Extraction of Organic Compounds Involved in the Kinetic Resolution of *rac*-2-Pentanol by *n*-Hexane by Imidazolium-based Ionic Liquids: Liquid-Liquid Equilibrium

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Abstract

This paper focuses on the use of ionic liquids (1-butyl-3-methylimidazolium methylsulphate, [bmim$^+$][MeSO$_4^-$], and 1-ethyl-3-methylimidazolium acetate, [emim$^+$][Ac$^-$]) to extract organic compounds involved in the racemic resolution of *rac*-2-pentanol (*rac*-2-pentanol, vinyl butyrate, *rac*-2-pentyl butyrate or butyric acid) from a mixture of one of these organic compounds with *n*-hexane. Liquid–liquid equilibrium data were experimentally obtained for seven ternary systems comprising an ionic liquid + *rac*-2-pentanol, vinyl butyrate, *rac*-2-pentyl butyrate or butyric acid + *n*-hexane at *T*=303.15 K and atmospheric pressure. Binodal curves were measured applying the well-known procedure based on the observance of the cloud point while the compositions of the tie lines were calculated from refractive index and density measurements (the phase rich in the ionic liquid) and by gas cromatography (the phase rich in *n*-hexane). Selectivity values and the solute distribution ratio were utilized to test the possibility of the use of these ionic liquids as extractive solvents of the organic compounds implicated in

36   the kinetic separation of the *R*- and *S*-enantiomers of *rac*-2-pentanol. The liquid-liquid

37   equilibrium data of the ternary systems examined here have not previously been described in

38   the literature.

1. Introduction

42   During the last decades, the interest for enantiopure chemicals has greatly increased in the

43   pharmaceutical industry, largely due to the fact that when chiral mixtures are used as drugs, one

44   of the enantiomers usually presents biological activity, whereas the other may be harmful or

45   toxic or shows antagonism. For this reason, a great variety of enantioseparation techniques

46   exist, although among other types of technique, kinetic resolution using membranes such as

47   supported liquid membranes (SLMs) has attracted great attention [1]. SLMs are porous

48   structures whose cavities contain a liquid. Their main advantages are the small quantity of liquid

49   necessary for the process and the combination in a unique stage of the extraction and stripping

50   processes [2]. However, their industrial development has been scarce, primarily because of the

51   low stability and the problems associated with the long-term usage of the SLMs. Furthermore,

52   SLMs with conventional organic solvents may deteriorate because of liquid evaporation and

53   their dissolution in the surrounding medium and migration from the pores of the support under

54   a low pressure gradient. Moreover, from an environmental point of view, the organic solvents

55   most widely employed for processes involving liquid membranes possess high vapour pressure

56   and high toxiciy, meaning that their presence could involve serious hazards [1]. The

57   incorporation of ionic liquids (ILs) [1,3] in SLMs has demonstrated an important increase in

58   their stability enabling long-term experiments for separating the reactants and products of

59   transesterification reactions. Several works in the literature have checked the improvement on

60   the SLM stability when they contain ILs [4,5]. The most noteworthy feature of the ILs is their

61   negligible vapour pressure at room temperature and atmospheric pressure [6] which has led to

them being called "green solvents". This property, their high capillary force due to their

relatively high viscosity and the possible modulation of their solubility in a specific medium

makes the use of ILs a stable and environmentally friendly alternative for the selective transport

of organic compounds [3,7].

Furthermore, ILs can be designed for particular applications by the selection of the chemical

nature of both the anion and the cation constituents [8]. Accordingly, they have also been called

"designer solvents". Solute-solvent interactions in solution are determined by the cation and

anion pair that constitutes the ionic liquid. In this context, specific ILs can be used to accomplish

the selective extraction of *rac*-2-pentanol by supported ionic liquid membranes. In this case, *S*-

2-pentanol has special interest because it is a racemic intermediate involved in obtaining some

anti-Alzheimer drugs which restrict the release and the synthesis of β-amyloid peptide [9]. The

stoichiometric scheme for the racemic resolution of 2-pentanol by transesterification with a

vinyl ester catalysed by a lipase is shown in Scheme 1.
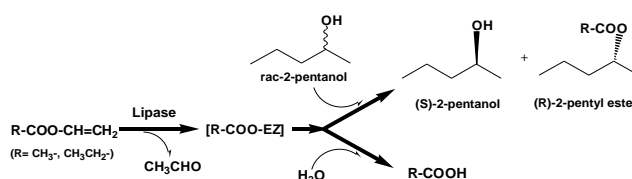
Scheme 1. Stoichiometric scheme of racemic resolution of *rac*-2-pentanol catalysed by a lipase

[1].

For liquid-liquid extraction processes, the essential equilibrium properties of the solvent phase

are important. The measurement of liquid-liquid equilibrium (LLE) data is a widely used

method for evaluating the ability of a solvent through the calculation of standard variables such

as selectivity (S) or solute distribution coefficient (β). In order to extract *S*-2-pentanol

selectively from the reaction medium (i.e. *n*-hexane), knowledge of the LLE data of the ternary

86   systems (ionic liquid + *n*-hexane + an organic compound present in the kinetic resolution of

87   *rac*-2-pentanol) is very convenient. Our research group has already published several studies of

88   this same system using ILs and we have obtained promising results ([emim⁺][EtSO₄⁻],

89   [bmim⁺][BF₄⁻] and [bmim⁺][NTf₂⁻] [10]; [emim⁺][NTf₂⁻] and [hmim⁺][NTf₂⁻] [11]). In addition,

90   we have also studied the LLE of other ternary systems (ionic liquid + *n*-hexane + organic

91   compounds implicated in the racemic separation of *rac*-1-phenylethanol) [12]. The selective

92   extraction of *rac*-1-phenylethanol is of special relevance because *R*-1-phenylethanol is broadly

93   employed in pharmaceutical and fine chemical industry [13]. In addition, our previous works

94   [10-12] on the application of ILs in separation processes showed the growing interest of

95   increasing the quantity of available physico-chemical data related to extraction processes.

96

97   LLE data of ternary systems involving ILs have been widely studied by a great many authors

98   [10-12,14-46]. The present work is an extension of our investigation into the extraction potential

99   of ILs for the separation of specific compounds involved in the kinetic resolution of racemic

100   alcohols. The principal goal of this paper was to evaluate the LLE of seven ternary systems

101   which contain an ionic liquid, *n*-hexane and an organic compound implicated in the kinetic

102   resolution of *rac*-2-pentanol (*rac*-2-pentanol, vinyl butyrate, *rac*-2-pentyl butyrate or butyric

103   acid) at 303.15 K and *p*=0.1MPa. The binodal curves and the tie line data for these ternary

104   systems were also determined in the above mentioned conditions. From the features of the

105   binodal curves and the tie line data, valuable insights can be achieved concerning the potential

106   extractive capability of the ILs.

107

108   On the basis of previous results [10,11], it could be inferred that more hydrophilic ILs may be

109   more selective for the extraction of the target compounds. In consequence, (i) 1-butyl-3-

110   methylimidazolium methylsulphate, [bmim⁺][MeSO₄⁻] and (ii) 1-ethyl-3-methylimidazolium

111 acetate, [emim$^+$][Ac$^-$] have been chosen in this paper. LLE data for the system [emim$^+$][Ac$^-$] +

112 *n*-hexane+vinyl butyrate have not been included because vinyl acetate was formed as result of

113 the transesterification reaction between [emim$^+$][Ac$^-$] and vinyl butyrate and the reactive

114 extraction process is beyond this work. Furthermore, the ILs are regenerated removing the

115 organic compound by vacuum distillation. Figures S1 and S2 show the ^{1}H-NMR results and

116 GC-MS spectra of the *n*-hexane phase as evidence of the presence of vinyl acetate.

117

2. Experimental

2.1. Materials

120 The ILs 1-butyl-3-methylimidazolium methylsulphate, [bmim$^+$][MeSO$_4$$^-$] (purity > 0.99), and

121 1-ethyl-3-methylimidazolium acetate, [emim$^+$][Ac$^-$] (purity > 0.95) were provided from Iolitec.

