$ in combination with pyridinium cations provide superior capacity and selectivity [14]. Since real petrochemical streams, e.g. naphtha, consist of a large variety of components, it is important that, in addition to toluene and *n*-heptane, also (liquid + liquid) equilibrium data for ionic liquids with other important constituents of petrochemical streams are generated. For this reason, the objective of this work is to determine (liquid + liquid) equilibrium (LLE) data for 3-methyl-*N*-butylpyridinium dicyanamide in various ternary mixtures with benzene, cumene, and *p*-xylene as aromatics and *n*-hexane and *n*-nonane as paraffins over a broad composition range. The experimental phase compositions were correlated with the non-random two liquids (NRTL) activity coefficient model for the ternary systems (3-methyl-*N*-butylpyridinium dicyanamide + benzene + *n*-hexane), (3-methyl-*N*-butylpyridinium dicyanamide + cumene + *n*-nonane), (3-methyl-*N*-butylpyridinium dicyanamide + *p*-xylene + *n*-hexane), at $T = 303.15$ K and 328.15 K and $p = 0.1$ MPa.

2. Experimental section

2.1. Materials and methods

The ionic liquid 3-methyl-*N*-butylpyridinium dicyanamide, [3-Mebupy][DCA], (>97%) and *p*-xylene ($\geq 99.9\%$) were purchased from Merck. Benzene ($\geq 99\%$), cumene (98%), *n*-hexane ($\geq 99\%$), *n*-nonane ($\geq 95\%$), ethylbenzene ($\geq 99\%$), and acetone (p.a. >99%) were purchased from Fluka. Prior to the experiments, the ionic liquid has been dried in a rotary evaporator (Büchi Rotavapor R-200) at 100°C and under reduced pressure. Subsequent, the water

* Corresponding author. Tel.: +31 40 247 2424; fax: +31 40 246 3966.
E-mail address: a.hansmeier@tue.nl (A.R. Hansmeier).

content of [3-Mebupy][DCA] has been determined by means of Karl–Fischer titration and was found to be 900 ppm.

2.2. Equipment and experimental procedure

Liquid–liquid extraction experiments were carried out in jacketed glass vessels with a volume of about 70 ml. The vessels were closed with a PVC-cover through which a stirrer shaft was lead. For each experiment 10 ml of the feed and 20 ml ionic liquid have been added and the mixture was stirred (1200 rpm) for 15 min to reach equilibrium [5]. After stirring, the two phases were allowed to settle for about 1 h. For phase mixing two stainless steel propellers, one in the bottom phase and one at the phase interface, with an electronic stirrer (Ika Eurostar) were used. In order to maintain constant temperature (± 0.1 K) a water bath (Julabo F32-MW) was used. A more detailed description of the experimental procedure was reported earlier by Meindersma *et al.* [5].

2.3. Analysis

After equilibrium was reached, a sample of 0.5 ml of each phase was taken and analysed by gas chromatography (Varian CP-3800). Acetone was added to the samples to avoid phase splitting and to maintain a homogeneous mixture. Ethylbenzene (0.2 ml for the raffinate samples and 0.1 ml for the extract phase samples) was used as internal standard for the GC-analysis. The compositions of toluene and heptane in the samples were analysed by a Varian CP-3800 gas chromatograph with an WCOT fused silica CP-SIL 5CB column (50 m $\times$ 0.32 mm; DF = 1.2) and a Varian 8200 Auto-Sampler. Since ionic liquids have no vapour pressure and they cannot be analyzed by GC only the hydrocarbons of the feed were analyzed and the amount of ionic liquid was calculated by means of a mass balance. For a ternary mixture, only two components need to be analyzed; the third one, the ionic liquid, was determined by a mass balance of the measured mass fractions of toluene and heptane. In order to avoid inaccuracy of the analysis caused by fouling of the gc by the ionic liquid a liner and a pre-column have been used. Furthermore, measurements were carried out in duplicate to increase accuracy.

The deviation in the calibration curves of 1% and a possible contamination of the gas chromatograph can cause a variance in the mole fractions (estimated on 1%). The averages of the two measurements were used in our results. The relative average deviation in the compositions is about 2.5%.

