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1 Imidazolium and pyridinium-based ionic liquids for the 2 cyclohexane/cyclohexene separation by liquid-liquid extraction

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9 Abstract

10 The separation of olefins/paraffins is a challenge for the petrochemical industry due to the
11 close boiling points of these hydrocarbons. In this work we have studied the feasibility of
12 different imidazolium and pyridinium-based ionic liquids (ILs) as alternative solvents in the
13 cyclohexane/cyclohexene separation. Five ILs have been studied, namely 1-butyl-4-
14 methylpyridinium tricyanomethanide ([4bmpy][TCM]), bis(1-ethyl-3-methylimidazolium)
15 tetrathiocyanatocobaltate ([emim]₂[Co(SCN)₄]), bis(1-butyl-3-methylimidazolium)
16 tetrathiocyanatocobaltate ([bmim]₂[Co(SCN)₄]), 1-ethyl-4-methylpyridinium
17 bis(trifluoromethylsulfonyl)imide ([4empy][Tf₂N]), and 1-butyl-4-methylpyridinium
18 bis(trifluoromethylsulfonyl)imide ([4bmpy][Tf₂N]). Experimental liquid-liquid equilibrium
19 (LLE) data were obtained for the equimolar ternary mixtures {cyclohexane (1) + cyclohexene
20 (2) + IL (3)} at $T = (298.2, 313.2 \text{ and } 328.2) \text{ K}$ and atmospheric pressure in order to study the
21 effect of the temperature on the extractive properties. Afterwards, LLE data for every ternary
22 system was determined at the best temperature and for the whole cyclohexane/cyclohexene
23 composition range. These ILs have shown promising results in terms of distribution ratio and
24 selectivity, showing the [4bmpy][TCM] IL the best extractive properties at 298.2 K and
25 atmospheric pressure. The Non-Random Two Liquids (NRTL) model was used to
26 successfully correlate the experimental LLE data.

27
28 **Keywords:** Cyclohexane/cyclohexene separation; liquid-liquid extraction; ionic liquids;
29 NRTL model.

30

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31 **1. Introduction**

32 The separation of olefins from paraffins by distillation process involves both large
33 energetic costs and capital investment due to the close relative volatilities of these compounds
34 [1]. To overcome this drawback, the separation of close boiled compounds is commonly
35 performed via extractive or azeotropic distillation [2, 3], and pressure swing adsorption (PSA)
36 [1]. In the last decades, different technologies have been studied as alternative to conventional
37 cyclohexane/cyclohexene separation processes, namely membranes technologies [4] and
38 liquid-liquid extraction with ionic liquids (ILs) [5].

39 Liquid-liquid extraction with ILs rises as a new separation technology, which could
40 operate at mild process conditions. The use of ILs as extractive solvents would improve the
41 capacities and selectivities with respect to conventional organic solvents and would decrease
42 the solvent losses in the process [6]. Domanska *et al.* have reported that imidazolium- and
43 pyridinium-based ILs with cyano anions, such as [DCA]⁻ [3, 6-9], [TCM]⁻ [3, 6], or [Tf₂N]⁻
44 [3, 6, 7], show high solvation properties and give satisfying results in the liquid-liquid
45 extraction for the hexane/hex-1-ene and the cyclohexane/cyclohexene separation. Different
46 works based on activity coefficients at infinite dilution have also reported high selectivity
47 and/or acceptable distribution ratio for the hexane/hex-1-ene and the
48 cyclohexane/cyclohexene separation, using mainly imidazolium and pyridinium-based ILs
49 with different anions: dicyanamide, [DCA]⁻ [10-15], tricyanomethanide, [TCM]⁻ [16, 17],
50 bis(trifluoromethylsulfonyl)imide, [Tf₂N]⁻ [14, 18-23], and thiocyanate, [SCN]⁻ [5, 24, 25].

51 In this work we have studied the separation of cyclohexane/cyclohexene by liquid-liquid
52 extraction using different imidazolium- and pyridinium-based ILs. Five ILs have been
53 studied, namely 1-butyl-4-methylpyridinium tricyanomethanide ([4bmpy][TCM]), bis(1-
54 ethyl-3-methylimidazolium) tetrathiocyanatocobaltate ([emim]₂[Co(SCN)₄]), bis(1-butyl-3-
55 methylimidazolium) tetrathiocyanatocobaltate ([bmim]₂[Co(SCN)₄]), 1-ethyl-4-
56 methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf₂N]), and 1-butyl-4-
57 methylpyridinium bis(trifluoromethylsulfonyl)imide ([4bmpy][Tf₂N]). New experimental
58 LLE data have been reported for the ternary systems {cyclohexane (1) + cyclohexene (2) + IL
59 (3)}. We have selected pyridinium-based ILs because this cation improves the extractive
60 capacity of the IL in aromatic/aliphatic separations [26, 27]. The tetrathiocyanatocobaltate-
61 based ILs have been selected because the presence of transition metal salts also improves the
62 separation of aromatics and olefins from alkanes [28, 29]. In our previous work, we also
63 corroborated that the values of distribution ratio of aromatics for [emim]₂[Co(SCN)₄] and
64 [bmim]₂[Co(SCN)₄] ILs in the separation of aromatic hydrocarbons from a pyrolysis gasoline

65 were substantially higher than those for the [emim][SCN] and [bmim][SCN] ILs [30]. Against
66 this background, herein we have decided to study the effectiveness of the five above-
67 mentioned ILs in the cyclohexane/cyclohexene separation.

68 First, LLE data have been determined for the equimolar ternary systems {cyclohexane (1)
69 + cyclohexene (2) + IL (3)} at $T = (298.2, 313.2 \text{ and } 328.2) \text{ K}$ and atmospheric pressure.
70 Once the best temperatures for every system have been selected, the LLE data have been
71 determined for the whole cyclohexane/cyclohexene composition range. Finally, the NRTL
72 model has been used to correlate the experimental data of the five ternary systems.

