Selective Extraction of Organic Compounds from Transesterification Reaction Mixtures by Using Ionic Liquids

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*In this article, we describe assays carried out to determine the suitability of 13 ionic liquids based on 1-*n*-alkyl-3-methylimidazolium and* n*-alkylpyridinium cations and a wide range of anions (hexafluorophophate, bis{(trifluoromethyl)sulfonyl}imide, tetrafluoroborate, methylsulfate, 2(2-methoxyethoxy)ethylsulfate, ethylsulfate,* n*-octylsulfate, dicyanamide, nitrate, tetrafluoroborate and chloride) to carry out the selective separation of the organic compounds involved in a transesterification reaction (butyl butyrate, vinyl butyrate, 1-butanol, and butyric acid) from hexane solutions. The assayed ionic liquids were shown to be suitable solvents for the selective separation of the target compounds, the extraction process being controlled by the hydrophobicity of the compounds. The anion composition of the ionic liquid was seen to strongly influence the average extraction ratio, the highest value being reached with the chloride-based ionic liquid. As regards the cation composition of the ionic liquids, it was seen that the average distribution ratio increased with decreasing length of alkyl chain.* © 2010 American Institute of Chemical Engineers *AIChE J,* 56: 1213–1217, 2010
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Introduction

Liquid/liquid extraction is a very effective separation method for recovering and separating organic compounds in the chemical industry. Traditionally, solvent extraction has involved partitioning a solute between two immiscible phases, typically an organic solvent and an aqueous solution. However, the use of volatile organic solvents (VOS) in chemical processes has a detrimental impact on the environment and on human health. Consequently, greener and cleaner extraction methods are being sought.

Ionic liquids (ILs) have recently been revealed as interesting clean alternatives to classical organic solvents in a wide range of chemical,[1] biochemical,[2,3] separation,[4,5] and electrochemical[6] applications. Ionic liquids (ILs) are organic salts that are liquid in a temperature range around or below room temperature. They normally consist of an organic cation, the most commonly used being dialkylimidazolium, *N*-alkylpyridinium and tetraalkylammomium salts, and a polyatomic inorganic anion such as [BF_4^-], [PF_6^-], and [NTf_2^-]. The most important advantage of ILs is their nondetectable vapor pressure, which makes them environmentally benign solvents compared with volatile organic solvents (VOSs). They also

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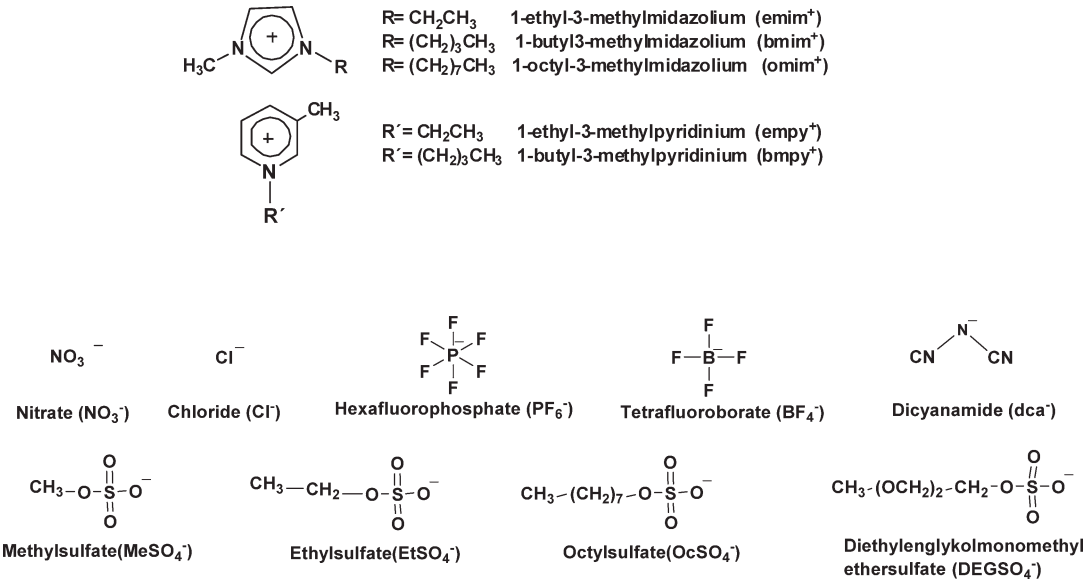