122 All other chemicals were supplied by Sigma-Aldrich (purity > 0.98). The ILs and the organic

123 compounds were dried under vacuum in the presence of anhydrous phosphorus pentoxide and

124 kept in a desiccator to avoid any moisture absorption (Table 1). The water contents of the ILs

125 and the organic compounds was determined with a Karl Fischer coulometric titrator (Metrohm,

126 831 KF). The values of the water content were low in all cases ($w < 0.001$). The standard

127 uncertainty, u, of the water content measurements was $u(w)$=0.1 µg/mL. The structures and

128 molecular weight are depicted in Table 2 together with the refractive index and density values

129 of the pure ILs measured in this work and those found in the literature. The same samples of

130 butyric acid, vinyl butyrate, *rac*-2-pentyl butyrate, and *rac*-2-pentanol with the same physical

131 properties as in [11] were used.

132

133 **Table 1**. Sample Table.

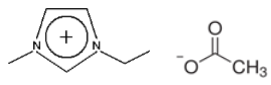| Chemical Name	Source	Initial Mole Fraction Purity	Purification Method
[bmim$^+$][MeSO$_4^-$][a]	Iolitec	0.99	Vacuum drying
[emim$^+$][Ac$^-$][b]	Iolitec	0.95	Vacuum drying
Butyric acid	Sigma-Aldrich	0.99	Vacuum drying
Vinyl butyrate	Sigma-Aldrich	0.99	Vacuum drying
rac-2-Pentyl butyrate	Sigma-Aldrich	0.99	Vacuum drying
rac-2-Pentanol	Sigma-Aldrich	0.98	Vacuum drying
n-Hexane	Sigma-Aldrich	0.99	Vacuum drying

134 [a][bmim$^+$][MeSO$_4^-$] = 1-butyl-3-methylimidazolium methylsulphate
135 [b][emim$^+$][Ac$^-$] = 1-ethyl-3-methylimidazolium acetate
136

137 **Table 2.** Refractive index (n) measured at λ=589nm and density (ρ) of pure compounds at T=

138 303.15 K and p=0.1MPa.[a]

139

140

Compounds	Molecular weight (g mol^{-1})	Structure	n		ρ (g/cm^3)	
			This work	Lit.	This work	Lit.
[bmim$^+$][MeSO$_4^-$]	250.32		1.47771	1.4779[b] 1.47704[c] 1.47805[d] 1.4765[e]	1.20401	1.2041[k] 1.205253[l] 1.2055[m] 1.20627[n] 1.20448[o] 1.2023[p] 1.2025[b] 1.2087[c] 1.20881[d] 1.1983[e]
[emim$^+$][Ac$^-$]	170.21		1.49717	1.49861[f] 1.49867[g] 1.49854[h] 1.49949[i] 1.4981[j]	1.09504	1.09516[f] 1.0951[q] 1.0952[g] 1.09472[r] 1.0972[s] 1.0962[i] 1.09664[j] 1.0946[t]

141 [a]Standard uncertainties u are $u(\rho)$=0.00005 g/cm^3 with $u(T^p)$ = 0.03 K and $u(n)$=0.00004 (nD) with $u(T^n)$ = 0.02 K. Standard
142 uncertainty in pressure was $u(P)$=10kPa. [b] Soriano *et al.* [47]. [c] Singh *et al.* [48]. [d] Pereiro *et al.* [49]. [e] Miran Beigi *et al.* [50].
143 [f] Araújo *et al.* [51]. [g] Oliveira *et al.* [52]. [h] Almeida *et al.* [53]. [i] Freire *et al.* [54]. [j] Fröba *et al.* [55]. [k] García-Miaja *et al.* [56].
144 [l] Pal *et al.* [57]. [m] Mac Dowell *et al.* [58]. [n] Fernández *et al.* [59]. [o] Iglesias-Otero *et al.* [60]. [66,p] Sibiya *et al.* [61]. [q] Rabari *et*
145 *al.* [62]. [r] Quijada-Maldonado *et al.* [63]. [s] Stevanovic *et al.* [64]. [t] Banerjee *et al.* [65].
146

147 After use, the ILs have been regenerated following procedures previously published in the

148 literature with other organic solvents [66]. Briefly, organic compound (2-pentanol, vinyl

149 butyrate, 2-pentyl butyrate or butyric acid)/hexane mixtures can be removed from the ILs on a

150 rotary evaporator at 80°C and 80 mbar. The ILs were kept in a desiccator until reuse.

151

152   *2.2 Experimental Procedure*

153 When possible, the binodal curves of the ternary systems were obtained at 303.15 K and

154 atmospheric pressure through the titration of two-component mixtures of known compositions

155 with the third component. The disappearance of turbidity in the sample was taken as the end

156 point, as in the cloud point method [10-12,16,18,35,46].

157 Tie line data for the ternary systems studied were obtained from measurements of the

158 compositions of the conjugate phases for several mixtures with a known global composition of

159 the three components within the two-phases region. For this, the ternary mixtures were

160 introduced into a 5 ml glass cell, shaken vigorously for 10 minutes using a vortex mixer and

161 then for 1h using a magnetic stirrer before leaving overnight to allow the separation into two

162 phases and to ensure equilibrium between them [10-12, 16, 18, 25]. The tube was tightly closed

163 to prevent vaporization or the absorption of humidity from the ambient. The temperature was

164 regulated using a thermostatic bath with a standard uncertainty value of $u(T)$=0.5 K.

165 The index of refraction of the ionic liquid-rich phase and the pure compounds was measured

166 using a RX-5000α refractometer from ATAGO (λ=589nm). Earlier, the refractive index of the

167 ternary mixtures was correlated with their respective concentrations by calibration curves in

168 order to obtain the component concentrations in this phase. Standard uncertainties were

169 $u(T^n)$=0.02 K and $u(n)$=0.00004 (nD). The density of the ionic liquid-rich phase, which was

170 also correlated with concentration, and the density of the pure compounds were measured with

171   an Anton Paar DMA-4500 vibrating-tube densimeter. In this case, standard uncertainties were

172    $u(T^p)$=0.03 K and $u(\rho)$=0.00005 g/cm^3. Therefore, the calibration method was used to measure

173   the refractive index and density of the ionic liquid-rich phase at 303.15 K by preparing

174   calibration plots of the refractive index and density from several known phase compositions

175   (see Figures 1 to 14 in [67]).

176   The component concentrations in the hexane-rich phase was determined by gas

177   chromatography (GC). In this phase, the ionic liquid concentration cannot be measured due to

178   the negligible vapour pressure of ILs. An internal standard was used to calculate the mole

179   fractions of the two other compounds of the mixture, obtaining the ionic liquid mole fraction

180   by difference. The standard uncertainty of the mole fraction compositions for multiple GC

181   measurements was estimated as $u(x)$=0.0002.

182   All the tie lines were examined to assure that they crossed through the composition of the initial

183   mixture. The standard uncertainties of the procedure used to determine the binodal curve points

184   were $u(x)$=0.006, $u(T)$=0.5 K and the standard uncertainties for the composition of the tie lines

185   were $u(x)$=0.003, $u(T)$=0.5 K and $u(P)$ =10 kPa. All the measurements were made in triplicate.

186   *2.3 Gas chromatographic analysis*

187   GC analysis was carried out with an Agilent HP-7890A instrument equipped with auto sampler

188   and FID detector and a Supelco Beta Dex^{TM}120 16612-03 capillary column (30m $\times$ 0.25mm $\times$

189   0.25μm). The fixed conditions were: carrier gas (He) at 10 psi (39.436 mL/min total flow);

190   temperature program: 50 ºC, 25min; 10 ºC/min, 100 ºC; 25 min; split ratio: 50/1; injector:22

191   ºC, detector: 300 ºC. The following retention times of the peaks were determined: hexane, 4.7

192   min; ethyl propionate (internal standard), 9.9 min; vinyl butyrate, 14.5 min; (*R*)-2-pentanol,

193   21.9 min; (*S*)-2-pentanol, 22.4 min; (*S*)-2-pentylbutyrate, 35.7 min; (*R*)-2-pentylbutyrate, 36.4

194   min; and butyric acid, 40.9 min. The average values were calculated by injecting the samples

195   at least three times. Previously, calibration curves using stock solutions of the pure compounds

196   were obtained in order to calculate the concentrations of the *n*-hexane-rich phase.