73 2. Experimental

74 2.1. Chemicals

75 The ILs, namely 1-butyl-4-methylpyridinium tricyanomethanide ([4bmpy][TCM]), bis(1-
76 ethyl-3-methylimidazolium) tetrathiocyanatocobaltate ([emim]₂[Co(SCN)₄]), bis(1-butyl-3-
77 methylimidazolium) tetrathiocyanatocobaltate ([bmim]₂[Co(SCN)₄]), 1-ethyl-4-
78 methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf₂N]), and 1-butyl-4-
79 methylpyridinium bis(trifluoromethylsulfonyl)imide ([4bmpy][Tf₂N]), were purchased from
80 Iolitec GmbH with a mass purity higher than 0.98. Water and halides content were determined
81 by the supplier using Karl-Fischer titration and Ion Chromatography, respectively.
82 Cyclohexane and cyclohexene were supplied by Sigma-Aldrich with a mass purity of 0.995
83 and 0.990, respectively. The compound chemical specifications are listed in Table 1. ILs were
84 stored in a desiccator and handled in a glove box under dry nitrogen to avoid their hydration.
85 All chemicals were used as received from the suppliers without further purification.

86 2.2. Experimental procedure and analysis

87 Hydrocarbons and ILs were gravimetrically added to 8 mL vials using a Mettler Toledo XS
88 205 balance with a precision of $\pm 1 \times 10^{-5} \text{ g}$. The LLE was reached in a Labnet Vortemp 1550
89 shaking incubator for 5 h at $T = (298.2, 313.2 \text{ and } 328.2 \pm 0.3) \text{ K}$. To reach the complete
90 phase separation, the vials were moved to a Labnet Accublock dry bath for 12 h at $T = (298.2,$
91 $313.2 \text{ and } 328.2 \pm 0.5) \text{ K}$. Triplicate samples from the raffinate phase were analysed in an
92 Agilent 7890A gas chromatograph (GC) equipped with a flame ionization detector (FID). The
93 extract phase was analysed following the multiple headspace extraction (MHE) method.
94 Triplicate samples of 100 μL from the extract phase were added to 20 mL vials and analysed
95 using an Agilent 7890A GC coupled with a Headspace Sampler Agilent 7697A. A detailed
96 description of both analytical methods can be found in our previous work [31].

97 **Table 1.**Compound chemical specifications.

Chemical name	Supplier	CAS number	Mass fraction purity	Analysis method	Water content/wt.% ^d	Halide content/10 ⁻⁶ b
[4bmpy][TCM]	Iolitec GmbH	1312925-66-8	0.98	NMR ^a and IC ^b	0.0129	< 500
[emim] ₂ [Co(SCN) ₄]	Iolitec GmbH	1255925-80-4	0.99	NMR ^a and IC ^b	0.0040	< 500
[bmim] ₂ [Co(SCN) ₄]	Iolitec GmbH	1245942-47-5	0.99	NMR ^a and IC ^b	0.0210	< 500
[4empy][Tf ₂ N]	Iolitec GmbH	712355-03-8	0.99	NMR ^a and IC ^b	0.0076	< 100
[4bmpy][Tf ₂ N]	Iolitec GmbH	475681-62-0	0.99	NMR ^a and IC ^b	0.0048	< 100
Cyclohexane	Sigma–Aldrich	110-82-7	0.995	GC ^c	-	-
Cyclohexene	Sigma–Aldrich	110-83-8	0.99	GC ^c	-	-

98 ^aNuclear Magnetic Resonance99 ^bIon Chromatography100 ^cGas Chromatography101 ^dKarl-Fischer titration102 **3. Results and discussion**103 *3.1. Temperature effect on the experimental liquid-liquid equilibria*

104 The LLE data were determined for the equimolar ternary systems {cyclohexane (1) +
 105 cyclohexene (2) + [4bmpy][TCM] or [emim]₂[Co(SCN)₄] or [bmim]₂[Co(SCN)₄] or
 106 [4empy][Tf₂N] or [4bmpy][Tf₂N](3)} at $T = (298.2, 313.2 \text{ and } 328.2)$ K and atmospheric
 107 pressure.

108 The hydrocarbon distribution ratios (D_i) and the cyclohexene/cyclohexane selectivity ($\alpha_{2,1}$)
 109 for the ternary systems {cyclohexane (1) + cyclohexene (2) + IL (3)} were calculated from
 110 the experimental compositions of the raffinate and extract phases with the following
 111 equations:

$$112 \quad D_i \left(\frac{g}{g} \right) = \frac{w_i^{\text{II}}}{w_i^{\text{I}}} \quad (1)$$

$$113 \quad \alpha_{2,1} = \frac{D_2}{D_1} \quad (2)$$

114 where w_i is the mass fraction for the hydrocarbon i , and superscript I and II refer to the
 115 raffinate and extract phases, respectively. The results for the composition of both phases and
 116 the extractive properties at $T = (298.2, 313.2 \text{ and } 328.2)$ K and atmospheric pressure are
 117 shown in Table S1 in the Supplementary Material.

118 Figure 1 represents the extractive properties obtained for the five ILs in the equimolar
 119 ternary systems {cyclohexane (1) + cyclohexene (2) + IL (3)} at $T = (298.2, 313.2 \text{ and } 328.2)$
 120 K and atmospheric pressure. As can be seen, the temperature has an opposite effect on the
 121 extractive properties for the most of the studied ILs. Related to the cyclohexene distribution
 122 ratio, the SCN and Tf₂N-based ILs show an increase in this property with temperature;
 123 meanwhile the TCM-based IL shows a decrease. The TCM and Tf₂N-based ILs are the ILs

124 with the higher temperature influence on the cyclohexene distribution ratio. Related to the
125 cyclohexene/cyclohexane selectivity, the temperature has a lower effect on it, decreasing its
126 value at higher temperatures. As a consequence of these results, a previous temperature
127 analysis could improve the extractive properties of every ternary system.