Figure 1. Ions involved in the assayed ILs.

show good chemical and thermal stability and can be used at high temperatures.[7] Additionally, the physical-chemical properties of ionic liquids, such as their hydrophobicity, density, viscosity, melting point, polarity, and solvent properties, can be tailored by varying the substitutive group on the cation or the combined anion.[8,9] Indeed, this feature is a key factor for realizing successful extraction processes because appropriate combinations of the cationic and anionic parts of the solvent can be made. To date, several authors have been successful in the field of extraction, for instance, isolation of metal species[10–12] and organic compounds such as phenolic compounds,[13] organic acids,[14] amino acids,[15] azo dyes,[16] S-compounds in diesel oil,[17] and antibiotics.[18]

The aim of this work was to evaluate the extraction of organic compounds involved in a transesterification reaction (vinyl butyrate, 1-butanol, butyl butyrate, and butyric acid) from hexane solutions by using environmentally friendly solvents, such as ionic liquids. Water cannot be used as extraction agent in these processes because the hydrolysis of the vinyl ester could take place. For this purpose, 13 ionic liquids consisting of 1-*n*-alkyl-3-methylimidazolium and 1-*n*-alkyl-3-methylpyridinium cations combined with a wide range of anions, including hexafluorophosphate, bis(trifluoromethylsulfonyl) imide, tetrafluoroborate, methylsulfate, 2(2-methoxyethoxy) ethylsulfate, ethylsulfate, *n*-octylsulfate, dicyanamide, nitrate, acetate, tetrafluoroborate, and chloride, were used as extraction agent (see Figure 1). The extraction process was studied by means of the solute distribution ratio and the extraction efficiency of the ionic liquid at 303.15 K. More specifically, the effect of cation and anion composition on the efficiency of the extraction process was studied. The results of this study will be used in future integrated reaction/separation processes.

Experimental

Chemicals

The ionic liquids, 1-ethyl-3-methylimidazolium ethylsulfate [emim$^+$][EtSO$_4^-$] (purity > 99%), 1-butyl-3-methylimidazolium methylsulfate [bmim$^+$][MeSO$_4^-$] (purity > 99%), 1-butyl-3-methylimidazolium diethyleneglycol monomethylether sulfate [bmim$^+$][MDEGSO$_4^-$] (purity > 99%), 1-ethyl-3-methylpyridinium ethylsulfate [empy$^+$][EtSO$_4^-$] (purity > 99%), 1-butyl-3-methylimidazolium chloride [bmim$^+$][Cl$^-$] (purity > 99%), 1-butyl-3-methylimidazolium tetrafluoroborate [bmim$^+$][BF$_4^-$] (purity > 99%), 1-butyl-3-methylpyridinium tetrafluoroborate [bmpy$^+$][BF$_4^-$] (purity > 99%), 1-octyl-3-methylimidazolium tetrafluoroborate [omim$^+$][BF$_4^-$] (purity > 99%), 1-butyl-3-methylimidazolium octylsulfate [bmim$^+$][OctSO$_4^-$] (purity > 99%), 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim$^+$][PF$_6^-$] (purity > 99%), and 1-octyl-3-methylimidazolium hexafluorophosphate [omim$^+$][PF$_6^-$] (purity > 99%) were purchased from Solvent Innovation GmbH (Cologne, Germany). The ionic liquids were dried under anhydrous phosphorous pentoxide in vacuum and were stored in a desiccator to prevent any absorption of moisture.