197   **3. Results and discussion**

198   *3.1. Experimental liquid-liquid equilibrium data*

199   The LLE data of seven ternary systems were determined: [bmim$^+$][MeSO$_4^-$] + *rac*-2-pentanol

200   + *n*-hexane; [bmim$^+$][MeSO$_4^-$] + butyric acid + *n*-hexane; [bmim$^+$][MeSO$_4^-$] + *rac*-2-pentyl

201   butyrate + *n*-hexane; [bmim$^+$][MeSO$_4^-$] + vinyl butyrate + *n*-hexane; [emim$^+$][Ac$^-$] + *rac*-2-

202   pentanol + *n*-hexane; [emim$^+$][Ac$^-$] + butyric acid + *n*-hexane; [emim$^+$][Ac$^-$] + *rac*-2-pentyl

203   butyrate + *n*-hexane. The composition of the conjugate phases for the three-component mixtures

204   (ionic liquid + extracting organic compound + *n*-hexane), was calculated from the tie line data

205   and is shown in Tables 3 and 4. The binodal curves and tie lines are represented in Figures 1 to

206   7. Binodal data, when they exist, of the ternary systems are collected in Table 5.

207

208   Slope of the tie lines (STL) and tie line length (TLL) are two important characteristics of a

209   phase diagram which can be calculated at different compositions with eq 1 and 2, respectively

210   [68-71]:

211    $$STL = \frac{x_1' - x_1''}{x_3' - x_3''} \tag{1}$$

212    $$TLL = [(x_1' - x_1'')^2 + (x_3' - x_3'')^2]^{1/2} \tag{2}$$

213   where x'_1, x'_3 are mole fractions of the ionic liquid and *n*-hexane, respectively, in the top phase

214   (hexane-rich phase), and x''_1, x''_3 are mole fractions of the ionic liquid and *n*-hexane,

215   respectively, in the bottom phase (ionic liquid-rich phase). The calculated values of STL and

216   TLL have been included in Tables 3 and 4.

217

218   For the determination of the appropriateness of a solvent to carry out successful liquid-liquid

219   extraction processes, the *S* and the *β* need to be calculated. In our case, the *β* provides the solvent

220   capacity of an ionic liquid, which is directly related to the quantity needed for the extraction

221   process. To act as a good extraction solvent, high values of these parameters are required. The

222   S and the β to extract the organic compound from the mixture may be calculated by means of

223   the following expressions [10-12,14,16,18]:

224    $$S = \frac{x_2'' x_3'}{x_2' x_3''}$$ (3)

225    $$\beta = \frac{x_2''}{x_2'}$$ (4)

226   where x_2', x_3' are mole fractions of the extracting compound and n-hexane, respectively, in the

227   hexane-rich phase, and x_2'', x_3'' are mole fractions of the extracting compound and n-hexane,

228   respectively, in the ionic liquid-rich phase. S and β values were calculated from the tie line data

229   and are also shown in Tables 3 and 4.

230

231 **Table 3.** Measured LLE data (in mole fraction) for ternary mixtures [bmim$^+$][MeSO$_4^-$] (x_1) +

232 2nd component (butyric acid, *rac*-2-pentyl butyrate or *rac*-2-pentanol) (x_2) + *n*-hexane (x_3),

233 experimental selectivity (S) and solute distribution coefficient (β), slope (STL) and length

234 (TLL) of the tie lines at T=303.15 K and p=0.1MPa.[a]

Ionic liquid (1)	[bmim$^+$][MeSO$_4^-$]							
Organic Component (2)	Hexane-rich phase		Ionic liquid-rich phase		S	β	STL	TLL
	x'_1	x'_2	x''_1	x''_2				
rac-2-Pentanol								
	0.007	0.250	0.200	0.450	3.817	1.798	-0.492	0.438
	0.005	0.227	0.377	0.383	5.383	1.684	-0.705	0.645
	0.001	0.113	0.424	0.354	12.457	3.128	-0.638	0.787
	0.000	0.074	0.574	0.263	20.152	3.546	-0.752	0.955
	0.000	0.058	0.729	0.151	20.234	2.585	-0.888	1.098
Butyric Acid								
	0.009	0.544	0.090	0.662	2.197	1.218	-0.405	0.215
	0.005	0.433	0.153	0.621	3.556	1.433	-0.440	0.366
	0.004	0.254	0.201	0.591	8.352	2.331	-0.369	0.570
	0.000	0.125	0.238	0.552	18.483	4.432	-0.357	0.707
	0.000	0.071	0.309	0.481	30.043	6.769	-0.430	0.783
	0.000	0.025	0.354	0.456	92.659	18.079	-0.451	0.861
rac-2-Pentyl Butyrate								
	0.000	0.855	0.899	0.101	-	0.118	-6.196	0.911
	0.000	0.751	0.900	0.100	-	0.133	-3.609	0.934
	0.000	0.619	0.929	0.071	-	0.114	-2.441	1.004
	0.000	0.415	0.939	0.061	-	0.147	-1.605	1.106
	0.000	0.295	0.949	0.051	-	0.173	-1.347	1.182
	0.000	0.106	0.959	0.041	-	0.389	-1.072	1.311
Vinyl Butyrate								
	0.000	0.876	0.696	0.304	-	0.348	-5.596	0.707
	0.000	0.760	0.750	0.250	-	0.329	-3.125	0.787
	0.000	0.599	0.800	0.200	-	0.334	-1.994	0.895
	0.000	0.450	0.840	0.156	-	0.346	-1.535	1.008
	0.000	0.293	0.920	0.080	-	0.273	-1.301	1.160
	0.000	0.116	0.980	0.020	-	0.175	-1.108	1.320

[a] Standard uncertainties are $u(x)$=0.003, $u(T)$=0.5 K and $u(P)$=10 kPa.

235

236

Table 4. Measured LLE data (in mole fraction) for ternary mixtures [emim$^+$][Ac$^-$] (x$_1$) + 2nd component (butyric acid, *rac*-2-pentyl butyrate or *rac*-2-pentanol) (x$_2$) + *n*-hexane (x$_3$), experimental selectivity (*S*) and solute distribution coefficient (*β*), slope (STL) and length (TLL) of the tie lines at *T*=303.15 K and *p*=0.1MPa.[a.]

Ionic liquid (1)	[emim$^+$][Ac$^-$]							
Organic Component (2)	Hexane-rich phase		Ionic liquid-rich phase		*S*	*β*	STL	TLL
	x'_1	x'_2	x''_1	x''_2				
rac-2-Pentanol								
	0.000	0.002	0.404	0.356	673.698	161.909	-0.533	0.859
	0.000	0.003	0.489	0.312	546.189	104.033	-0.606	0.944
	0.000	0.003	0.559	0.271	479.633	82.000	-0.677	0.998
	0.000	0.004	0.675	0.195	383.196	49.949	-0.778	1.100
	0.000	0.005	0.757	0.131	215.142	26.240	-0.865	1.157
Butyric Acid								
	0.000	0.018	0.156	0.565	110.420	31.394	-0.222	0.720
	0.000	0.003	0.228	0.543	947.451	217.320	-0.296	0.802
	0.000	0.001	0.272	0.519	3093.870	648.375	-0.344	0.835
	0.000	$5·10^{-4}$	0.317	0.480	4712.139	959.400	-0.398	0.857
	0.000	$5·10^{-4}$	0.398	0.423	4733.650	846.800	-0.485	0.912
	0.000	$4·10^{-4}$	0.579	0.269	4432.065	673.500	-0.683	1.026
rac-2-Pentyl Butyrate								
	0.000	0.885	0.613	0.387	-	0.437	-5.312	0.624
	0.000	0.762	0.804	0.196	-	0.258	-3.375	0.838
	0.000	0.619	0.822	0.178	-	0.287	-2.158	0.906
	0.000	0.491	0.908	0.092	-	0.187	-1.784	1.041
	0.000	0.288	0.940	0.060	-	0.209	-1.320	1.179
	0.000	0.124	1.000	0.000	-	0.000	-1.142	1.329

[a] Standard uncertainties are *u(x)*=0.003, *u(T)*=0.5 K and *u(P)*=10 kPa.

