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Industrial application of ionic liquids for the recoveries of spent paint solvent

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ABSTRACT

The recovery of industrially valuable organic solvents from liquid waste, generated in chemical processes, is economically crucial to countries which need to import organic solvents. In view of this, the main objective of this study was to determine the ability of selected ionic liquids, namely, 1-ethyl-3-methylimidazolium ethylsulphate, [EMIM][ESO4] and 1-ethyl-3-methylpyridinium ethylsulphate, [EMpy][ESO_4] to recover aromatic components from spent paint solvents. Preliminary studies done on the liquid waste, received from a paint manufacturing company, showed that the aromatic components were present in the range of (6–21)% by volume. The separation of the aromatic components was performed with the ionic liquids listed above. The phases, resulting from the separation of the mixtures, were analysed with a gas chromatograph (GC) coupled to a FID detector. Chromatograms illustrate that the chosen ZB-Wax-Plus column gave excellent separation of all components of interest from the mixtures, including the isomers of xylene. The concentrations of aromatics recovered from the spent solvents were found to be in the % ranges of (13 — 33) and (23–49), respectively for imidazolium and pyridinium based ionic liquids. These results also show that there is a significant correlation between π-character of ionic liquids and the level of extraction. It is therefore concluded that ionic liquids have the potential for macro-scale recovery of re-useable solvents present in liquid waste emanating from paint manufacture.

1. Introduction

Oil paint manufacturing companies are significant users of aromatic and aliphatic hydrocarbons as solvents in their various processing units. This is evident from literature reports [1–3] which focus on the health hazards of aromatic solvents used by paint and allied industries. The pollution is not confined to the atmosphere; there is also the danger of pollution of the land if the residues from oil paint manufacture are dumped in landfill sites. The 'waste' from oil paint making processes comprises of unused pigments and solvents. In this context the solvent component is referred to as 'spent solvent'. It is noteworthy that the spent solvents contain significant amounts of aromatic species such as toluene, ethyl benzene and xylene isomers, known by the acronym, TEX. The spent solvents also contain other organic species such as aliphatic hydrocarbons. Although aromatic solvents are generally shunned because of their classification as carcinogens [4], they do play an irreplaceable role in many chemical-based manufacturing processes. This study was therefore aimed at recoveries of aromatic solvents from waste organic mixtures emanating from oil-paint manufacture. In the interest of promoting 'green chemistry' [5,6], ionic liquids (ILs) were selected as extracting agents. ILs is emerged as a new class of solvents for the replacement of volatile organic solvents in different separation as well as industrial processes to reduce both economic and environmental pollution [7]. ILs is used in a wide range of commercial, industrial and incredible applications. Preliminary studies in our laboratories showed that the concentration of aromatic components in spent paint solvents vary between 6 and 21% by volume. Since aromatic solvents are generally costlier to manufacture than aliphatic ones, their recoveries using economically viable methods is very important. In processes where aromatic solvents are utilized as reaction media [8], it would reduce manufacturing costs if the aromatic components could be recovered on a macro scale and reused. Currently, the recovery of aromatic solvents (on an industrial scale) from mixtures containing aliphatic solvents is generally done by distillation or by using extracting solvents such as sulfolane [9,10]. It has been shown [11] that sulfolane is not effective in cases where the concentration of the aromatic components is <20%. Furthermore, distillation is not suitable for separating azeotropic mixtures.

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Although the recovery of organic solvents from spent paint solvents was performed on a laboratory scale, the experimental design for this project incorporated the following considerations:

- The chosen laboratory method [12] for synthesis of the selected IL has potential for adaption to an industrial-scale synthesis of the IL.
- The stability [13] of the IL was such that it was recovered unchanged at the end of the extraction, that is, it is unaffected by exposure to air and moisture.
- The IL meets the requirements for a 'green solvent' [14] so that it is not hazardous to the environment.
- The ILs should be selected on some rational basis [15].
- The ILs shows no loss of extraction ability on repeated reuse [16].

It is noted that there are several reports on the uses of ionic liquids for micro-extraction of BTEX [17,18] but none of them is associated with the extraction of aromatic components from non-aqueous mixtures. There are also several recent reports [19–22] on the extraction of organic liquids using ionic liquids. However they are restricted to binary and ternary systems whereas this project addresses the extraction of organic liquids from multi-component systems. Moreover, this project is an addition to our contributions [12,13,16] on the synthesis of ionic liquids and their application for the extraction of organic liquids from mixtures of organic liquids.