Synthesis of ionic liquids

1-Butyl-3-methylimidazolium dicyanamide, [bmim$^+$][dca$^-$]. [bmim$^+$][Cl$^-$] (52.2 g, 0.3 mol) was dissolved in acetone (50 mL) and sodium dicyanamide (28.6 g, 0.32 mol) was added. The mixture was stirred for 20 h at room temperature, then kept at −20°C for 1 day and filtered. The filtrate was evaporated by rotary evaporation, yielding a slightly yellow ionic liquid (53.4 g, 90%). This product was purified by column chromatography over active alumina, yielding a colorless ionic liquid (49.8 g, 84%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.99 (t, 3H), 1.41 (m, 2H), 1.92 (m, 2H), 4.03 (s, 3H), 4.26 (t, 2H), 7.50 (m, 2H), 9.17 (s, 1H).

1-Butyl-3-methylimidazolium nitrate, [bmim$^+$][NO$_3^-$]. A column was packed with 250 g of Dowex 1X8-200 anion-exchange resin and flushed thoroughly with a 1 M sodium nitrate solution (0.5 L), then with Milli-Q water. The [bmim$^+$][Cl$^-$] (26.3 g, 0.15 mol) was dissolved in Milli-Q water (200 mL) and the resulting solution was slowly run

Table 1. IL/Hexane Distribution Ratio and Extraction Percentage Values of 1-Butanol (BuOH), Vinyl Butyrate (VB), Butyl Butyrate (BB), and Butyric Acid (BA) in the Assayed ILs

	D_{VB}	D_{BuOH}	D_{BB}	D_{BA}	E_{VB}	E_{BuOH}	E_{BB}	E_{BA}
[bmim$^+$][Cl$^-$]	0.21	34.68	0.08	435.8	17.03	97.20	7.69	99.77
[bmim$^+$][NO$_3^-$]	0.29	14.66	0.04	241.8	22.56	93.62	3.97	99.59
[emim$^+$][EtSO$_4^-$]	0.29	12.98	0.08	248.2	22.23	92.85	7.10	99.60
[empy$^+$][EtSO$_4^-$]	0.29	17.36	0.06	127.2	22.77	94.55	5.70	99.22
[bmim$^+$][OctSO$_4^-$]	0.57	29.78	0.26	317.8	36.44	96.75	20.57	99.69
[bmim$^+$][MDEGSO$_4^-$]	0.36	15.29	0.12	151.6	26.57	93.86	10.50	99.34
[bmim$^+$][MeSO$_4^-$]	0.45	15.80	0.18	204.7	30.97	94.05	15.16	99.51
[bmim$^+$][dca$^-$]	0.67	12.96	0.29	138.5	40.17	92.83	22.28	99.28
[omim$^+$][BF$_4^-$]	0.82	9.18	0.41	14.97	45.17	90.18	28.95	93.74
[bmim$^+$][BF$_4^-$]	0.41	4.87	0.14	8.30	28.84	82.98	12.57	89.25
[bmpy$^+$][BF$_4^-$]	0.28	4.22	0.16	9.74	21.88	80.84	13.72	90.69
[omim$^+$][PF$_6^-$]	0.68	3.63	0.35	1.57	40.48	78.40	25.93	61.09
[bmim$^+$][PF$_6^-$]	0.47	2.46	0.17	1.12	31.97	71.10	14.53	52.83

through the column and eluted with Milli-Q water (1 L). The eluate was collected and concentrated under reduced pressure. The residue was dried extensively under vacuum over phosphorous pentoxide. [bmim$^+$][NO$_3^-$] was obtained in a near-quantitative yield.^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.94 (t, 3H), 1.36 (m, 2H), 1.87 (m, 2H), 4.01 (s, 3H), 4.25 (t, 2H), 7.52 (m, 2H), 9.78 (s, 1H).