243   **Table 5.** Binodal data (in mole fraction) at T= 303.15 K and p=0.1MPa for ternary mixtures

244   ionic liquid ([bmim$^+$][MeSO$_4^-$] or [emim$^+$][Ac$^-$]) (x$_1$) + 2nd component (*rac*-2-pentanol or

245   butyric acid) (x$_2$) + *n*-hexane (x$_3$).[a]

| [bmim$^+$][MeSO$_4^-$] | | | |
| *rac*-2-Pentanol | | Butyric acid | |
x_1	x_2	x_1	x_2
0.006	0.000	0.006	0.000
0.006	0.278	0.013	0.580
0.028	0.325	0.031	0.678
0.031	0.332	0.054	0.691
0.064	0.437	0.202	0.587
0.127	0.474	0.337	0.452
0.287	0.429	0.480	0.330
0.402	0.373	0.927	0.000
0.543	0.287	-	-
0.927	0.000	-	-
[emim$^+$][Ac$^-$]			
rac-2-Pentanol		Butyric acid	
x_1	x_2	x_1	x_2
0.008	0.000	0.008	0.000
0.039	0.151	0.025	0.354
0.087	0.253	0.045	0.497
0.117	0.297	0.065	0.525
0.165	0.352	0.098	0.573
0.258	0.371	0.199	0.552
0.438	0.341	0.254	0.532
0.539	0.280	0.435	0.396
0.719	0.161	0.573	0.283
0.930	0.000	0.770	0.129
-	-	0.930	0.000

[a]Standard uncertainties are $u(x)$=0.006, $u(T)$=0.5 K and $u(P)$=10 kPa.

Figure 1. Experimental binodal curve and tie lines for ternary mixture of [bmim+][MeSO4-] + *rac*-2-Pentanol + *n*-hexane at 303.15 K. (○) binodal point; (●) tie line end points.

Figure 2. Experimental binodal curve and tie lines for ternary mixture of [bmim+][MeSO4-] + Butyric Acid + *n*-hexane at 303.15 K. (○) binodal point; (●) tie line end points.

Figure 3. Experimental tie lines for ternary mixture of [bmim$^+$][MeSO$_4$$^-$] + *rac*-2-Pentyl Butyrate + *n*-hexane at 303.15. (•) tie line end points.
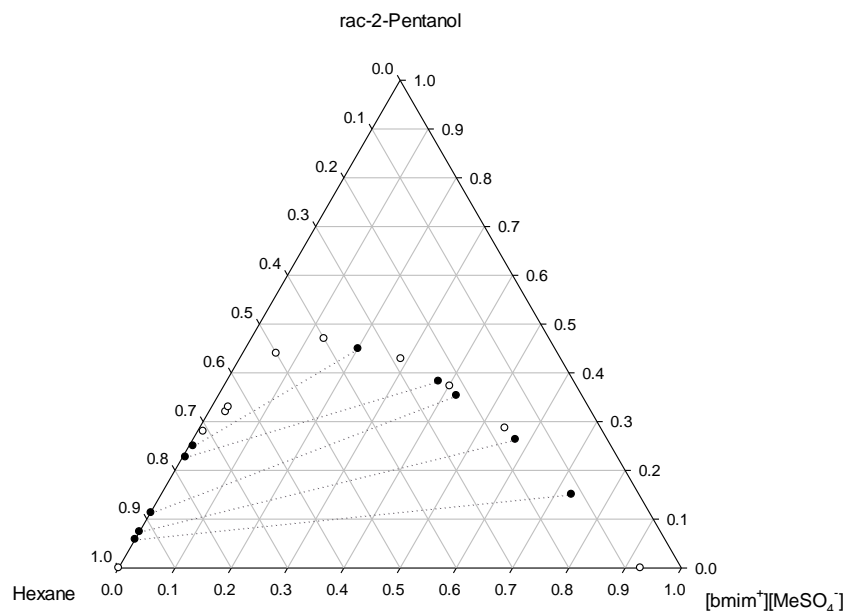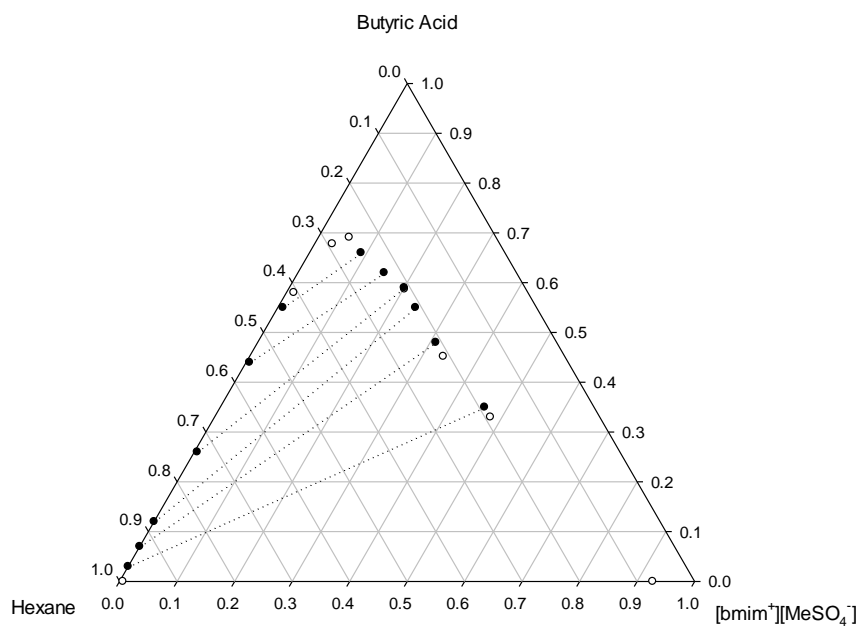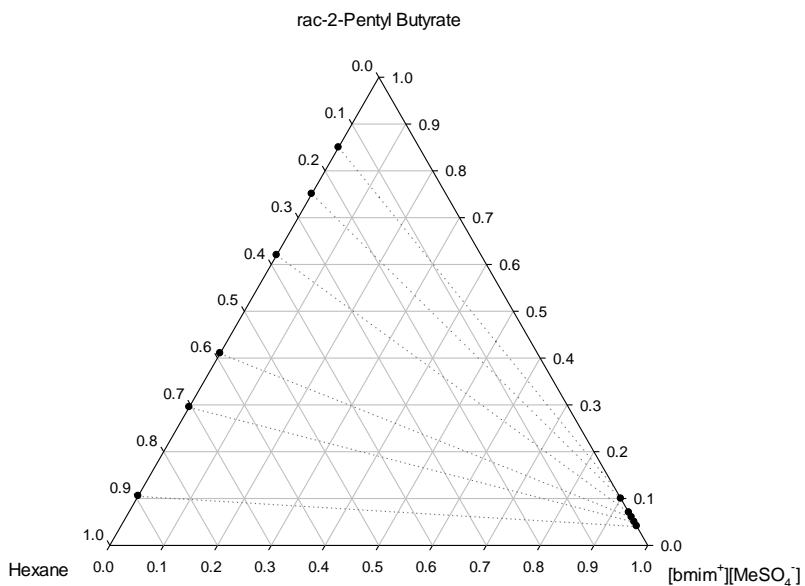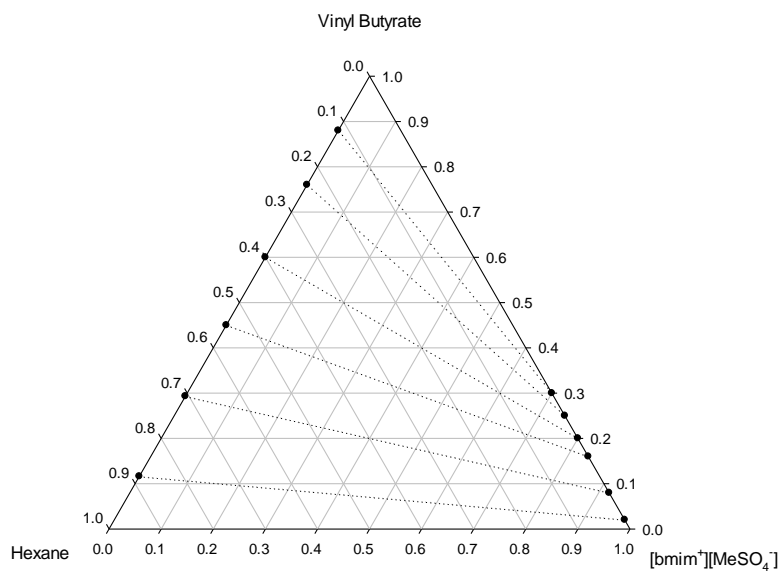
Figure 4. Experimental tie lines for ternary mixture of [bmim$^+$][MeSO$_4$$^-$] + Vinyl Butyrate + *n*-hexane at 303.15 K. (•) tie line end points.