2. Experimental

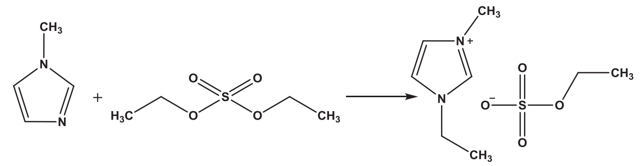
2.1. Materials

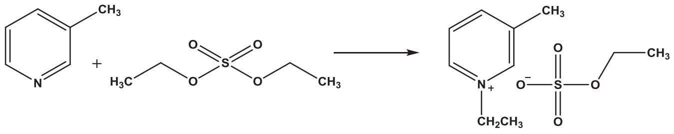
Diethylsulphate (≥99%), 1-methylimidazole (≥99%), and 3-methylpicoline were purchased from Fluka. Toluene (≥99.9%), benzene (≥99.9%), ethyl benzene, *m*-xylene (≥99%), *o*-xylene (≥99%), *p*-xylene (≥99%) and *n*-hexane (≥99%) were purchased from Merck. Karl-Fischer reagent was purchased from Riedel-de-Haen. Samples of spent solvents were obtained from Plascon Paints, one of the major manufacturers of paints in South Africa. The ionic liquids 1-ethyl-3-methylimidazolium ethylsulphate, [EMIM] [ESO_4] and 1-ethyl-3-methylpyridinium ethylsulphate, [EMpy][ESO_4] were synthesized in our laboratory using modifications of documented methods.

2.2. Procedures

2.2.1. Synthesis and characterization of ionic liquids

The ionic liquid, 1-ethyl-3-methylimidazolium ethylsulphate, was synthesized using modifications of reported procedures [23,24] while 1-ethyl-3-methylpyridinium ethylsulfate was produced by adapting a documented [25] method. Since the project was aimed at establishing procedures suitable for industrial use, the most amenable method was chosen. For the synthesis of imidazolium and pyridinium-based ionic liquids, quarternization reactions, whereby the ionic liquid cations are formed from the tertiary amines using alkylating agents such as alkyl halides and dialkyl sulphates, proved to be very suitable. Quarternization of 1-ethyl-3-methylimidazolium ethylsulfate and 1-ethyl-3-methylpyridinium ethylsulfate proceeds as follows:





In illustration of the principles described above, the following procedure was used for the synthesis of 1-ethyl-3methylimidazolium ethyl sulphate:

Diethylsulfate(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 diethylsulfate was complete, the reaction mixture was stirred for 5 h 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 h using a rotary evaporator; to remove organic solvents and water before the characterization measurements.

2.2.2. Determination of water content in the ionic liquids

The water content of the ionic liquid was determined using a Karl–Fischer Coulometer [Metrohm 756]. Ionic liquids were tested immediately after drying under high vacuum for 48 h and it was found that the water content was below 850 ppm for both the ionic liquids used in this work.

2.2.3. Analysis of spent solvent waste mixtures

Spent paint solvent mixtures were analysed for the concentration by volume of aromatic components present in each. A known volume of each spent solvent mixture was distilled using a rotary evaporator (to collect all volatile organic components including aromatic and aliphatic hydrocarbons as the most important ones). The volume of the distilled liquid was carefully measured and then analysed for the percentage (by volume) of each aromatic component present in the distillate, using GC fitted with capillary column and an FID detector. The concentrations in the raw samples were calculated using the original volume of the raw sample. The results for the above are given in Table 1.

2.2.4. Extraction in stages using freshly-prepared ionic liquids

Aliquots of distillates from spent paint solvents were extracted with freshly-prepared ionic liquids under controlled conditions, using purpose-made water jacketed reaction vessels through which water from a thermostatically controlled tank was circulated. The extraction of aromatic components (toluene, ethyl-benzene and isomers of xylenes, known by the acronym TEX) from the measured samples, using the ionic liquids listed above, was carried out at constant temperature of 40 °C and atmospheric pressure. Aliquots (10 mL) of the spent solvent were placed in the reaction vessels (at 40 °C), followed by addition of ionic liquid (20 mL). The mixture was agitated vigorously using a magnetic stirrer for 5 h in order to allow for intimate contact between the two phases. The equilibrium mixture was then transferred into a separating funnel and allowed to settle for at least 12 h at room temperature to ensure that complete phase separation had occurred. 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 alkane-rich phase as the raffinate phase. The ionic liquid was recovered from the mixtures using a rotary evaporator to remove organic solvents

Table 1
Concentrations of aromatic components in spent paint solvent samples.