3. LLE data correlation

The phase equilibrium data for the described systems were correlated with the non-random two liquids (NRTL) model derived by Renon and Prausnitz in 1968. It was shown earlier that this model is a good approach for the description of LLE and VLE for systems containing ionic liquids [15–18]. The objective function for the regression of the NRTL-parameters is the equality of the activity for each component in both phases. With the assumption of equilibrium in the liquid phase, the referring equation is:

$$x_i^R = \gamma_i^E / \gamma_i^R \cdot x_i^E, \quad (1)$$

where x_i^R is the composition of component i in the raffinate phase, x_i^E the composition of component i in the extract phase, γ_i^E the activity coefficient of component i in the extract phase and γ_i^R the activity coefficient of component i in raffinate phase. The activity coefficients were determined by means of Gibbs excess free energy. Hence, the required parameters for the binary interactions were calculated according to

$$\tau_{ij} = a_{ij} + b_{ij}/T, \quad G_{ij} = \exp(-\alpha_{ij}\tau_{ij}), \quad \alpha_{ij} = \alpha_{ji}, \quad (2)$$

whereas τ_{ij} and G_{ij} are NRTL-parameters, which are calculated via the non-randomness parameter, α_{ij} , and the parameters a_{ij} and b_{ij}/K . The model parameters of the NRTL equation (a_{ij} , a_{ji} , b_{ij}/K and b_{ji}/K) were determined via data regression using ASPEN Plus 12.1. The values of the non-randomness parameter, α , were assigned to 0.3 for the interaction aromatic/aliphatic and regressed for the interaction aromatic/IL and aliphatic/IL, see table 1. The parameters obtained describe the three ternary systems investigated in this work well, however, the application to similar systems is not recommended. Moreover, in recently published work investigating the ternary system (toluene + n -heptane + ionic liquid) with the chemically alike ionic liquids [BMIM][DCA], [BMIM][SCN], and [3-Mebupy][DCA] significantly different parameters for all three systems were obtained [19].

Since the concentration of the ionic liquid in the raffinate phase is very low, while it is very large in the extract phase the constraints for the ionic liquids in the data properties were left out in order to avoid numerical problems. This has been done according to Seiler *et al.* [20], who suggests treating the IL as non-dissociating solvent. The negligible vapour pressure for the ionic liquids was represented by means of the Antoine equation and, in order to be able to fulfill the equation for the equality of fugacity and to circumvent numerical problems, calculated to be $<10^{-2}$ Pa. In order to obtain sound results for the ternary systems (3-methyl- N -butylpyridinium dicyanamide + benzene + n -hexane) and (3-methyl- N -butylpyridinium dicyanamide + cumene + n -nonane) the standard deviation was adjusted to 1×10^{-5} for (3-methyl- N -butylpyridinium dicyanamide + benzene + n -hexane) and to 1×10^{-4} for cumene and 1×10^{-6} for n -nonane in case of (3-methyl- N -butylpyridinium dicyanamide + cumene + n -nonane). Additionally, for the system (3-methyl- N -butylpyridinium dicyanamide + benzene + n -hexane) the data points $x_{\text{benzene}} = 0.8350$ [mole/mole] and $x_{\text{benzene}} = 0.7610$ [mole/mole] at $T = 303.15$ K and 328.15 K, respectively have been weighed with a factor five. The same procedure has been applied for the system (3-methyl- N -butylpyridinium dicyanamide + p -xylene + n -hexane) for the values $x_{p\text{-xylene}} = 0.8370$ [mole/mole] and $x_{p\text{-xylene}} = 0.8020$ [mole/mole] at $T = 303.15$ K and 328.15 K, respectively. The values for the regressed binary interaction parameters are given in table 1.

4. Results and discussion

The experimental LLE data for the ternary systems ([3-Mebupy][DCA] + benzene + n -hexane), ([3-Mebupy][DCA] + cumene + n -nonane) and ([3-Mebupy][DCA] + p -xylene + n -hexane) at $T = 303.15$ and $T = 328.15$ K and $p = 0.1$ MPa are reported in tables 2 to 4.