Figure 5. Experimental binodal curve and tie lines for ternary mixture of [emim⁺][Ac⁻] + *rac*-2-Pentanol + *n*-hexane at 303.15 K. (○) binodal point; (●) tie line end points.

Figure 6. Experimental binodal curve and tie lines for ternary mixture of [emim⁺][Ac⁻] + Butyric Acid + *n*-hexane at 303.15 K. (○) binodal point; (●) tie line end points.

Figure 7. Experimental tie lines for ternary mixture of [emim$^+$][Ac$^-$] + *rac*-2-Pentyl Butyrate + *n*-hexane at 303.15 K. (•) tie line end points.

246   Figures 3, 4 and 7 show that for the studied ternary systems involving esters (*rac*-2-pentyl

247   butyrate or vinyl butyrate) the immiscibility region occupies all the possible compositions,

248   covering the total area of the diagram; therefore, [bmim$^+$][MeSO$_4^-$] and [emim$^+$][Ac$^-$] can be

249   considered as extraction solvents for *rac*-2-pentyl butyrate or vinyl butyrate. These systems do

250   not present binodal curve. However, as can be seen in Figures 1, 2, 5 and 6, ternary systems

251   that contain *rac*-2-pentanol or butyric acid present a binodal curve and, as a result, a region with

252   one phase. The curve indicates the boundaries of the homogeneous (with one phase) (on or

253   upper the curve) and heterogeneous (with two phase) (below the curve) domains. The amount

254   of *rac*-2-pentanol or butyric acid needed to make *n*-hexane and the ionic liquid completely

255   miscible is known from the intersection of the biphasic curve with the broken line. For both

256   ILs, the (ionic liquid + *rac*-2-pentanol + *n*-hexane) systems show a greater area corresponding

257   to a single phase than the (ionic liquid + butyric acid + *n*-hexane) systems. However, for both

258   ILs, the results show that the slope of the tie lines were higher for the (ionic liquid + *rac*-2-

259   pentanol + *n*-hexane) systems than for the (ionic liquid + butyric acid + *n*-hexane) systems. The

260   calculated values of STL and TLL (Tables 3 and 4) support these facts. As regard to the slope

261   of the tie lines, we found that for all the studied systems which present a miscibility region

262   (Figures 1, 2, 5 and 6), the tie lines clearly sloped towards the *n*-hexane vertex, indicating that

263   these components (*rac*-2-pentanol and butyric acid) are more soluble in the ionic liquid-rich

264   layer than in the hexane-rich layer, thus favouring the extraction of the organic compound from

265   organic compound-hexane mixtures into the ionic liquid-rich phase. Furthermore, the use of

266   ILs as extractive solvents is also favoured by the ease which they can be recycled due to their

267   extremely low vapour pressure, which, in turn, increases the economic and environmental

268   incentives for their use. By contrast, for the studied systems without binodal curve (Figures 3,

269   4 and 7), the tie lines sloped towards the ionic liquid vertex. From this, it can be deduced that

270   these organic compounds (*rac*-2-pentyl butyrate and vinyl butyrate) show higher solubility in

271   the hexane-rich phase than in the ionic liquid-rich phase, meaning that the use of these ILs as

272   extraction solvents for these esters would be unsuitable. However, the use of *n*-hexane as

273   extraction solvent for an ionic liquid-ester mixture is more appropriate.

274

275   According to our results, we conclude that the slopes of the tie lines and the extraction efficiency

276   of the assayed ILs for the recovery of the target compounds from organic compounds-hexane-

277   ionic liquid ternary mixtures is closely related to the relative polarity and hence to the

278   hydrophilicity/hydrophobicity of the organic component and the ionic liquid. These results

279   agree with those reported in previous works by the authors [10-12]. However, from our results

280   it is also clear that the most relevant influence on the LLE data obtained is the organic

281   compound structure, together with the characteristics of the phases in equilibrium, because

282   similar results were found for both ILs with the same organic compound. Taking into account

283   the experimental and predicted values of the octanol-water partition coefficient of the studied

284   organic compounds found in the literature [72,73], we can establish the following order for their

285   hydrophilicity: Butyric acid > *rac*-2-pentanol > vinyl butyrate > *rac*-2-pentyl butyrate.

286   Therefore, it seems that the greater the hydrophilicity of the target compound, the greater the

287   suitability of the [bmim$^+$][MeSO$_4$$^-$] and [emim$^+$][Ac$^-$] to act as extraction solvents. This is

288   mainly due to the hydrophilic character of the ILs used whose octanol-water partition

289   coefficient was also determined in a previous paper [6]. In contrast, *n*-hexane is a very

290   hydrophobic compound [74].

291

292   Determination of the experimental *S* values from the tie line data was not possible for all the

293   systems because the *n*-hexane concentration in the ionic liquid-rich phase was undetectable in

294   some cases, especially when the binodal curve could not be calculated. When possible, *S* values

295   are shown in Tables 3 and 4. They were far larger for the systems involving [emim$^+$][Ac$^-$] than

296   [bmim$^+$][MeSO$_4$$^-$], underlining the higher extraction efficiency of [emim$^+$][Ac$^-$] for *rac*-2-

297   pentanol and butyric acid. In addition, for both ILs the extraction efficiency towards butyric

298   acid was higher than towards *rac*-2-pentanol, especially in the case of [emim$^+$][Ac$^-$], which was

299   probably due to the higher hydrophilicity of butyric acid. Therefore, we can conclude that

300   [emim$^+$][Ac$^-$] is a very suitable solvent for extracting butyric acid and *rac*-2-pentanol from *n*-

301   hexane.

302   The *β* values, which are also shown in Tables 3 and 4, confirm the trends mentioned above

303   based on an analysis of the slope of the tie lines and the *S* values. Both ILs showed higher *β* for

304   *rac*-2-pentanol and butyric acid than for the esters, being the difference higher when

305   [emim$^+$][Ac$^-$] was used.

306   Figures 8 to 11 plot the values of *β* and *S* obtained for these two ILs (and others studied in

307   previous works [10,11]) as a function of the mole fraction of organic compound in the *n*-hexane-

308   rich phase for the three-component systems. For comparison purposes, Figures 8 and 9 depict

309   the results obtained for ternary systems involving ILs with the [emim$^+$] cation, whereas Figures

310   10 and 11 collate the results found for systems with the [bmim$^+$] cation. Figures 8 to 11 show

311   that the values of both parameters generally lessen as the solute mole fraction in the n-hexane

312   phase becomes greater for all the systems, when going through the tie line end composition.

