

Utilization of Ionic Liquids for the Separation of Organic Liquids from Industrial Effluents

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Received 15 August 2011, revised 15 April 2012, accepted 29 June 2012.

ABSTRACT

The recovery of aromatic organic solvents from mixtures containing aliphatic compounds has economic as well as environmental significance. This is so because viable methods have not been established for the recovery from mixtures in which the components of value are 20 % (v/v) or less. In the light of this, we investigated the efficacy of selected ionic liquids to recover aromatic solvents from prepared mixtures. We used 1-ethyl-3-methylimidazolium ethyl sulfate [EMIM][EtSO₄] and 1-ethyl-3-methylpyridinium ethyl sulfate [EMpy][EtSO₄] to separate and recover aromatic hydrocarbons (less than 10 % (v/v)) from aromatic/aliphatic hydrocarbon mixtures, namely, benzene, toluene, ethyl benzene and *o*-xylene (BTEX) from *n*-heptane at 40 °C. The same aromatic components were used with *n*-hexane as an alkane and 1-ethyl-3-methylpyridinium ethyl sulfate [EMpy][EtSO₄] as an ionic liquid. The concentrations of the aromatic components used were in the range of 2.5–10 % (v/v) for the following multi-systems at 40 °C:

- Benzene + toluene + ethyl benzene + *o*-xylene + *n*-heptane + [EMIM][EtSO₄].
- Benzene + toluene + ethyl benzene + *o*-xylene + *n*-hexane + [EMIM][EtSO₄].
- Benzene + toluene + ethyl benzene + *o*-xylene + *n*-hexane + [EMpy][EtSO₄].

The % removal of each aromatic, the ionic liquid selectivity trend, as well as its lifetime, and the distribution pattern of aromatic components in the ionic liquid obtained by gas chromatography were used to determine the capability of [EMIM][EtSO₄] and [EMpy][EtSO₄] as extracting solvents for low concentration BTEX.

KEYWORDS

Ionic liquids, solvent extraction, BTEX, aromatic hydrocarbons, aliphatic hydrocarbons.

1. Introduction

The recovery of organic solvents from effluents emanating from industries such as oil refineries is important for several reasons. Among these, the more salient ones are:

- Saving in costs involved in purchasing replacement stocks.
- Decreasing pollution of the environment linked with the disposal of waste effluent.
- Creating openings for small to medium-sized businesses to get involved in separation industries.
- Reuse of valuable resources.

It has been reported^{1–6} that in the petrochemical industries, liquid extraction is the most widely used process for the separation of benzene, toluene, ethyl benzene and xylenes (BTEX) from aliphatic hydrocarbons because their separations cannot be carried out in an efficient and economic way by energy-intensive methods due to the close proximity of the boiling points of the hydrocarbons.¹ Currently some conventional organic solvents, used by many industries for this purpose, include sulfolane, ethylene glycols, *N*-methylpyrrolidone, *N*-formylmorpholine, and *N*-methylimidazole amongst others. However, these solvents are generally toxic, flammable, and their recovery is tedious as it requires several steps.² Sulfolane is one of the most appropriate solvents employed for this separation due to its physical-chemical properties and much research involving its liquid-liquid equilibria in aromatic/aliphatic mixtures has been reported.^{3–10} Although sulfolane is currently the most widely used solvent in the petroleum industry, its

viability is limited to mixtures containing 20 % and/or more of the target aromatic hydrocarbons.¹⁰ Unless alternative techniques are developed, petroleum effluents containing less than the extractable amounts need to be treated as waste.

Our search of the literature has shown that there is only one report¹¹ which has directly addressed the challenge of developing a method for recovering aromatic hydrocarbons from mixtures containing less than 20 % of useful components by using a pilot plant. Furthermore, it involved the chemical engineering aspect, namely, the design of a laboratory-scale separator using ionic liquids to effect the initial separation. This study was motivated by the following observations, regarding the limitations of sulfolane as an extracting solvent, namely:

- It is only suitable for mixtures with 20–65 % aromatic hydrocarbons content.
- Additional separation steps are required to purify the raffinate, extract and solvent streams.
- Regeneration of the spent sulfolane is very costly.