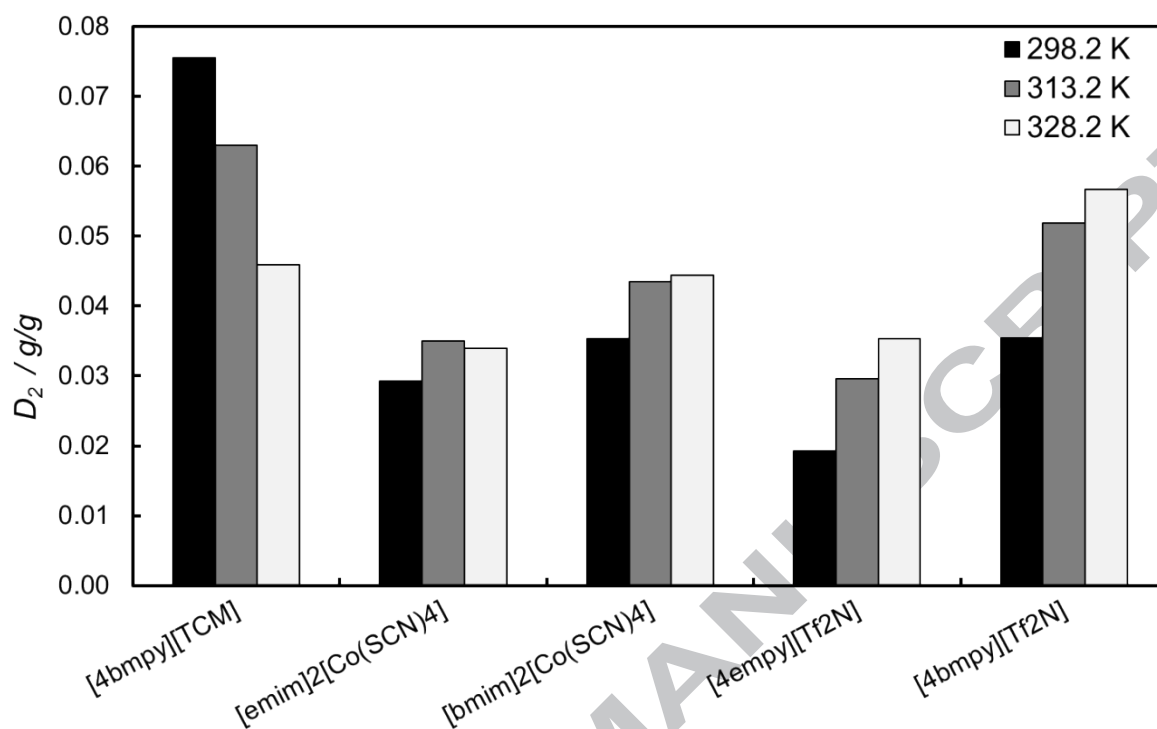
128 The selected temperatures for every IL have been $T = 298.2$ K for [4bmpy][TCM],
129 [emim]₂[Co(SCN)₄], and [bmim]₂[Co(SCN)₄], and $T = 328.2$ K for [4empy][Tf₂N] and
130 [4bmpy][Tf₂N]. We have chosen the temperatures at which the cyclohexene distribution ratio
131 presents the higher value for [4bmpy][TCM], [4empy][Tf₂N], and [4bmpy][Tf₂N]. Related to
132 [emim]₂[Co(SCN)₄] and [bmim]₂[Co(SCN)₄], and due to the higher temperature influence on
133 the cyclohexene/cyclohexane selectivity than on the cyclohexene distribution ratio, we have
134 chosen the temperature at which the cyclohexene/cyclohexane selectivity presents the higher
135 value.

136 3.2. Liquid-liquid extraction of cyclohexene from cyclohexane

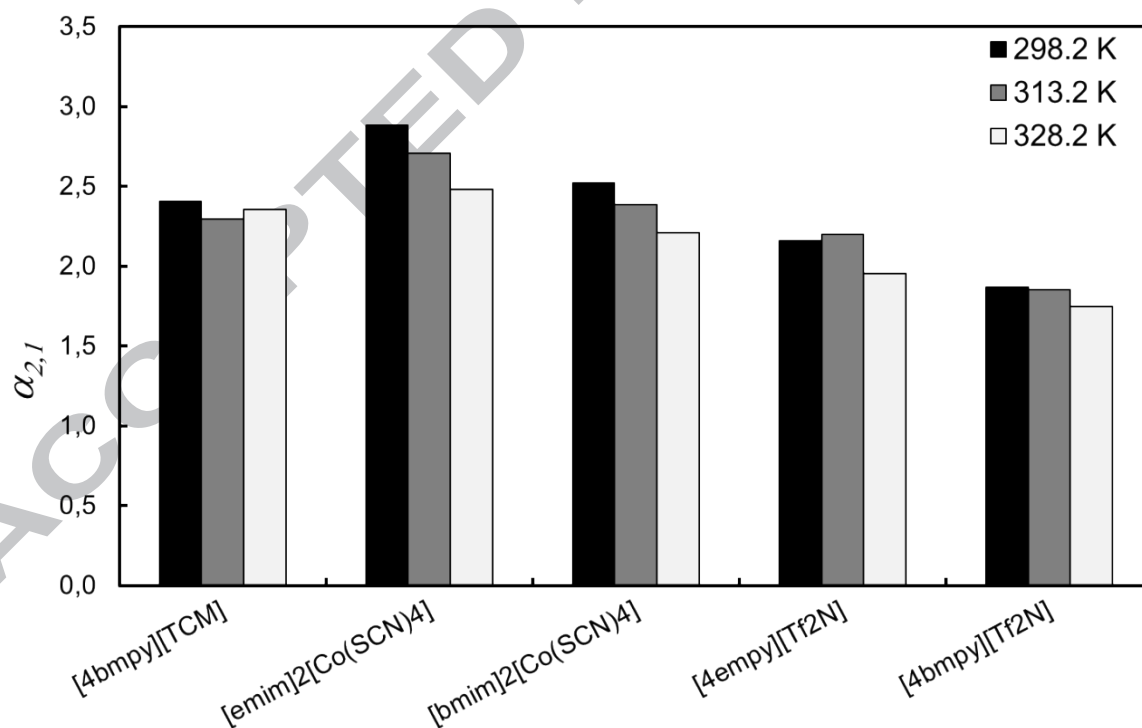
137 Figure 2 represents the experimental LLE data obtained at atmospheric pressure for the
138 systems {cyclohexane (1) + cyclohexene (2) + [4bmpy][TCM] or [emim]₂[Co(SCN)₄] or
139 [bmim]₂[Co(SCN)₄] (3)} at $T = 298.2$ K, as well as for the systems {cyclohexane (1) +
140 cyclohexene (2) + [4empy][Tf₂N] or [4bmpy][Tf₂N] (3)} at $T = 328.2$. These data are also
141 reported in Table S2 in the Supplementary Material.