313   The same conclusions were reached from our previous results [10-12].
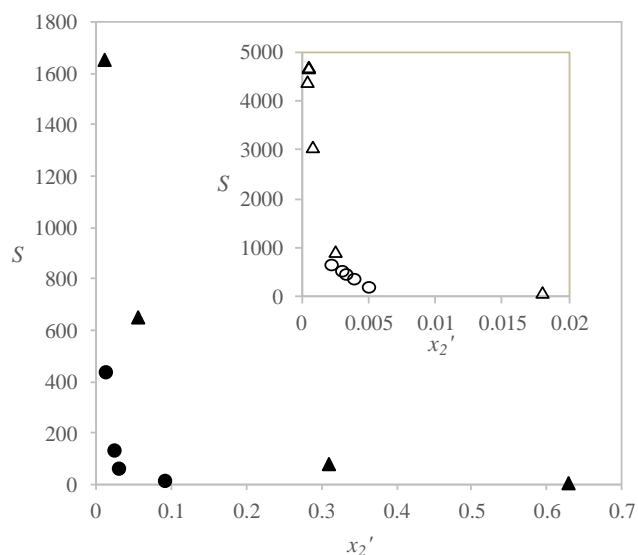
314

315   **Figure 8**. Comparison between the experimental selectivity (S) as a function of the mole

316   fraction of solute in the hexane-rich phase (x_2') for some of the ternary systems involving

317   [emim$^+$] cation studied in this paper and values obtained in a previous work for [emim$^+$] [EtSO$_4^-$

318   ]: ○ {[emim$^+$] [Ac$^-$] + rac-2-Pentanol + n-hexane}, Δ {[emim$^+$] [Ac$^-$] + Butyric Acid + n-

319   hexane} and (● {[emim$^+$] [EtSO$_4^-$] + rac-2-Pentanol + n-hexane}, ▲ {[emim$^+$] [EtSO$_4^-$] +

320   Butyric Acid + n-hexane}[10]).

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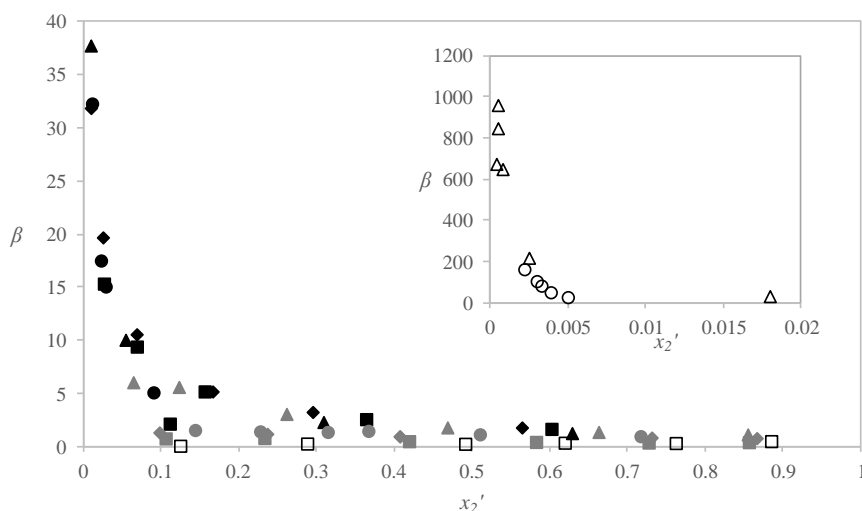
Figure 9. Solute distribution coefficient (β) as a function of the mole fraction of solute in the hexane-rich phase (x_2') for ternary systems containing [emim$^+$] cation: ○ {[emim$^+$] [Ac$^-$] + *rac*-2-Pentanol + *n*-hexane}, Δ {[emim$^+$] [Ac$^-$] + Butyric Acid + *n*-hexane}, □ {[emim$^+$] [Ac$^-$] + *rac*-2-Pentyl Butyrate + *n*-hexane}, (● {[emim$^+$] [EtSO$_4^-$] + *rac*-2-Pentanol + *n*-hexane}, ▲ {[emim$^+$] [EtSO$_4^-$] + Butyric Acid + *n*-hexane}, ■ {[emim$^+$] [EtSO$_4^-$] + *rac*-2-Pentyl Butyrate + *n*-hexane}, ◆ {[emim$^+$] [EtSO$_4^-$] + Vinyl Butyrate + *n*-hexane}[10]) and (●{[emim$^+$] [NTf$_2^-$] + *rac*-2-Pentanol + *n*-hexane}, ▲ {[emim$^+$] [NTf$_2^-$] + Butyric Acid + *n*-hexane}, ■ {[emim$^+$] [NTf$_2^-$] + *rac*-2-Pentyl Butyrate + *n*-hexane}, ◆ {[emim$^+$] [NTf$_2^-$] + Vinyl Butyrate + *n*-hexane}[11]).

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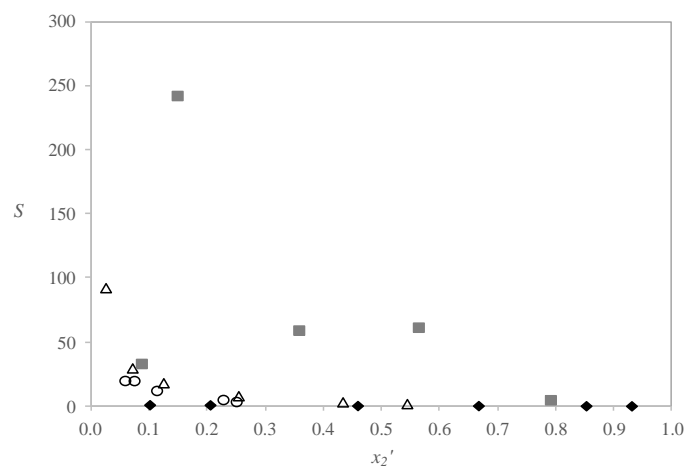
Figure 10. Comparison between the experimental selectivity (S) as a function of the mole fraction of solute in the hexane-rich phase (x_2') for some of the ternary systems involving [bmim$^+$] cation studied in this paper and values obtained in a previous work for [bmim$^+$] [BF$_4^-$] and [bmim$^+$] [NTf$_2^-$]: ○ {[bmim$^+$] [MeSO$_4^-$] + *rac*-2-Pentanol + *n*-hexane}, Δ {[bmim$^+$] [MeSO$_4^-$] + Butyric Acid + *n*-hexane} and (♦ {[bmim$^+$] [BF$_4^-$] + Vinyl Butyrate + *n*-hexane}, ■ {[bmim$^+$] [NTf$_2^-$] + *rac*-2-Pentyl Butyrate + *n*-hexane}[10]).

343
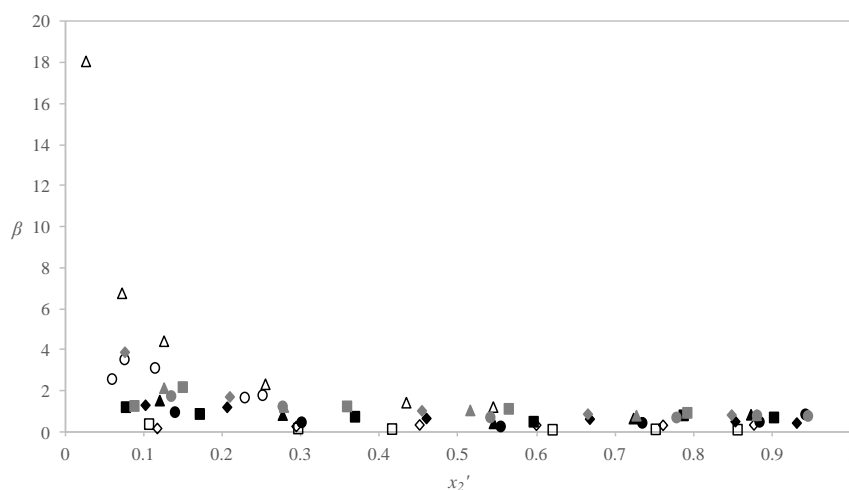
Figure 11. Solute distribution coefficient (β) as a function of the mole fraction of solute in the hexane-rich phase (x_2') for ternary systems containing [bmim$^+$] cation: ○ {[bmim$^+$] [MeSO$_4^-$] + *rac*-2-Pentanol + *n*-hexane}, Δ {[bmim$^+$] [MeSO$_4^-$] + Butyric Acid + *n*-hexane}, □ {[bmim$^+$] [MeSO$_4^-$] + *rac*-2-Pentyl Butyrate + *n*-hexane}, ◇ {[bmim$^+$] [MeSO$_4^-$] + Vinyl Butyrate + *n*-hexane} and (● {[bmim$^+$] [BF$_4^-$] + *rac*-2-Pentanol + *n*-hexane}, ▲ {[bmim$^+$] [BF$_4^-$] + Butyric Acid + *n*-hexane}, ■ {[bmim$^+$] [BF$_4^-$] + *rac*-2-Pentyl Butyrate + *n*-hexane}, ◆ {[bmim$^+$] [BF$_4^-$] + Vinyl Butyrate + *n*-hexane}, ●{[bmim$^+$] [NTf$_2^-$] + *rac*-2-Pentanol + *n*-hexane}, ▲ {[bmim$^+$] [NTf$_2^-$] + Butyric Acid + *n*-hexane}, ■ {[bmim$^+$] [NTf$_2^-$] + *rac*-2-Pentyl Butyrate + *n*-hexane}, ◆ {[bmim$^+$] [NTf$_2^-$] + Vinyl Butyrate + *n*-hexane}[10]).