On the other hand, ionic liquids have many useful properties such as: zero or low solubility of aliphatic hydrocarbon in the ionic liquid, high separation factor or selectivity and distribution coefficient, easy recovery of the ionic liquid from both the extract and the raffinate phases, fast mass transport from the feed phase to the ionic liquid phase, high thermal and chemical stability, high heat and electrical conductivities, high solubility in both polar and non-polar organic and inorganic substances and high turnover frequencies.^{11–13} In addition, ionic liquids have gained in appeal because traditional distillation systems are

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considered as unsafe for reasons of environmental protection due to high volatility of organic solvents.¹⁴ In view of this the introduction of cleaner technologies has engaged the attention of both academics and industrialists.

In view of the above it is apparent that very little work has been done on the extraction of aromatic liquids from mixtures of hydrocarbon waste generated by oil refinery industries. This study therefore investigated the efficacy of two ionic liquids 1-ethyl-3-methylimidazolium ethyl sulfate [EMIM][EtSO₄] and 1-ethyl-3-methylpyridinium ethyl sulfate [EMpy][EtSO₄] as a means of recovering aromatic solvents from selected aliphatic solvents. These ionic liquids have been chosen primarily due to the scarcity of data in the literature for the selected systems, as well as the fact that they are relatively simple to synthesize and characterize. The concentrations of the components were varied from 2.5 to 10 % (v/v) and the targeted fractions were analyzed by GC-FID to determine the % recovery by mass.

2. Experimental

2.1. Chemicals

Ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate (≥ 98.5 %), diethyl sulfate (≥ 99 %), and 1-methylimidazole (≥ 99 %), 3-methylpicoline were purchased from Fluka. Toluene (≥ 99.9 %), benzene (≥ 99.9 %), *m*-xylene (≥ 99 %), *o*-xylene (≥ 99 %), *p*-xylene (≥ 99 %), (*n*-heptane (≥ 99 %), *n*-hexane, and 1-butanol (≥ 99 %) were purchased from Merck. Acetone-*d*₆ (≥ 99.5 %) was purchased from Aldrich.

2.2. Experimental Procedure

2.2.1. Synthesis and Characterization of Ionic Liquids

Ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate was synthesized according to the procedures described elsewhere^{9,15–17} as follows: Diethyl sulfate (0.44 mol, 58 mL) was slowly added drop-wise to an ice-cooled mixture of 1-methylimidazole (0.44 mol, 35 mL) and toluene (1.88 mol, 200 mL) under an inert atmosphere of argon. When the addition of diethyl sulfate was complete, the reaction mixture was stirred for 5 hours at room temperature to allow the reaction to go to completion. At the end of this period, the lower layer (ionic liquid phase) was separated from the mixture by using a separating funnel and then washed three times with a total volume of 100 mL toluene. The crude product was dried at 70 °C under reduced pressure for 3 hours in a rotary evaporator to remove organic solvents and water before the characterization measurements. The final product was then subjected to various qualitative analytical methods for characterization purposes such as ¹H NMR using acetone-*d*₆ as solvent.²¹ The characteristics of the products were verified by FTIR-ATR and UV-Visible spectrometry. The spectra obtained from both techniques were compared with spectra of standard 1-ethyl-3-methylimidazolium ethyl sulfate. The water content and densities were determined with a Karl-Fischer titration and densitometer respectively.^{21–24} The ionic liquids were stored in a moisture-free environment such as desiccators and always analyzed for moisture content before use. The ionic liquid 1-ethyl-3-methylpyridinium ethyl sulfate [EMpy][EtSO₄] was also synthesized and characterized using the experimental procedure described above.

2.2.2. Extraction and Separation of Aromatic Components

Mixtures containing benzene, toluene, ethyl benzene and *o*-xylene (BTEX) in the concentration range 2.5–10 % (v/v) for

each component in *n*-heptane or *n*-hexane were prepared. The extraction of benzene, toluene, ethyl benzene and *o*-xylene (BTEX) from the mixture using 1-ethyl-3-methylimidazolium ethyl sulfate or 1-ethyl-3-methylpyridinium ethyl sulfate was carried out at constant temperature of 40 °C using jacketed vessels and a thermostatically controlled water-bath. The experimental mixture (10 mL) was placed in a jacketed vessel at 40 °C, followed by addition of ionic liquid (20 mL).²¹ The mixture was agitated vigorously using a magnetic stirrer for 3 hours in order to allow an intimate contact between the two phases. The equilibrium mixture was then transferred into a separating funnel and allowed to settle for at least 12 hours at room temperature to ensure complete phase separation.^{21,25–27} This operation was also subjected to a 4-hour settling period for comparison purposes. The phases were then separated and stored in suitable sample vials for analysis. The ionic liquid-rich phase is referred to as the extract phase and the *n*-alkane-rich phase as the raffinate phase. The ionic liquid was recovered from the mixtures using a rotary evaporator to remove organic solvents and water.