142 The experimental LLE data for the binary systems {cyclohexane (1) + IL (2)} and
143 {cyclohexene (1) + IL (3)} are represented along with the literature data in Figure 3, to
144 compare the results of various ILs with common anions ([TCM]⁻, [SCN]⁻, and [Tf₂N]⁻) and
145 cations ([emim]⁺, [bmim]⁺, and [4bmpy]⁺) [3, 6, 32]. These data can also be found in Table
146 S3 in the Supplementary Material. It can be observed some deviations between both
147 experimental and literature data. Experimental cyclohexane solubility in ILs is lower than that
148 reported by Domanska *et al.* [3, 6, 32], showing a difference by a factor of two for the
149 [4bmpy][Tf₂N] IL [32]. These deviations could be attributed to: the lower hydrocarbon
150 solubility in the ILs and, therefore, the higher uncertainties; and the IL purity and further
151 purification made by these authors to remove any volatile chemicals and water from the IL
152 [7]. Related to the cyclohexene solubility, the experimental data follow the expected tendency
153 for this system. It can be confirmed that: first, cyclohexene solubility is higher than
154 cyclohexane solubility; second, pyridinium cations present higher extractive capacity than
155 imidazolium cations; and third, the ability of the IL to solubilize hydrocarbons is increased
156 with longer alkyl cation side-chains [33, 34].

157 To check the reliability of the LLE data, herein we have used the Othmer-Tobias
 158 correlation [35]:



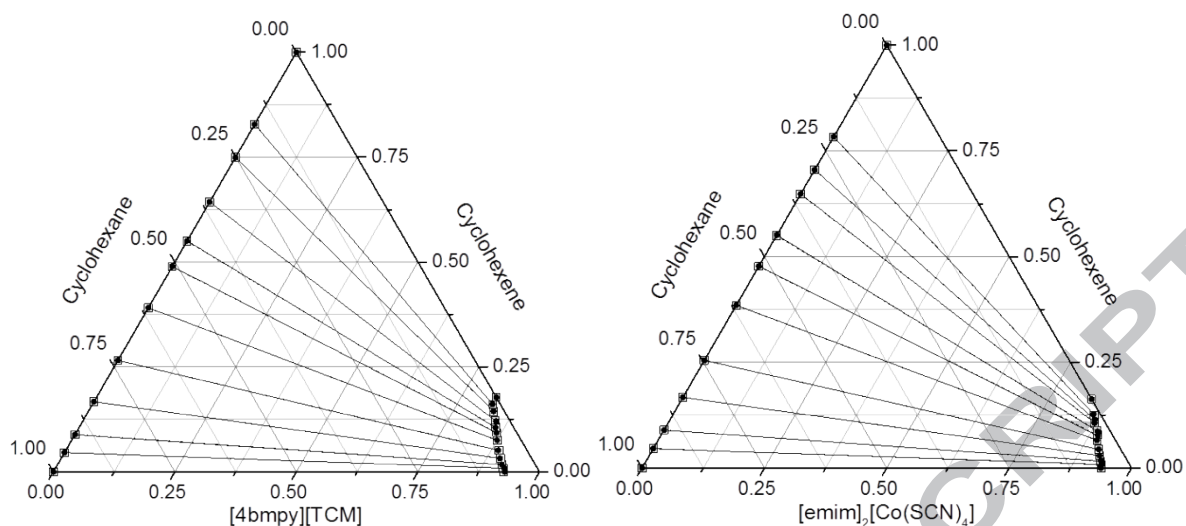
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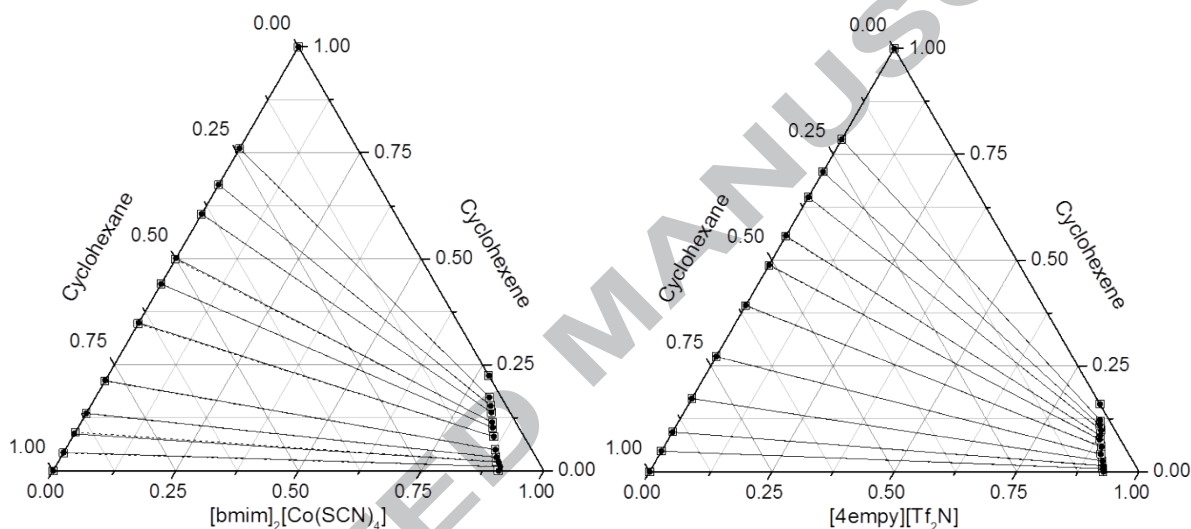
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Figure 1. Cyclohexene distribution ratio and cyclohexene/cyclohexane selectivity for the equimolar ternary systems {cyclohexane (1) + cyclohexene (2) + IL (3)} as a function of temperature and $P = 0.1$ MPa.