Together with the LLE data tables 2 to 4 include the corresponding values for the solute distribution ratio (β_i) and the selectivity (S), which are widely used parameters to characterize the suitability of a solvent in liquid–liquid extraction. The distribution coefficients β_i are directly calculated from the mole fractions in extract and raffinate phase at equilibrium. β_i is defined as the ratio of the mole fractions of the component in the extract phase (ionic liquid) and in the raffinate phase (organic phase). Their calculation is easily made from the experimental compositions of the tie line ends, according to the following expressions:

$$\beta_{\text{aromatic}} = x_{\text{arom}}^{\text{IL}} / x_{\text{arom}}^{\text{org}}, \quad (3)$$

$$\beta_{\text{aliphatic}} = x_{\text{aliph}}^{\text{IL}} / x_{\text{aliph}}^{\text{org}}, \quad (4)$$

The selectivity S is derived from the ratio of the distribution coefficients, according to:

$$S = \beta_{\text{arom}} / \beta_{\text{aliph}}. \quad (5)$$

TABLE 1

Binary interaction parameters for the correlation of the experimental LLE data of the ternary systems (aromatic + aliphatic + ionic liquid) by the NRTL model at $T = 303.15$ K and 328.15 K.

Binary parameter	a_{ij}	a_{ji}	b_{ij}/K	b_{ji}/K	α
Benzene + <i>n</i> -hexane	3.368	−3.786	449.6	1781.3	0.3
Benzene + [3-Mebupy][DCA]	0.050	0.864	147.1	432.5	−0.1744
<i>n</i> -Hexane + [3-Mebupy][DCA]	−0.131	5.984	−271.5	1603.7	0.2693
<i>p</i> -Xylene + <i>n</i> -hexane	−1.224	0.523	299.3	1087.2	0.3
<i>p</i> -Xylene + [3-Mebupy][DCA]	1.929	0.679	237.4	−197.8	0.1032
<i>n</i> -Hexane + [3-Mebupy][DCA]	6.111	5.644	583.5	1426.2	0.3436
Cumene + <i>n</i> -nonane	−2.256	−0.718	507.8	651.1	0.3
Cumene + [3-Mebupy][DCA]	−0.265	1.129	−256.9	350.3	−0.5026
<i>n</i> -Nonane + [3-Mebupy][DCA]	1.191	1.482	146.2	189.6	−0.3465

TABLE 2

Composition of the experimental tie lines and values of the solute distribution ratio (β) and selectivity (S) for the ternary system (benzene (1) + *n*-hexane (2) + [3-Mebupy][DCA] (3)) at $p/\text{MPa} = 0.1$ and $T = 303.15$ K and 328.15 K.

<i>n</i> -Hexane-rich phase			[3-Mebupy][DCA]-rich phase			β		S
x_1	x_2	x_3	x_1	x_2	x_3	Benzene	<i>n</i> -Hexane	Exp.
$T = 303.15$ K								
0.0000	0.9990	0.0010	0.0000	0.0240	0.9760	–	0.0240	–
0.0660	0.9340	0.0000	0.0960	0.0250	0.8790	1.45	0.0268	54.1
0.1340	0.8650	0.0010	0.1590	0.0210	0.8200	1.19	0.0243	49.0
0.2200	0.7790	0.0010	0.2370	0.0190	0.7440	1.08	0.0244	44.3
0.2940	0.7050	0.0010	0.2990	0.0210	0.6800	1.02	0.0298	34.2
0.4110	0.5880	0.0010	0.3590	0.0200	0.6210	0.87	0.0340	25.6
0.4850	0.5150	0.0010	0.4230	0.0190	0.5580	0.87	0.0369	23.6
0.5740	0.4250	0.0010	0.4780	0.0190	0.5030	0.83	0.0447	18.6
0.6860	0.3130	0.001	0.5490	0.0180	0.4340	0.80	0.0575	13.9
0.8350	0.1640	0.0010	0.6270	0.0130	0.3600	0.75	0.0793	9.5
0.9990	0.0000	0.0010	0.7420	0.0000	0.2580	0.74	–	–
$T = 328.15$ K								
0.0000	0.9990	0.0010	0.0000	0.0300	0.9700	–	0.0300	–
0.0810	0.9180	0.0010	0.0900	0.0250	0.8850	1.11	0.0272	40.8
0.1480	0.8510	0.0010	0.1470	0.0240	0.8290	0.99	0.0282	35.1
0.2370	0.7630	0.0000	0.2220	0.0260	0.7520	0.94	0.0341	27.6
0.3310	0.6690	0.0000	0.2830	0.0230	0.6940	0.85	0.0344	24.7
0.4320	0.5670	0.0010	0.3450	0.0220	0.6330	0.80	0.0388	20.6
0.5450	0.4540	0.0010	0.4140	0.0210	0.5650	0.76	0.0463	16.4
0.6410	0.3580	0.0010	0.4200	0.0200	0.5600	0.66	0.0559	11.8
0.7610	0.2390	0.0000	0.5360	0.0160	0.4480	0.70	0.0669	10.5
0.9990	0.0000	0.0010	0.7000	0.0000	0.3000	0.70	–	–