2.2.3. Analysis of Phase Mixtures by GC-FID

The aromatic components (BTEX) in each phase were analyzed by GC-FID fitted with a ZB-Wax-Plus capillary column (30 m × 0.25 mm × 0.25) and a guard column (5 m × 0.25 mm) to protect the analytical column.^{21,26}

The following GC parameters were used for the analysis of the phases:

Column oven: 40 °C [2 min → 115 °C] (20 °C min⁻¹)

Carrier gas: nitrogen; column flow

Injector: 250 °C; split ratios 1:100 raffinate phase and 1:25 for the extract phase

Detector: FID; 250 °C

Standards of BTEX, covering the concentration range of the prepared mixtures, were used for calibration of the instrument. The concentrations and the peak areas were used to construct calibration curves, and the BTEX concentrations were calculated by means of the linear equation. Since the ionic liquids contain a small amount of toluene from the synthesis stage, a blank analysis was also carried out to adjust the results. The reused ionic liquids were also analyzed for BTEX content for the same purpose before extraction. A known volume of each phase was mixed thoroughly with an equal volume of 1-butanol in a suitable vial for GC analysis to prevent phase splitting and to maintain a homogeneous mixture during analyses. The vials were sealed with silicon septa through which a micro syringe needle was used to draw 1 μL of each sample for GC analysis.

3. Results and Discussion

All samples and standards were analyzed under the same conditions as described above.

Experiments were devised to investigate the effects of:

- Varying the concentrations of BTEX components
- Varying the phase settling periods
- Varying the nature of alkanes
- Varying the nature of the cations in the ionic liquids
- Increasing the number of extraction stages

3.1. The Effect of Varying the Concentrations of BTEX Components

Multi-system Mixture: BTEX + [EMIM][EtSO₄] + *n*-heptane

The percentage amounts of BTEX components present in both

Table 1 Variation of BTEX concentration in *n*-heptane over a 12-hour settling period for [EMIM][EtSO₄] (R = Raffinate, E = Extract).

Concentration of individual components/% (v/v)	Benzene/% (m/v)			Toluene/% (m/v)			Ethyl benzene/% (m/v)			<i>o</i> -Xylene/% (m/v)		
	R	E	R+E	R	E	R+E	R	E	R+E	R	E	R+E
2.5	57	34	91	67	15	82	72	11	83	77	14	91
5.0	56	30	86	77	12	89	71	10	81	76	10	86
7.5	55	28	83	75	13	88	79	9	88	74	10	84
10.0	55	24	79	75	12	87	80	8	88	74	10	84

Table 2 Variation of BTEX concentration in *n*-heptane over a 4-hour settling period for EMIM][EtSO₄] (R = Raffinate, E = Extract).

Concentration of individual components/% (v/v)	Benzene/% (m/v)			Toluene/% (m/v)			Ethyl benzene/% (m/v)			<i>o</i> -Xylene/% (m/v)		
	R	E	R+E	R	E	R+E	R	E	R+E	R	E	R+E
2.5	63	32	95	61	18	79	64	8	72	64	9	73
5.0	61	30	91	70	14	84	68	7	75	65	8	73
7.5	61	26	87	72	13	85	73	7	80	68	8	76
10.0	58	21	79	71	11	82	74	6	80	69	7	76

the extract and raffinate phases are shown in Table 1 for their individual concentration range of 2.5–10 % (v/v). The values for the extract phases indicate a general decrease with increasing concentration of the BTEX components. This indicates that the amount of ionic liquid required for extraction should be increased proportionally with increasing concentration of BTEX components in order to ensure optimum and efficient separation. The results in Table 1 also reveal a general increase in percentages extracted in the following order: *ethyl benzene* ≤ *o-xylene* < *toluene* < *benzene*. This phenomenon can be explained in terms of the structures of the aromatic hydrocarbons. Benzene is the smallest molecule with the least steric hindrance and strongest π -systems whereas *o*-xylene is crowded with two methyl groups while ethyl benzene is sterically hindered by a longer ethyl group thus causing relatively weaker π -systems.¹⁹