167



168



169

170 **Figure 2.** Liquid-liquid equilibria at $P = 0.1$ MPa for the ternary systems {cyclohexane (1) +
 171 cyclohexene (2) + [4bmpy][TCM] or [emim]₂[Co(SCN)₄] or [bmim]₂[Co(SCN)₄] (3)} at $T =$
 172 298.2 K, and {cyclohexane (1) + cyclohexene (2) + [4empy][Tf₂N] or [4bmpy][Tf₂N] (3)} at
 173 $T = 328.2$ K. Solid lines and full points represent experimental tie-lines whereas dashed lines
 174 and empty squares are the regressed data using the NRTL model.

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

where w_1^{I} is the cyclohexane mass fraction in the raffinate phase, w_3^{II} is the IL mass fraction in the extract phase, and a and b are the parameters of the Othmer-Tobias correlation.

In Table 2, the fitting parameters (a, b), the regression coefficients (R^2), and the standard deviations of this fit (σ) are listed. As can be observed, R^2 values higher than 0.99 and small σ values were obtained for the LLE data of the five ternary systems. Therefore, the consistence of the experimental LLE data was confirmed.

3.3. Regression of the liquid-liquid equilibrium data using NRTL model

In this work we have used the NRTL model to successfully correlate the LLE data [36, 37]. Aspen Plus Simulator has been used to calculate the binary interaction parameters $\Delta g_{ij}/R$ and $\Delta g_{ji}/R$, and the non-randomness parameter (α_{ij}) has been fixed at 0.30, the most employed value in the data correlation for systems containing ILs [38-40].

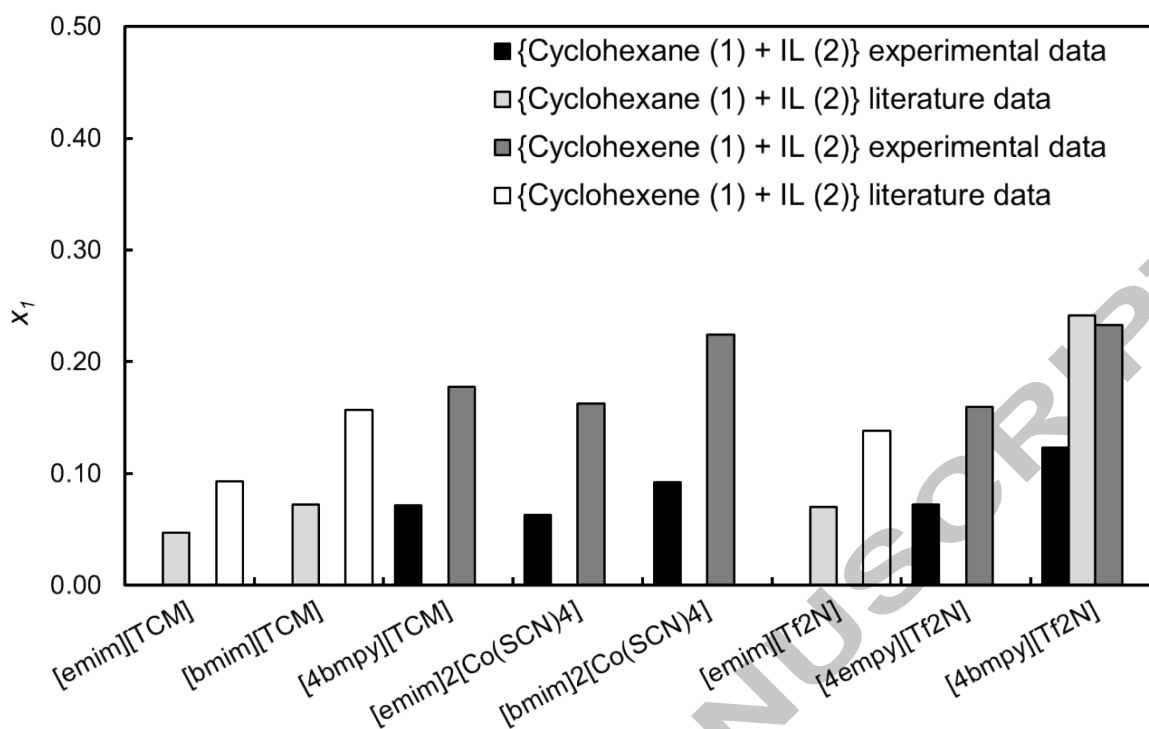
Table 3 summarizes the NRTL model parameters and the root mean square deviations (*rmsd*) calculated as follows:

$$rmsd = \left\{ \frac{\sum_i \sum_l \sum_m (x_{ilm}^{\text{exptl}} - x_{ilm}^{\text{calc}})^2}{6k} \right\}^{1/2} \quad (3)$$

Table 2. Parameters of the Othmer–Tobias correlation (a , b), regression coefficients (R^2), and standard deviations (σ) for the LLE data at $P = 0.1$ MPa for the systems {cyclohexane (1) + cyclohexane (2) + [4bmpy][TCM] or [emim]₂[Co(SCN)₄] or [bmim]₂[Co(SCN)₄] (3)} at $T = 298.2$ K, and {cyclohexane (1) + cyclohexane (2) + [4empy][Tf₂N] or [4bmpy][Tf₂N] (3)} at $T = 328.2$ K^a.

a	b	R^2	σ
-2.9189	0.2084	0.9975	0.0149
-3.900	0.2063	0.9923	0.0246
-3.5736	0.2084	0.9945	0.0206
-3.6070	0.1625	0.9916	0.0297
-3.1082	0.1466	0.9960	0.0126

^a Standard uncertainties (u) are: $u(T) = 0.1$ K; $u(P) = 1$ kPa.