According to previous LLE data results [10,11] obtained by our group for ternary systems (ionic liquid + *n*-hexane + an organic compound present in the kinetic resolution of *rac*-2-pentanol) some conclusions can be derived. Specifically, we have already examined the suitability of five ILs ([emim$^+$][EtSO$_4^-$], [bmim$^+$][BF$_4^-$] and [bmim$^+$][NTf$_2^-$] [10] and [emim$^+$][NTf$_2^-$] and [hmim$^+$][NTf$_2^-$] [11]) for selectively extracting these organic compounds (*rac*-2-pentanol, vinyl butyrate, *rac*-2-pentyl butyrate or butyric acid) from *n*-hexane-organic compound mixtures at 298.2 and 303.15 K, respectively, and *p*=0.1MPa. As mentioned above, the extraction capacity of the ionic liquid generally depends on the organic component and the characteristics of the phases in equilibrium, but some tendencies can be established. As regard the effect of the anion

364   (for ILs with the same cation) on the extractive capacity of the ionic liquid, we found the

365   following sequences: $[emim^+][Ac^-] > [emim^+] [EtSO_4^-] > [emim^+][NTf_2^-]$ and $[bmim^+][MeSO_4^-]$

366     $] > [bmim^+][BF_4^-] \approx [bmim^+][NTf_2^-]$. Therefore, in general terms, it can be inferred that an

367   augment in the hydrophobicity of the ILs will lead to poorer extraction of the target compounds.

368   We found even larger differences for the extractive capability in the sequence containing the

369     $[emim^+]$ cation. However, for the ILs of the sequence containing the $[bmim^+]$ cation the results

370   were poorer than with the $[emim^+]$ cation, probably because an increase in the length of the

371   alkyl chain of the cation has more effect on the hydrophobicity of the ionic liquid than the anion.

372   Due to all the arguments presented above, we can affirm that both $[emim^+][Ac^-]$ and

373     $[bmim^+][MeSO_4^-]$ can be used as efficient extraction agents of *rac*-2-pentanol and butyric acid

374   from organic compound-*n*-hexane mixtures, although $[emim^+][Ac^-]$ is more selective than

375     $[bmim^+][MeSO_4^-]$.

376

377   **4. Conclusions**

378   Ternary LLE data were determined for ternary mixtures of an ionic liquid ($[bmim^+][MeSO_4^-]$

379   and $[emim^+][Ac^-]$) + *n*-hexane + an organic compound present in the kinetic resolution of *rac*-

380   2-pentanol (*rac*-2-pentanol, vinyl butyrate, *rac*-2-pentyl butyrate and butyric acid) at 303.15K

381   and *p*=0.1MPa.

382   The results showed that the studied ILs could be used as successful solvents for the selective

383   extraction of *rac*-2-pentanol and butyric acid, both the *S* and the *β* being higher when

384     $[emim^+][Ac^-]$ was used. However, the outcome revealed that these ILs are not suitable for the

385   extraction of vinyl butyrate or *rac*-2-pentyl butyrate from an *n*-hexane medium due to the higher

386   hydrophobicity of these esters compared with *rac*-2-pentanol or butyric acid. These results

387   reveal the suitability of $[bmim^+][MeSO_4^-]$ and $[emim^+][Ac^-]$ for selective extraction from a

388 hexane reaction medium. For all the systems, β and S values generally decreased when the

389 solute mole fraction in the hexane phase increased.

390

391 **Acknowledgements**

395

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632

Extraction of Organic Compounds Involved in the Kinetic Resolution of *rac*-2-Pentanol from *n*-Hexane by Imidazolium-based Ionic Liquids: Liquid-Liquid Equilibrium

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SUPPORTING INFORMATION
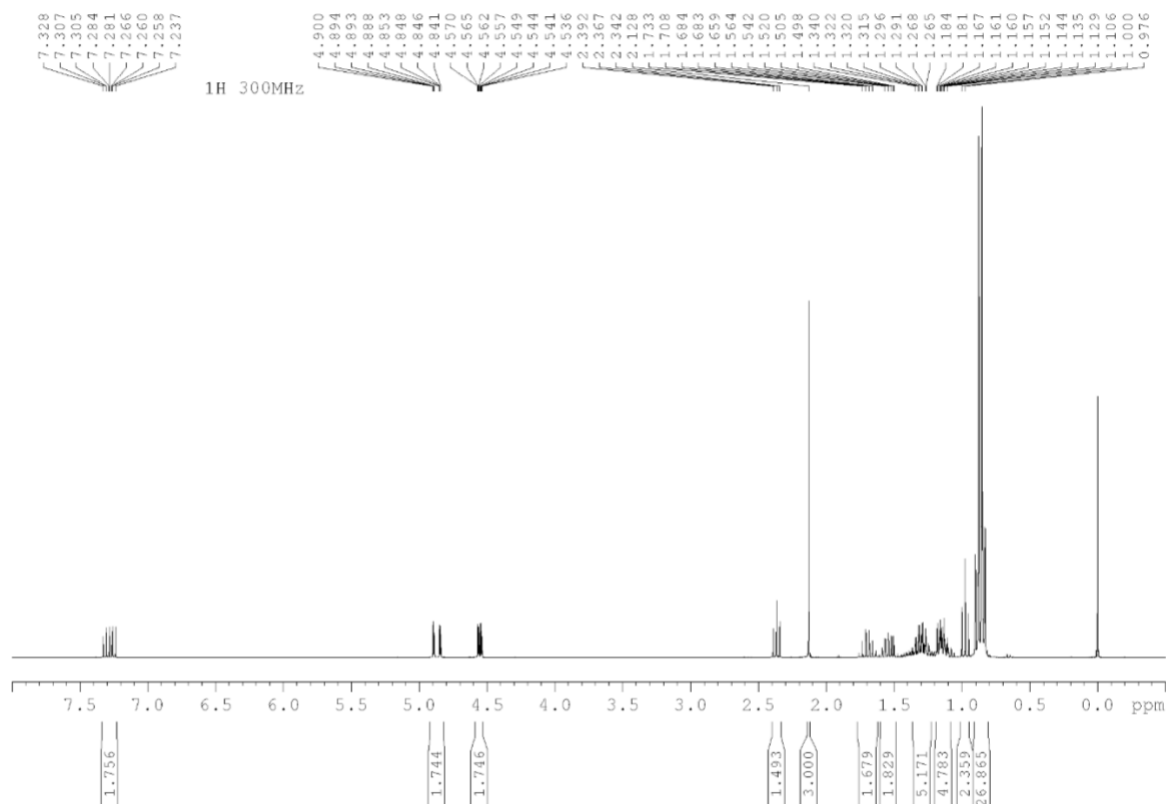
Figure S1. ^{1}H-NMR spectrum of the *n*-hexane phase obtained from the [emim$^+$][Ac$^-$] + *n*-hexane + vinyl butyrate system.
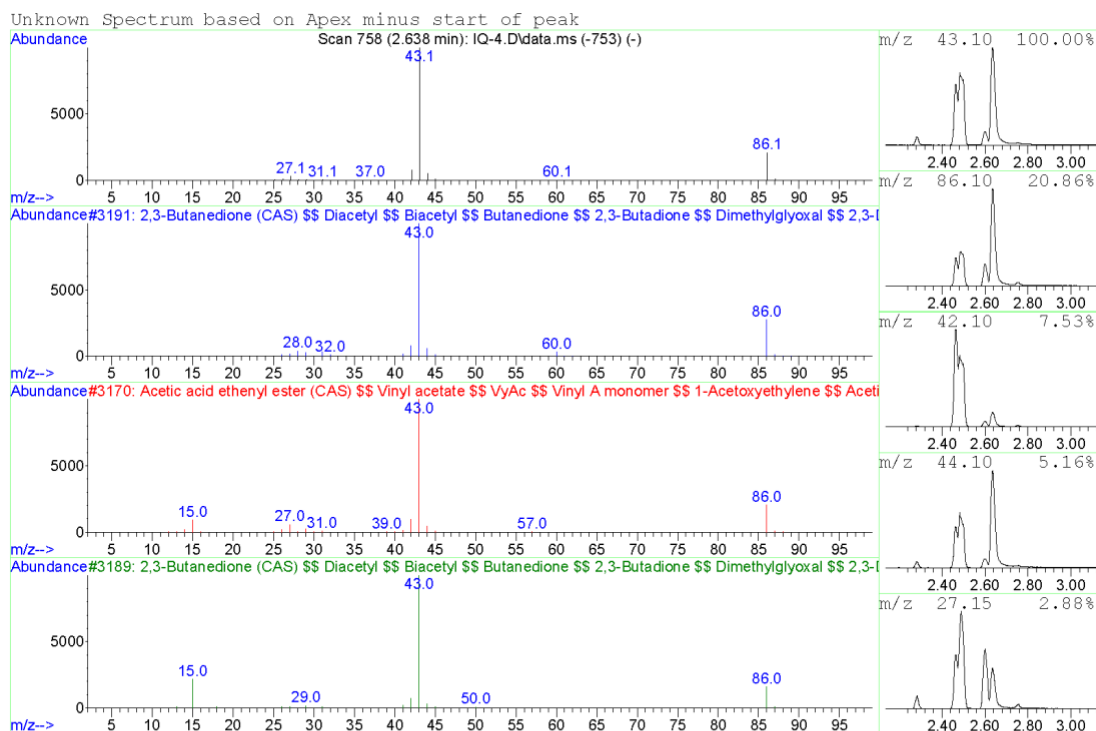
657   ^{1}H-NMR spectrum of the *n*-hexane phase obtained from the [emim$^+$][Ac$^-$] + *n*-hexane + vinyl