In addition, it appears that the longer the alkyl chains that are attached to the aromatic rings, the more difficult it is for the molecules to organize themselves in a sandwich structure. This phenomenon supports the observation made by Meindersma *et al.*¹¹ that alkyl substitution on the aromatic ring affect the molecular interaction in the preferred functional groups. Based on BTEX structures, it can be argued that π - π interactions strongly influence the BTEX interactions with the ionic liquids. According to Poole *et al.*²⁰ the ionic liquid may form a single phase with the mixture in which it has a higher affinity for one component over the other (often hydrogen bonding more strongly with one component than the other). Hansmeier *et al.*²¹ reported that ionic liquids and aromatic solutes organize themselves in a sandwich structure in which 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.

The concentrations of the alkane components are relatively

lower in the extract phases relative to the raffinate phases as shown in Tables 1 and 2. The ionic liquids used show much higher affinities toward the BTEX components than for the alkanes. In both ionic liquids, the alkanes have very small peak areas (at 2.72 min) in the extract phases compared to the peak areas in the raffinate phases. Therefore, the extract phase is said to be ionic liquid-rich and the raffinate phase alkane-rich. It was also established by FTIR and ¹H-NMR spectroscopy that the raffinate phases contained no ionic liquid.

3.2. The Effect of Varying the Phase Settling Periods

The percentage amounts of individual components of BTEX present in both raffinate and extract phases for the concentration range 2.5–10 % (v/v) when using a 4-hour settling period are shown in Table 2. It appears that the extraction values for a 4-hour settling time are slightly lower than those of a 12-hour settling period. The slight difference observed suggests that the ionic liquid in question is almost capable of achieving a complete phase separation within 4 hours after extraction. However, all operations in this study were conducted for a 12-hour settling period to ensure maximum equilibration.

3.3. The Effect of Varying the Nature of the Alkanes

Multi-system Mixture: BTEX + [EMIM][EtSO₄] + *n*-hexane

The extraction results using *n*-hexane as an alkane are shown in Table 3. These values do not differ significantly from those obtained for heptane under similar conditions. In general, however, the former are slightly lower than the latter. This is attributed to the chain lengths of alkanes which influence the interaction between BTEX solutes and ionic liquids. Gonzalez *et al.*⁹ reported that an increase in the chain length of the alkanes leads to an increase in the size of the immiscibility region. They also concluded that the selectivity values were higher for the systems

Table 3 Variation of BTEX concentration in *n*-hexane over a 12-hour settling period for [EMIM][EtSO₄] (R = Raffinate, E = Extract).

Concentration of individual components (%v/v)	Benzene (%m/m)			Toluene (%m/m)			Ethyl benzene (%m/m)			<i>o</i> -Xylene (%m/m)		
	R	E	R+E	R	E	R+E	R	E	R+E	R	E	R+E
2.5	51	26	77	69	15	84	64	9	73	64	11	75
5.0	51	18	69	68	13	81	70	9	79	70	10	80
7.5	55	18	73	71	12	83	75	8	83	75	9	84
10.0	54	17	71	71	12	83	77	8	85	77	9	86

Table 4 Variation of BTEX concentration in *n*-hexane over a 12-hour settling, period for [EMpy][EtSO₄] (R = Raffinate, E = Extract).

Concentration of individual components/ % (v/v)	Benzene/% (m/v)			Toluene/% (m/v)			Ethyl benzene/% (m/v)			<i>o</i> -Xylene/% (m/v)		
	R	E	R+E	R	E	R+E	R	E	R+E	R	E	R+E
2.5	56	36	92	78	24	102	74	15	89	71	15	86
5.0	48	33	81	71	22	93	76	13	89	73	15	88
7.5	49	35	84	68	19	87	76	12	88	71	15	86
10.0	53	31	84	77	19	96	84	13	97	78	15	93

Table 5 Effect of extraction stages for [EMIM][EtSO₄] and [EMpy][EtSO₄].