197

198 **Figure 3.** Liquid-liquid equilibria at $P = 0.1$ MPa for the binary systems {cyclohexane (1) +
 199 IL (2)} and {cyclohexene (1) + IL (2)}. The systems with [4bmpy][TCM], [emim][TCM],
 200 [bmim][TCM], [emim]₂[Co(SCN)₄], [bmim]₂[Co(SCN)₄], and [emim][Tf₂N] ILs are at $T =$
 201 298.2 K, meanwhile systems with [4empy][Tf₂N] and [4bmpy][Tf₂N] ILs are at $T = 328.2$ K
 202 [3, 6, 32].

203 where x is the mole fraction of each component, k is the number of tie-lines, and the
 204 subscripts i , l , and m refer to the component, phase, and tie-line, respectively.

205 In Figure 2, it can also be seen the regressed tie-lines. The estimated tie-lines by the
 206 NRTL model are coincident with the experimental tie-lines, which means that the LLE for
 207 the five studied ternary systems at $T = (298.2$ and $328.2)$ K and atmospheric pressure were
 208 successfully fitted to the NRTL model.

209 3.4. Extractive properties of the ILs

210 In Figure 4 the experimental values for cyclohexene distribution ratio and
 211 cyclohexene/cyclohexane selectivity at atmospheric pressure are represented for the systems
 212 {cyclohexane (1) + cyclohexene (2) + [4bmpy][TCM] or [emim]₂[Co(SCN)₄] or
 213 [bmim]₂[Co(SCN)₄]} at $T = 298.2$ K, and {cyclohexane (1) + cyclohexene (2) +
 214 [4empy][Tf₂N] or [4bmpy][Tf₂N]} at $T = 328.2$ K. In the same figures, it has been included
 215 the literature data for the ternary systems {cyclohexane (1) + cyclohexene (2) +
 216 [emim][TCM] or [bmim][TCM] or [emim][Tf₂N]} at $T = 298.2$ K [6, 11]. We have decided to

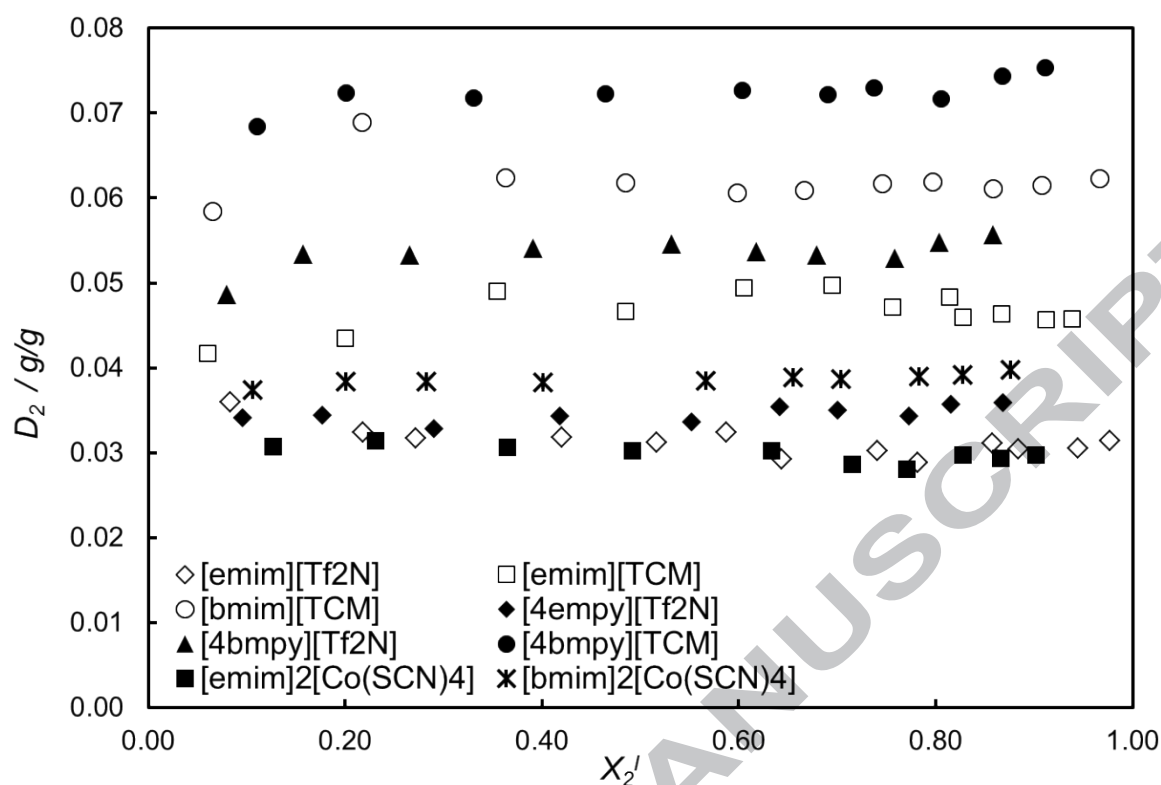
217 compare cyclohexene distribution ratios in mass basis since Canales *et al.* recommended to
 218 use the mass fraction basis to adequately compare the extractive properties of ILs and avoid
 219 the influence of their molar mass [41].

220 As can be seen in Figure 4, the five studied ILs show distribution ratio and selectivity
 221 values similar or even higher than those previously reported in the literature. First, it is
 222 observed that the ILs with longer alkyl cation side-chains show higher values of cyclohexene
 223 distribution ratio but lower values of cyclohexene/cyclohexane selectivity (or vice versa). It is
 224 well known that for aromatic/aliphatic separation, as well as herein for
 225 cyclohexane/cyclohexene separation, there is a clear trade-off between capacity and
 226 selectivity [42, 43]. Second, the pyridinium-based ILs show higher values of cyclohexene
 227 distribution ratios and selectivities than those of the imidazolium-based ILs. Final, ILs with
 228 the [TCM]⁻ anion show the highest values of both distribution ratio and selectivity except
 229 when they are compared to tetrathiocyanatocobaltate-based ILs, which show lower
 230 distribution ratio values but also the highest selectivity values.