Extraction of organic compounds from transesterification reaction mixtures

Extraction was performed at 303.15 K. 0.75 mL of a synthetic mixture of all reaction products (0.1 M) was brought into contact with 0.75 mL of pure IL. The phase-contacting experiments were carried out in carefully stoppered glass vessels. The mixture was shaken vigorously for 5 min to facilitate the transfer of compounds into the ionic liquid phase before being left at a constant temperature for 10 min to complete phase separation. After that, samples were taken from the hexane-rich phase by penetrating the silicone septum with a glass syringe with a stainless-steel needle. Samples were taken from the vials during three sampling events occurring over a 10 to 30 min period, the equilibrium concentrations being already reached in 10 min. The composition of the organic phase before ($C_{H(0)}$) and after shaking ($C_{H(1)}$) with the IL phase was analyzed by GC, as described in the next section (GC analysis). The distribution ratios of a given compound between the IL and the hexane solution were calculated by the following equation:

$$D = \left(\frac{C_{H(0)} - C_{H(1)}}{C_{H(1)}}\right)\frac{V_H}{V_{IL}} = \frac{C_{IL}}{C_{H(1)}} \quad (1)$$

These also allow the extraction percentage (E) to be calculated by

$$E = \frac{C_{IL}}{C_{IL} + C_{H(1)}} \times 100 \quad (2)$$

where C_{IL} and $C_{H(1)}$ refer to the equilibrium concentration of the compounds in the ionic liquid and in the hexane phases, respectively. It should be noted that the ionic liquids used in this work are immiscible with the hexane phase. Determinations were made in triplicate to ensure the repeatability of the tests and the mean values are reported. The repeatability of the assay, as measured by the relative standard deviation, was 3% or less.

GC analysis

GC analysis was performed with an Agilent 6890 N instrument equipped with FID detector and a Nukol^{TM} capillary column (15 m $\times$ 0.53 mm $\times$ 0.5 μm, Supelco), using ethyl hexanoate as internal standard. The chromatographic conditions were as follows: carrier gas (N_2) at 1.89 psi (51 mL/min total flow); temperature program: 40°C, 4 min; 5°C/min, 135°C; split ratio: 7.9/1; detector: 220°C. The retention times of the peaks were as follows: *n*-hexane, 1.1 min; vinyl butyrate, 3.0 min; 1-butanol, 6.3 min; butyl butyrate, 8.8 min; ethyl hexanoate, 9.4 min; and butyric acid 21.6 min. Concentrations were calculated from calibration curves using stock solutions of pure compounds. The uncertainties after GC calibration on determined mole numbers was 0.01% or less.

Results and Discussion

Screening experiments with ionic liquid/hexane mixtures at 303.15 K

With the aim of evaluating the extraction of organic compounds involved in transesterification reaction mixtures from hexane solutions by using ionic liquids, the distribution ratio of four different compounds (vinyl butyrate, 1-butanol, butyl butyrate, and butyric acid) between *n*-hexane and the ionic liquids and the extraction percentage of these compounds were determined. For this purpose, 13 different ionic liquids consisting of 1-*n*-alkyl-3-methylimidazolium and 1-*n*-alkyl-3-methylpyridinium cations combined with a wide range of anions, including hexafluorophosphate, bis{(trifluoromethyl)-sulfonyl}imide, tetrafluoroborate, methylsulfate, 2(2-methoxyethoxy)ethylsulfate, ethylsulfate, *n*-octylsulfate, dicyanamide, nitrate, acetate, tetrafluoroborate, and chloride, were used (see Figure 1). The IL/hexane distribution ratio (D) and the extraction percentage (E) values for each compound using the different ionic liquids are presented in Table 1.

As can be seen from Table 1, appreciable differences in the distribution ratios between the organic compounds were observed, suggesting that the ionic liquids can be used for selective separation of the target compounds. The

distribution ratio for butyric acid and 1-butanol are always much greater than unity, which confirms the high extraction efficiency of the assayed ILs for these compounds. It is noteworthy that distribution ratio higher than 100 and consequently extraction percentage higher than 99% were obtained for butyric acid when the following ionic liquids were used as extractor solvent: [bmim$^+$][Cl$^-$], [bmim$^+$][NO$_3^-$], [emim$^+$][EtSO$_4^-$], [empy$^+$] [EtSO$_4^-$], [bmim$^+$][OctSO$_4^-$], [bmim$^+$][MDEGSO$_4^-$], [bmim$^+$][MeSO$_4^-$], and [bmim$^+$] [dca$^-$]. However, the values of the distribution ratios of vinyl butyrate and butyl butyrate with the assayed ionic liquids were not over unity. The important differences observed between butyric acid and 1-butanol, and vinyl butyrate and butyl butyrate enabled us to separate both groups of compounds with great efficiency.