The ternary diagrams for all three systems are depicted at both temperatures in figure 1. The binodal curves indicate that aromatic hydrocarbons are partially soluble in the tested ionic liquid. Solubility limits for the binary systems (aromatic + IL) and (paraffin + IL) are presented in tables 2 to 4. By comparing the different binary systems, it is apparent that the solubility of the studied aromatic hydrocarbons in the ionic liquid 3-methyl-*N*-butylpyridinium dicyanamide is influenced by length, number and order of the side chains of the aromatic ring. Hence, the solubility of the investigated aromatics decreases in the order of benzene > *p*-xylene > cumene with the following values $x_{\text{benzene}} = 0.74$ [mole/mole], $x_{p\text{-xylene}} = 0.40$ [mole/mole] and $x_{\text{cumene}} = 0.21$ [mole/mole] at $T = 303$ K. It was observed that the solubility of aliphatic hydrocarbons in the investigated ionic liquid decreases with increasing chain length of the molecules: *n*-hexane > *n*-nonane. Whereby the solubilities at $T = 303$ K are: $x_{n\text{-hexane}} = 0.08$ [mole/mole] ([3-Mebupy][DCA] + benzene + *n*-hexane), $x_{n\text{-hexane}} = 0.06$ [mole/mole] ([3-Mebupy][DCA] + *p*-xylene + *n*-hexane) and $x_{n\text{-nonane}} = 0.02$ [mole/mole], respectively.

4.1. Distribution coefficient

As illustrated by figure 2, the aromatic distribution coefficient decreases with increasing aromatic mole fraction, whereas the ali-

phatic distribution coefficient increases with increasing aromatic mole fraction. Holbrey *et al.* showed that ionic liquids and aromatic solutes organize in a sandwich structure, where the ionic liquid cations and the aromatic solutes interact in an alternating structure through π - π interactions with the ionic liquid anions arranged around this complex [21]. With increasing aromatics content the distance between aromatic solutes and cations becomes larger, reducing the strength of interaction and thereby the distribution coefficient. Additionally, the increased aromatics content of the ionic liquid increases the aliphatic distribution coefficient by enabling the aliphatic components to arrange themselves between the molecules.

With respect to temperature it is visible in figure 2 that, except for benzene, the aromatic distribution coefficient, β_{aromatic} , is almost temperature independent, while the aliphatic distribution coefficient increases with increasing temperature. Also this observation can be explained by increased molecular movements caused by increasing temperature, which breaks down the ordered sandwich like structure within the ionic liquid. As a consequence, the solubility due to the specific aromatic-ionic liquid π - π interactions is reduced, while at the same time the thermal expansion enables more aromatics to arrange themselves between the ions. Apparently both effects cancel out, resulting in a more or less constant aromatics distribution coefficient. For the aliphatics the break

TABLE 3

Composition of the experimental tie lines and values of the solute distribution ratio (β) and selectivity (S) for the ternary system (*p*-xylene (1) + *n*-hexane (2) + [3-Mebupy][DCA] (3)) at $p/\text{MPa} = 0.1$ and $T = 303.15\text{ K}$ and 328.15 K .