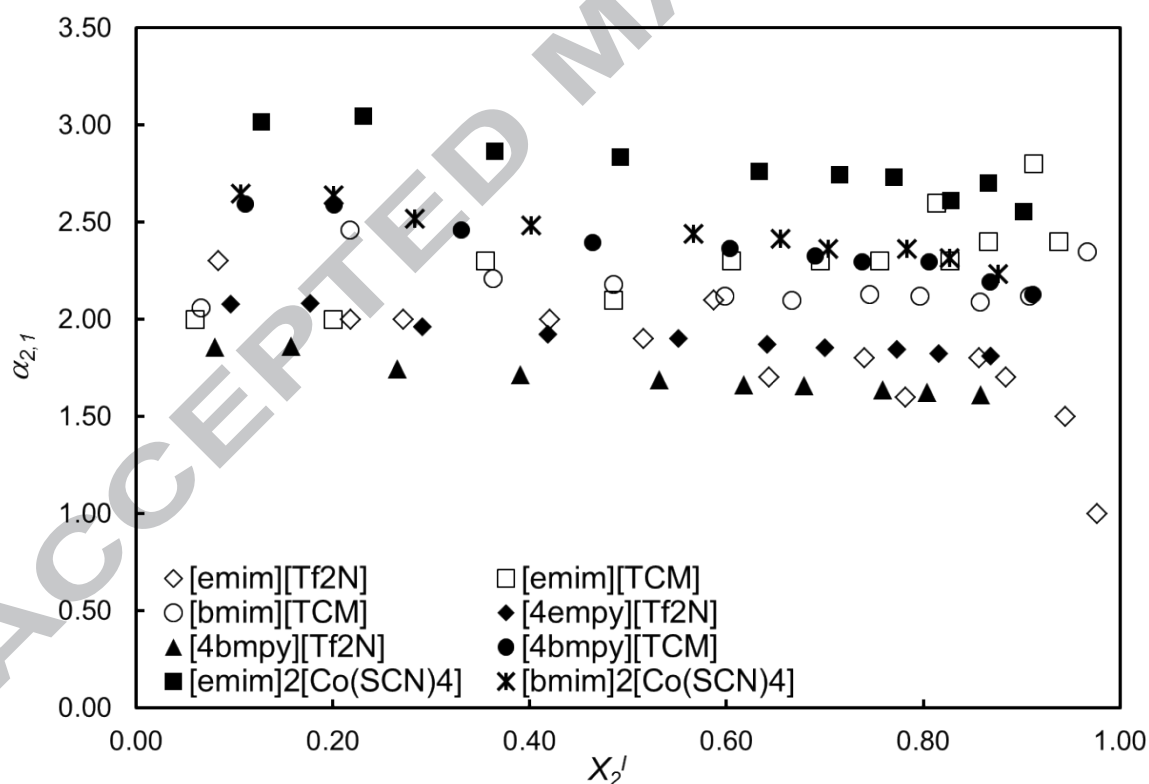
231 **Table 3.** Values of the NRTL parameters regressed from LLE data at $P = 0.1$ MPa for the
 232 systems {cyclohexane (1) + cyclohexene (2) + [4bmpy][TCM] or [emim]₂[Co(SCN)₄] or
 233 [bmim]₂[Co(SCN)₄] (3)} at $T = 298.2$ K, and {cyclohexane (1) + cyclohexene (2)
 234 + [4empy][Tf₂N] or [4bmpy][Tf₂N] (3)} at $T = 328.2$ K^a.

Component i - j	NRTL parameters			Rmsd
	$(\Delta g_{ij}/R)/K$	$(\Delta g_{ji}/R)/K$	α_{ij}	
Cyclohexane (1) + cyclohexene (2) + [4bmpy][TCM] (3)				
1 - 2	271.02	-279.53	0.30	0.0007
1 - 3	-835.78	1342.80	0.30	
2 - 3	402.57	610.04	0.30	
Cyclohexane (1) + cyclohexene (2) + [emim] ₂ [Co(SCN) ₄] (3)				
1 - 2	240.74	-281.24	0.30	0.0009
1 - 3	-897.14	1195.7	0.30	
2 - 3	780.32	418.17	0.30	
Cyclohexane (1) + cyclohexene (2) + [bmim] ₂ [Co(SCN) ₄] (3)				
1 - 2	253.61	-325.41	0.30	0.0016
1 - 3	-794.17	1020.4	0.30	
2 - 3	683.56	374.65	0.30	
Cyclohexane (1) + cyclohexene (2) + [4empy][Tf ₂ N] (3)				
1 - 2	315.97	-295.92	0.30	0.0008
1 - 3	-910.47	918.89	0.30	
2 - 3	504.07	638.22	0.30	
Cyclohexane (1) + cyclohexene (2) + [4bmpy][Tf ₂ N] (3)				
1 - 2	325.02	-283.49	0.30	0.0015
1 - 3	-744.51	562.64	0.30	
2 - 3	645.01	474.79	0.30	

235 ^a Standard uncertainties (u) are: $u(T) = 0.1$ K; $u(P) = 1$ kPa.



236



237

238 **Figure 4.** Cyclohexene distribution ratio and cyclohexene/cyclohexane selectivity at
 239 atmospheric pressure for the ternary systems {cyclohexane (1) + cyclohexene (2) +
 240 [4bmpy][TCM] or [emim]₂[Co(SCN)₄] or [bmim]₂[Co(SCN)₄] or [emim][Tf₂N] or
 241 [emim][TCM] or [bmim][TCM]} at $T = 298.2$ K, and {cyclohexane (1) + cyclohexene (2) +
 242 [4empy][Tf₂N] or [4bmpy][Tf₂N]} at $T = 328.2$ K. Black symbols are for experimental results
 243 and white symbols for literature data [6, 11].