As is evident from Table 1, the distribution ratio of the different compounds for all ionic liquids can be arranged as follows: butyric acid > 1-butanol > vinyl butyrate > butyl butyrate. This sequence can be related with the hydrophilic/hydrophobic character of the compounds. To establish a hydrophobicity sequence for the compounds, the Hildebrand solubility parameter (δ) was used. This parameter, defined as the square root of the cohesive energy density, provides a numerical estimate of the degree of interaction between compounds, and can be a good indication of solubility. Compounds with similar δ values are miscible in most proportions, while dissimilar values mean limited solubilities.[19] The solubility parameter of butyric acid is 24.5, 1-butanol 23.7, vinyl butyrate 17.7, and butyl butyrate 17.4. The nearer the solubility parameter of a target compound is to that of water, the more hydrophilic the compound, while the nearer the solubility parameter of the compound is to that of *n*-hexane, the more it is hydrophobic. Having in mind the solubility parameter of water ($\delta = 48$) and *n*-hexane ($\delta = 14.9$), the hydrophilic character of the assayed compounds can be arranged as follows: butyric acid > 1-butanol > vinyl butyrate > butyl butyrate. This sequence is in agreement with that obtained for the distribution ratio of the organic compounds, which confirms that an increase in the hydrophilic character of the assayed compounds results in an increase in their distribution ratio in the ionic liquids. This behavior could be explained by the hydrophilic nature of the assayed ionic liquids, which favors interaction with the more hydrophilic compounds. The relationship established between the distribution ratio and the hydrophilicity of the compounds suggests that the capability of a given ionic liquid to separate the target compounds can be assessed simply by evaluating the Hildebrand solubility parameter of each compound.

In order to find a numerical criterion to compare the ability of the different ionic liquids to separate the target compounds, a new parameter—the average distribution ratio—is introduced. The parameter can be defined as follows:

$$r\overline{D} = \frac{\sum_i^n rDi}{n} \quad \text{with} \quad rD_i > 1 \tag{3}$$

where rD_i is ratio between the distribution ratio of two compounds (e.g., 1-butanol and butyl butyrate) and n is the number of possible pairs of different compounds. rD_i can be expressed as follows:

Table 2. Average Distribution Ratio for the Assayed ILs

Ionic Liquid	*rD*
[bmim$^+$][Cl$^-$]	1326.2
[bmim$^+$][NO$_3^-$]	1184.6
[emim$^+$][EtSO$_4^-$]	725.1
[empy$^+$][EtSO$_4^-$]	482.0
[bmim$^+$][OcSO$_4^-$]	326.9
[bmim$^+$][MDEGSO$_4^-$]	316.0
[bmim$^+$][MeSO$_4^-$]	290.1
[bmim$^+$][dca$^-$]	127.8
[bmpy$^+$][BF$_4^-$]	23.6
[bmim$^+$][BF$_4^-$]	21.4
[omim$^+$][BF$_4^-$]	15.4
[bmim$^+$][PF$_6^-$]	5.6
[omim$^+$][PF$_6^-$]	4.5

$$rD_i = D_A/D_B \tag{4}$$

The average distribution ratio of the ionic liquid indicates its efficiency in separating compounds: the higher $r\overline{D}$, the more selective it is in separating the target compounds. An average distribution ratio near 1 means that the ILs are not useful for separating the compounds. The $r\overline{D}$ values for the different ionic liquids are shown in Table 2.

As can be seen from Table 2, significant differences in the average distribution ratio for the assayed ILs were found. The most effective IL for separating the target organic compounds was [bmim$^+$][Cl$^-$], which showed the highest average distribution ratio (1326.2) because of a combination of a high extraction percentage for butyric acid and 1-butanol (99.77 and 97.20, respectively) and a low extraction percentage for vinyl butyrate and butyl butyrate (17.03 and 7.69).