p-Xylene-rich phase			[3-Mebupy][DCA]-rich phase			β		S
x_1	x_2	x_3	x_1	x_2	x_3	p-Xylene	n-Hexane	Exp.
$T = 303.15\text{ K}$								
0.0000	0.9990	0.0010	0.0000	0.0250	0.9750	–	0.0250	–
0.0600	0.9390	0.0010	0.0320	0.0220	0.9460	0.53	0.0234	22.6
0.1310	0.8680	0.0010	0.0660	0.0230	0.9110	0.50	0.0265	18.9
0.2050	0.7940	0.0010	0.1020	0.0230	0.8750	0.50	0.0290	17.2
0.2870	0.7120	0.0010	0.1350	0.0230	0.8420	0.47	0.0323	14.6
0.3650	0.6340	0.0010	0.1690	0.0220	0.8090	0.46	0.0347	13.3
0.4620	0.5370	0.0010	0.2030	0.0200	0.7770	0.44	0.0372	11.8
0.5830	0.4160	0.0010	0.2440	0.0170	0.7390	0.42	0.0409	10.3
0.6970	0.3020	0.0010	0.2890	0.0140	0.6970	0.41	0.0464	8.8
0.8370	0.1620	0.0010	0.3440	0.0090	0.6470	0.41	0.0556	7.4
0.9990	0.0000	0.0010	0.4010	0.0000	0.5990	0.40	–	–
$T = 328.15\text{ K}$								
0.0000	1.0000	0.0010	0.0000	0.0260	0.9740	–	0.0260	–
0.0710	0.9290	0.0010	0.0340	0.0270	0.9390	0.48	0.0291	16.5
0.1450	0.8550	0.0010	0.0710	0.0280	0.9010	0.49	0.0327	15.0
0.2260	0.7740	0.0010	0.0990	0.0250	0.8760	0.44	0.0323	13.6
0.3220	0.6780	0.0010	0.1350	0.0240	0.8410	0.42	0.0353	11.9
0.3950	0.6050	0.0010	0.1620	0.0220	0.8160	0.41	0.0364	11.3
0.5040	0.4960	0.0010	0.2160	0.0230	0.7610	0.43	0.0464	9.3
0.6390	0.3610	0.0010	0.2590	0.0180	0.7230	0.41	0.0499	8.2
0.7350	0.2650	0.0010	0.2740	0.0140	0.7120	0.37	0.0528	7.0
0.8020	0.1980	0.0010	0.3070	0.0110	0.6820	0.38	0.0556	6.8
1.000	0.0000	0.0010	0.3810	0.0000	0.6190	0.38	–	–

TABLE 4

Composition of the experimental tie lines and values of the solute distribution ratio (β) and selectivity (S) for the ternary system (cumene (1) + *n*-nonane (2) + [3-Mebupy][DCA] (3)) at $p/\text{MPa} = 0.1$ and $T = 303.15\text{ K}$ and 328.15 K .

n-Nonane-rich phase			[3-Mebupy][DCA]-rich phase			β		S
x_1	x_2	x_3	x_1	x_2	x_3	Cumene	n-Nonane	Exp.
$T = 303.15\text{ K}$								
0.0000	0.9990	0.0010	0.0000	0.0064	0.9940	–	0.0064	–
0.0810	0.9170	0.0020	0.0250	0.0068	0.9680	0.31	0.0074	41.9
0.1780	0.8210	0.0010	0.0480	0.0064	0.9460	0.27	0.0078	34.6
0.2680	0.7310	0.0010	0.0700	0.0058	0.9240	0.26	0.0079	32.9
0.3530	0.6460	0.0010	0.0940	0.0059	0.9000	0.27	0.0091	29.7
0.4470	0.5510	0.0020	0.1130	0.0056	0.8810	0.25	0.0102	24.5
0.5560	0.4430	0.0010	0.1390	0.0046	0.8560	0.25	0.0104	24.0
0.6560	0.3430	0.0010	0.1710	0.0042	0.8250	0.26	0.0122	21.3
0.7830	0.2160	0.0010	0.1880	0.0027	0.8090	0.24	0.0125	19.2
0.8840	0.1150	0.0010	0.1860	0.0015	0.8130	0.21	0.0130	16.2
0.9990	0.0000	0.0010	0.2130	0.000	0.7870	0.21	–	–
$T = 328.15\text{ K}$								
0.0000	0.9990	0.0010	0.0000	0.0078	0.9920	–	0.0078	–
0.0820	0.9160	0.0020	0.0240	0.0075	0.9680	0.29	0.0082	35.4
0.1780	0.8210	0.0010	0.0480	0.0073	0.9450	0.27	0.0089	30.3
0.2670	0.7310	0.0020	0.0690	0.0068	0.9240	0.26	0.0093	28.0
0.3580	0.6400	0.0020	0.0890	0.0067	0.9040	0.25	0.0105	23.8
0.4540	0.5440	0.0020	0.1100	0.0063	0.8840	0.24	0.0116	20.7
0.5600	0.4390	0.0010	0.1350	0.0053	0.8600	0.24	0.0121	19.8
0.6550	0.3440	0.0010	0.1610	0.0046	0.8340	0.25	0.0134	18.7
0.7780	0.2200	0.0020	0.1750	0.0032	0.8220	0.22	0.0145	15.2
0.8410	0.1580	0.0010	0.1820	0.0024	0.8160	0.22	0.0152	14.5
0.9990	0.0000	0.0010	0.2730	0.0000	0.7270	0.27	–	–

down of the ordered structure within the ionic liquid is the dominating effect, resulting in a higher aliphatic solubility at higher temperatures. The reduced benzene capacity with increasing temperature can be explained from the same phenomena. Compared to the other studied aromatics, benzene is the smallest molecule with the least sterical hindrance and strongest π -system. Therefore, the interaction between benzene and the ionic liquid is, compared to the other aromatic hydrocarbons, the most strongly based on π -