Concentration of individual components/ % (v/v)	[EMIM][EtSO ₄] in extract/% (m/v)				[EMpy][EtSO ₄] in extract/% (m/v)			
	Benzene	Toluene	E/Benzene	<i>o</i> -Xylene	Benzene	Toluene	E/Benzene	<i>o</i> -Xylene
5.0 (1st stage)	21	15	10	12	38	25	15	18
5.0 (2nd stage)	12	21	7	8	25	27	11	12
5.0 (3rd stage)	12	21	8	8	25	27	11	12
Overall recovery	45	57	25	28	88	79	37	42
10.0 (1st stage)	19	14	9	10	35	22	15	17
10.0 (2nd stage)	18	13	8	9	20	26	10	11
10.0 (3rd stage)15	12	9	10	20	25	10	11	
Overall recovery	52	39	26	29	75	73	35	39

containing alkanes with longer chains in the following order: hexane < heptane < octane < nonane.

3.4. The Effect of Varying the Cation of the Ionic Liquid

Multi-System Mixture: BTEX + [EMpy][EtSO₄] + *n*-hexane

The results for using 1-ethyl-3-methylpyridinium ethyl sulfate as an ionic liquid are shown in Table 4. It appears that the values are higher than those obtained for 1-ethyl-3-methylimidazolium ethyl sulfate under similar conditions. The values suggest that the BTEX solutes interact more strongly with [EMpy][EtSO₄] than they do with the ionic liquid [EMIM][EtSO₄]. This could be attributed to the fact that the former contains a six-membered ring cation whereas the latter has a five-membered ring cation. This phenomenon enhances the solubility of the BTEX components in 1-ethyl-3-methylpyridinium ethyl sulfate. Meindersma *et al.*⁹ indicated in their study that the ionic liquids containing the ethyl-*N*-methylpyridinium cations have more aromatic character than the imidazolium-based ionic liquids which have relatively less π -character.

3.5. The Effect of Increasing the Extraction Stages

Multi-System Mixture: BTEX + [EMIM][EtSO₄] or [EMpy][EtSO₄] + *n*-hexane

The extraction results of the 5 and 10 % (v/v) mixtures are shown in Table 5 for both imidazolium-based and pyridinium-based ionic liquids. The nature of the results suggests that the recovery of the BTEX components from alkanes can be improved by increasing the number of extraction stages with ionic liquids. In both ionic liquids, the second stage values are slightly lower than those obtained in the first stages. Meindersma *et al.*¹¹ established that in order to achieve a toluene recovery of at least 98 %, the number of extraction stages must be at least six.

4. Conclusion

With regard to the effects of varying: (1) the concentrations of BTEX components, (2) the phase settling periods, (3) the nature of alkanes on extraction values, (4) the nature of cations in the

ionic liquids, and (5) the number of extraction stages, the conclusions are noted hereunder:

- The recovery values decrease with increasing concentrations of BTEX.
- The extraction values increase with increasing phase settling period.
- There was no significant difference between the extraction values obtained from *n*-hexane and *n*-heptane although the latter showed slightly higher values.
- The ionic liquid 1-ethyl-3-methylpyridinium ethyl sulfate showed higher recovery values than 1-ethyl-3-methylimidazolium ethyl sulfate.
- The recovery values increased with increasing number of extraction stages.

Overall, the most significant conclusion is: ionic liquids can be used to separate aromatic hydrocarbons, namely, benzene, toluene, ethylbenzene, and xylenes (BTEX components) from multi-system mixtures of aromatic/aliphatic solvents. Specifically the separation can be effected by using the ionic liquids, 1-ethyl-3-methylimidazolium ethyl sulfate [EMIM][EtSO₄] and 1-ethyl-3-methylpyridinium ethyl sulfate [EMpy][EtSO₄] under controlled conditions. It was found that 1-ethyl-3-methylpyridinium ethyl sulfate was more effective than 1-ethyl-3-methylimidazolium ethyl sulfate.

The method developed has commercial importance as it can be adapted for industrial plant scale usage and can be modified for automation. The latter can be exploited to increase the number of extraction stages to ensure optimum extraction.

Acknowledgements

Durban University of Technology (DUT) for financial support, and the University of KwaZulu-Natal for use of the NMR.

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