Bearing in mind the water miscible/immiscible character of the assayed ionic liquids (water miscible: [bmim$^+$][Cl$^-$],[bmim$^+$][NO$_3^-$],[emim$^+$][EtSO$_4^-$],[empy$^+$][EtSO$_4^-$],[bmim$^+$][OctSO$_4^-$], [bmim$^+$][MDEGSO$_4^-$], [bmim$^+$] [MeSO$_4^-$], [bmim$^+$][dca$^-$], [bmim$^+$][BF$_4^-$], [bmpy$^+$][BF$_4^-$]; water immiscible: [omim$^+$][BF$_4^-$], [omim$^+$][PF$_6^-$], [bmim$^+$] [PF$_6^-$], it can be concluded that the highest average distribution ratios were obtained when water miscible ionic liquids were used ($21.4 < r\overline{D} < 1326.2$). This underlines the relationship between the nature of the ionic liquid and their average distribution ratio.

Effect of the cation

Our aim was to investigate the influence of the ionic liquid composition on the recovery of organic compounds from hexane solutions. For that, a systematic study of ILs was carried out using ionic liquid based on the same anion, [BF$_4^-$] or [PF$_6^-$], and changing the cation ring (from imidazolium to pyridinium) or the chain length of the alkyl substituent in the imidazolium ring of the cation (from butyl to octyl). As can be observed in Table 1, the values of the distribution ratio for the compounds increased with increasing alkyl chain length of the cation of the ILs. This behavior was also reported by Fan et al.[13] for the selective separation of phenols. Regarding the average distribution ratio, it can be observed in Table 2 that the value of this parameter for [bmim$^+$][PF$_6^-$] was higher than that obtained for [omim$^+$][PF$_6^-$], which means that a decrease in the alkyl

chain length of the cation of the ionic liquid involves an increase in the average distribution ratio values. The same conclusion can be made when the $[omim^+][BF_4^-]$/$[bmim^+][BF_4^-]$ pair is compared. A decrease in the alkyl chain length has been correlated with an increase in the hydrophilicity of ILs, as measured by the octanol-water partition coefficients (K_{OW}).[20] Therefore, an increase in the hydrophilic character of the ionic liquid cation results in an increase in the average distribution ratio of the assayed compounds. Similar results were found by Meindersma et al.[21] who investigated the separation of toluene from heptane by extraction with ionic liquids, reporting that a shorter alkyl group on the imidazolium cation of the ionic liquids generally results in a higher selectivity in the separation.

Furthermore, although the average distribution ratio is quite similar for $[bmim^+][BF_4^-]$ and $[bmpy^+][BF_4^-]$, this parameter is significantly higher for $[emim^+][EtSO_4^-]$ with respect to $[empy^+][EtSO_4^-]$.

Effect of the anion

The influence of the anion composition of the ionic liquids on the average distribution ratio values can be appreciated by comparing this parameter for identical cations. As can be observed from Table 2, the average distribution ratio values increased for a given cation in the sequence: $[PF_6^-] < [BF_4^-] < [dca^-] < [MeSO_4^-] < [MDEGSO_4^-] < [OctSO_4^-] < [NO_3^-] < [Cl^-]$. By comparing cation and anion effects, the greatest effect on the average distribution ratio was observed by changing the nature of the anion of the ionic liquid.

Conclusions

The assayed ionic liquids are suitable solvents for the selective separation of transesterification reaction mixtures, especially the ionic liquid [bmim][Cl], which showed the highest average distribution ratio. The anion composition of the IL is the most important factor in the partitioning of these compounds into ILs from hexane solution. Regarding the cation composition of the ionic liquid, it was found that the distribution ratio for the compounds increased with increasing alkyl chain length of the cation of the ILs, while the average distribution ratio increased with decreasing alkyl chain length of the cation of the ILs. A relationship was established between the distribution ratio and the hydrophilicity of the compounds, which suggests that the capability of a given ionic liquid to separate the target compounds can be assessed simply by evaluating the Hildebrand solubility parameter of each compound.

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