π -interaction. Additionally its molecular movement is higher than that of the other aromatic components. Therefore, the reduction in the strength of π - π -interaction due to a break down of the sandwich structure at higher temperatures is the dominating phenomenon for benzene that decreases the benzene distribution coefficient. At the same time this creates more space for the aliphatic components to arrange themselves between the ionic liquid, explaining the stronger temperature dependence for β_{Hexane} in the

FIGURE 1. Ternary diagrams of the systems: at $T/K = 303.15$ (left) K and 328.15 (right) K, (Experiments: ■, solid lines; calculated: – dashed lines).

mixture ([3-Mebupy][DCA] + benzene + *n*-hexane) compared to ([3-Mebupy][DCA] + *p*-xylene + *n*-hexane).

4.2. Selectivity

In line with the effects of aromatics concentration and temperature on the distribution coefficients is the influence of these effects on the aromatic/aliphatic selectivity. The decrease of β_{aromatic} and increase of $\beta_{\text{aliphatic}}$ is expressed by a decrease in selectivity as it is apparent from figure 3.

From figure 1 it is obvious, that the solubility of the aromatics decreases in the following order: benzene > *p*-xylene > cumene. Whereas, evident from figure 3, this effect is the strongest for benzene with a significant sharp decrease in solubility and therewith selectivity. For other aromatic hydrocarbons the decrease in solubility is less strong. This is due to sterical hindering of the alkyl groups attached to the aromatic ring. The more and/or bigger the side chains, the more difficult it is for the molecules to organize in a sandwich structure [21] which is the likely reason for the decrease in selectivity. Thus, in general, the decrease in selectivity of the different systems follows the solubility. However, in this case

FIGURE 2a. (a) Aromatic distribution coefficient (β) dependent on the aromatic mole fraction in the raffinate phase (x) (♦ benzene, ▲ *p*-xylene, ● cumene; ♦, ▲, ● 302.15 K; ◇, △, ○ 328.15 K).

FIGURE 2b. (b) Aliphatic distribution coefficient (β) dependent on the aromatic mole fraction in the raffinate phase (x) (♦ *n*-hexane (benzene), ▲ *n*-hexane (*p*-xylene), ● *n*-nonane; ♦, ▲, ● 302.15 K; ◇, △, ○ 328.15 K).

FIGURE 3. Aromatic/aliphatic selectivity (S) dependent on the aromatic mole fraction in the raffinate phase (x) at $T = 303.02$ K (♦ benzene/*n*-hexane, ▲ *p*-xylene/*n*-hexane, ● cumene/*n*-nonane; — calculated).

TABLE 5

Root mean square deviation (δ) for the ternary mixtures (aromatic + aliphatic/olefine + ionic liquid).

Ternary system	δ	
	$T = 303.15$ K	$T = 328.15$ K
Benzene + <i>n</i> -hexane + [3-Mebupy][DCA]	0.0155	0.0088
<i>p</i> -Xylene + <i>n</i> -hexane + [3-Mebupy][DCA]	0.0056	0.0039
Cumene + nonane + [3-Mebupy][DCA]	0.0324	0.0250

due to the extreme low solubility of *n*-nonane the selectivities are in the order of benzene/*n*-hexane > cumene/*n*-nonane > *p*-xylene/*n*-hexane. Therewith, the conclusions drawn from figure 1 are verified by the graphs for the different aromatic selectivities shown in figure 3.