658   butyrate system was recorded on a Bruker Avance 200 (300 MHz, CDCl$_3$). The set of peaks

659   corresponding to δ 7.328-7.237, 4.900-4.841, 4.570-4.536 and 2.128 belongs to vinyl acetate.

660

661

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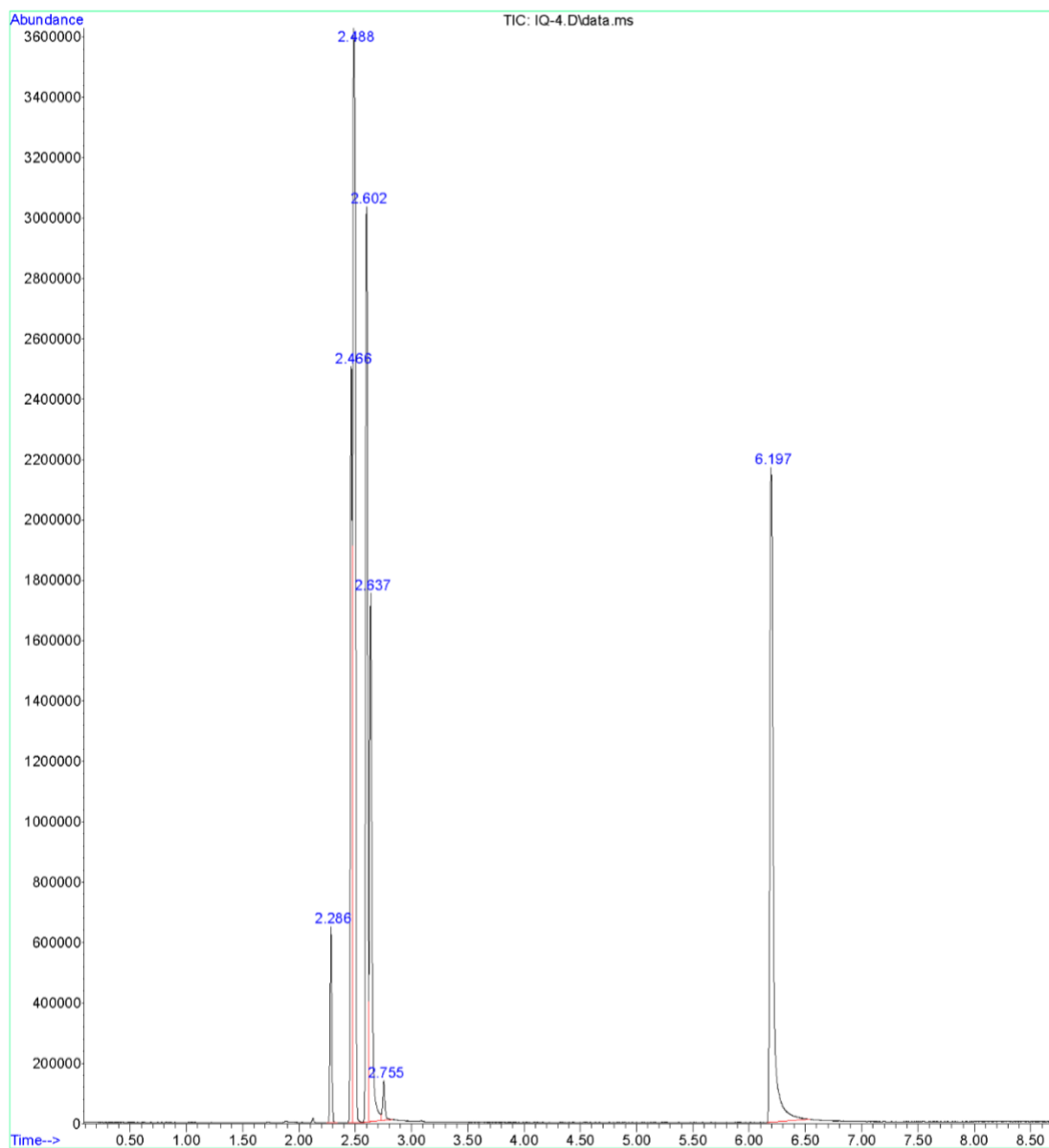
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    2 2-Pentanone                           1697 000107-87-9     9
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    2 Acetic acid ethenyl ester (CAS) ...   3170 000108-05-4    72
    3 2,3-Butanedione (CAS) $$ Diacety...   3189 000431-03-8    45
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Figure S2. GC-MS spectrum of the *n*-hexane phase obtained from the [emim$^+$][Ac$^-$] + *n*-hexane + vinyl butyrate system.

GC-MS analysis of the *n*-hexane phase of the [emim$^+$][Ac$^-$] + *n*-hexane + vinyl butyrate system was carried out with an Agilent 6890 instrument which was fitted with a mass detector Agilent Network 5973, using a HP-5 capillary column (30m x 0.25mm x 0.25μm). The fixed conditions were: carrier gas (He) (1 mL/min total flow); temperature program: 30 ºC, 5 min; 10 ºC/min, 180 ºC; split ratio: 600/1; injector: 200 ºC, detector: 230 ºC. The peak found at 2.637 min corresponds to vinyl acetate.