244 In Table 4 are shown the most recently results from literature for the selectivity ($S_{2,1}^\infty$)
 245 and capacity (D_2^∞) at infinite dilution for the cyclohexane/cyclohexene separation obtained by
 246 Domanska *et al.* Both extractive properties were calculated from the activity coefficients at
 247 infinite dilution, γ_{13}^∞ , for the binary systems {cyclohexane (1) + IL (2)} and {cyclohexene (1)
 248 + IL (2)} [10-15, 17, 44-47]. These results are useful to compare the IL separation ability and
 249 the IL potential for the cyclohexane/cyclohexene separation, though it is important to
 250 highlight that a whole experimental LLE data is necessary to completely define the system.
 251 The capacity at infinite dilution values are shown both in molar-basis and mass-basis to
 252 compare the results with our experimental data, taking into consideration the previously
 253 explained limitation. First, it can be seen that most of the [DCA]-based ILs present higher
 254 cyclohexene/cyclohexane selectivity values, but a lower cyclohexene capacity. Second, it is
 255 observed that molar-basis favours [Tf₂N]-based ILs because of their high molar mass,
 256 compared to the rest of ILs in the same table. If mass-basis capacities are compared, the best
 257 results are achieved with [bmpy][DCA] and [emim][TCM] ILs, which also present moderate
 258 cyclohexene/cyclohexane selectivity. Final, mass-basis extractive properties can be compared
 259 for [emim][TCM]: D_2 and $S_{2,1}$ values are comprised between 0.04 – 0.05 and 2.0 – 2.8,
 260 respectively (Figure 4), meanwhile $D_2^\infty = 0.04$ and $S_{2,1} = 2.24$. The [4bmpy][TCM] IL also
 261 presents well-balanced extractive properties, even higher than those reported for
 262 [bmpy][DCA] and [emim][TCM] ILs: D_2 and $S_{2,1}$ values in the interval 0.068 – 0.075 and 2.1
 263 – 2.6, respectively (Table S2 in the Supplementary Material). From these experimental data, it
 264 can be concluded that [4bmpy][TCM] would be the most promising IL to be used for the
 265 cyclohexene/cyclohexane separation, regarding its remarkable values for both cyclohexene
 266 distribution ratio and cyclohexene/cyclohexane selectivity.

267 4. Conclusions

268 The aim of this paper is to study the cyclohexane/cyclohexene separation by liquid-liquid
 269 extraction using five ILs, namely [4bmpy][TCM], [emim]₂[Co(SCN)₄], [bmim]₂[Co(SCN)₄],
 270 [4empy][Tf₂N], and [4bmpy][Tf₂N]. A first LLE determination has been made for the
 271 equimolar ternary systems {cyclohexane (1) + cyclohexene (2) + IL (3)} at $T = (298.2, 313.2$
 272 and 328.2) K and atmospheric pressure to fix the best temperature. The best extractive
 273 properties were obtained at $T = 298.2$ K for [4bmpy][TCM], [emim]₂[Co(SCN)₄], and
 274 [bmim]₂[Co(SCN)₄] ILs, and at $T = 328.2$ K for [4empy][Tf₂N] and [4bmpy][Tf₂N] ILs. LLE
 275 experimental results at the whole cyclohexene/cyclohexane composition range have shown
 276 the same order of values in the extractive properties for all the ILs. However, the
 277 [4bmpy][TCM] IL has shown the higher distribution ratio and selectivity values, near to the

278 maximum values showed by the [emim]₂[Co(SCN)₄] IL. The experimental LLE data were
 279 successfully fitted to the NRTL model.

280

281 **Table 4.** Selectivities, $S_{2,1}^\infty$, and capacities, D_2^∞ , at infinite dilution for several ILs from
 282 literature for the systems {cyclohexane (1) + cyclohexene (2) + IL (3)} at $T = 328.15$ K.

Ionic liquid	$S_{1,2}^\infty$	D_2^∞	
		mol·mol ⁻¹	g·g ⁻¹
[N-C ₃ OHMMor][DCA]	3.98	0.02	0.007
[EMMor][DCA]	3.04	0.02	0.008
[N-C ₃ OHPy][DCA]	2.79	0.03	0.012
[N-C ₃ OHmim][DCA]	2.64	0.03	0.012
[bzmim][DCA]	2.46	0.07	0.024
[amim][DCA]	2.51	0.05	0.022
[bmim][DCA]	2.19	0.09	0.036
[bmpy][DCA]	2.32	0.12	0.046
[emim][TCM]	2.24	0.10	0.040
[empyr][Lac]	2.17	0.048	0.019
[BCN ⁴ Py][NTf ₂]	2.07	0.14	0.026
[amim][NTf ₂]	1.79	0.15	0.031
[bzmim][NTf ₂]	1.77	0.19	0.034

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435 102 (2016) 39-47. **Highlights**

436 **Imidazolium and pyridinium-based ionic liquids for the**
437 **cyclohexane/cyclohexene separation by liquid-liquid extraction**

438 *Noemí Delgado-Mellado^a, Antonio Ovejero^a, Pablo Navarro^b, Marcos Larriba^a, Miguel*
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443

- 444
- 445 • The [4bmpy][TCM], [emim]₂[Co(SCN)₄], [bmim]₂[Co(SCN)₄], [4empy][Tf₂N] and [4bmpy][Tf₂N]
446 ILs are studied for this separation.
 - 447 • A first study of the temperature is made to determine its effect on the extractive properties.
 - 448 • LLE for ternary systems {cyclohexane (1) + cyclohexene (2) + IL (3)} are determined at the
449 optimal temperature.
 - 450 • The Non-random Two Liquids (NRTL) model is used to successfully correlate the experimental
451 data.
 - 452 • [4bmpy][TCM] reveals itself as the most promising IL in the cyclohexene/cyclohexane
453 separation.
- 454
455

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