4.3. Comparison of experimental and correlated data

As it is visible in figure 1, the experimental data are well correlated by the NRTL equation. Hence, there is a good agreement between experimental and calculated data and the tie lines in the ternary diagrams coincide in most cases. The validity of the model has been verified by means of the root mean square deviation (δ):

$$\delta = \left\{ \sum_i \sum_l \sum_m (x_{ilm}^{\text{exp}} - x_{ilm}^{\text{calc}})^2 / 6k \right\}^{1/2}, \quad (6)$$

where x is the mole fraction; the subscripts i , l and m provide a designation for the component, phase and the tie lines, respectively. The value k designates the number of tie lines. The values of the δ of the systems are listed in table 5. From these values it can be inferred that a good correlation of the experimental values with the NRTL model was obtained ($\delta < 0.0056$). The small deviations that arise are mainly due to the poor predictions of the low mole fractions for the ionic liquid in the raffinate phase and the aliphatic mole fraction in the extract phase.

Experimental and calculated values of the selectivities of the three measured ternary diagrams are compared in figure 3. It is apparent that for all measured ternary systems the values are in good agreement.

5. Conclusion

Liquid–liquid experimental data were determined for the ternary systems ([3-Mebupy][DCA] + benzene + *n*-hexane), ([3-Mebupy][DCA] + cumene + *n*-nonane) and ([3-Mebupy][DCA] + *p*-xylene + *n*-hexane at 303.15 K and 328.15 K). The ionic liquid [3-Mebupy][DCA] has the highest extraction capacity for benzene and the lowest for cumene. All experimental data can be adequately correlated with the NRTL model. The root mean square deviation values of the correlations are generally below 0.0056. The experimental and calculated (aromatic + aliphatic) selectivities are in good agreement with each other.

Acknowledgement

We acknowledge BP for financial support of this project.

References

- [1] W.A. Sweeny, P.F. Bryan, Kirk-Othmer, Encyclopedia of Chemical Technology (electronic version), John Wiley & Sons, 1992.
- [2] A. Heintz, Recent. J. Chem. Thermodyn. 37 (2005) 525–535.
- [3] C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, Wiley-VCH, Weinheim, 2003.
- [4] J. Lagowski, The Chemistry of Nonaqueous Solvents, Academic Press, New York, 1966.
- [5] G.W. Meindersma, A. Podt, A.B. de Haan, Fuel Process. Technol. 87 (2005) 59–70.
- [6] A. Arce, M. Earle, H. Rodriguez, K. Seddon, Green Chem. 9 (2006) 70–74.
- [7] U. Domanska, L. Mazurowska, Fluid Phase Equilib. 221 (2004) 73–82.
- [8] T. Letcher, P. Reddy, J. Chem. Thermodyn. 37 (2005) 415–421.
- [9] M. Krummen, P. Wasserscheid, J. Gmehling, J. Chem. Eng. Data 47 (2002) 1411–1417.
- [10] G. Foco, S. Bottini, N. Quezada, J. de la Fuente, C. Peters, J. Chem. Eng. Data 51 (2006) 1088–1091.
- [11] A. Arce, M. Earle, H. Rodriguez, K. Seddon, J. Phys. Chem. B 111 (2007) 4732–4736.
- [12] U. Domanska, A. Pobudkowska, Z. Zolek-Tryznowska, J. Chem. Eng. Data 52 (2007) 2345–2349.
- [13] D. Eike, J. Brennecke, E. Maginn, Ind. Eng. Chem. Res. 43 (2004) 1039–1048.

- [14] A. Hansmeier, G. Meindersma, A.B. de Haan, Conference Proceedings International Solvent Extraction Conference (ISEC): Tuscon, 2008, pp. 1331–1336.
- [15] U. Domanska, A. Marciniak, J. Chem. Thermodyn. 37 (2005) 577–585.
- [16] T. Letcher, N. Deenadayalu, J. Chem. Thermodyn. 35 (2003) 67–76.
- [17] G.W. Meindersma, A. Podt, A.B. de Haan, J. Chem. Eng. Data 51 (2006) 1814–1819.
- [18] G.W. Meindersma, A. Podt, A.B. de Haan, Fluid Phase Equilib. 247 (2006) 158–168.
- [19] A.R. Hansmeier, M. Minoves Ruiz, G.W. Meindersma, A.B. de Haan, J. Chem. Eng. Data, 2009. doi:10.1021/jc9004239.
- [20] M. Seiler, C. Jork, T. Schneider, W. Arlt, in: Proceedings of the International Conference on Distillation and Absorption: Baden-Baden, 2002, 30/9-2/10.
- [21] J.D. Holbrey, W.M. Reichert, M. Nieuwenhuyzen, O. Sheppard, C. Hardacre, R.D. Rogers, Chem. Commun. (2003) 476–477.

JCT 09-237