Aromatic components	Spent solvent mixture	
	Peak area	% (v/v)
Benzene	Nil	Nil
Toluene	18493790	21.0
Ethyl benzene	6168467	7.1
p-Xylene	6652490	7.7
m-Xylene	15830365	18.0
o-Xylene	7260821	8.2
Total aromatics		62.0

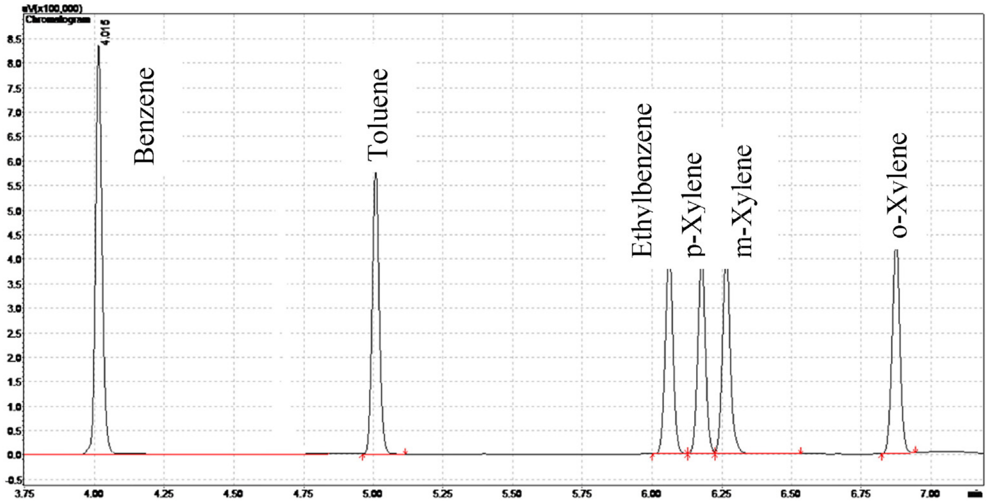


Fig. 1. Calibration chromatogram for determining composition of the spent solvent mixture.

and water. The recovered ionic liquids were used in experiments described under section.

2.2.5. Analysis of phase mixtures by GC-FID

The aromatic components (TEX) in each phase were analysed by FID-GC fitted with ZB-Wax-Plus capillary column (30 m × 0.25 mm × 0.25 μm) and a guard column.

(5 m × 0.25 mm) to protect the analytical column, with the following parameters:

Column oven: 40 °C [2 min → 115 °C] (20 °C/min)
Carrier gas: nitrogen; column flow
Injector: 250 °C; split ratio 1:100 for all samples
Detector: FID; 250 °C

Standards of TEX, covering the concentration range of the prepared mixtures, were used for the calibration of the instrument. The concentrations and the peak areas were used for the construction of the calibration curves and the TEX concentrations were calculated by means of a linear regression. Since the ionic liquids contain small amount of solvents from the synthesis stage, a blank analysis was also carried out to adjust the results for toluene. Furthermore, when regenerated ionic liquids were used in the extraction, blank analyses were performed to measure the residual aromatic components so that the extraction results are corrected. 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. All analyses in this study were based on external calibration standards of the aromatic components of interest.

3. Results and discussion

3.1. Determination of aromatic components in spent solvent mixtures

The spent solvent samples were obtained from the Plascon paint manufacturing company which had stored them in labelled tanks. This is referred to as 'spent solvent'. Prior to sampling, the storage tanks were agitated for about 3 min to homogenise the contents. These spent solvents were filtered and then distilled. The distillates were analysed, using GC-FID, to determine the concentration (%) of aromatic components. A guard column was used as a pre-column to prevent the non-volatile materials from entering the analytical column and, possibly, interfering with the analysis. Standards of appropriate concentration range of BTEX components were used to calibrate the instrument using linear graphs of concentrations versus peak areas. The chromatograms from the calibration experiments served to confirm that the aromatic components present in spent solvents were toluene, ethyl benzene *o*-xylene, *m*-xylene and *p*-xylene. The concentrations of toluene, ethyl-benzene and isomers of xylene are shown in Table 1. The aromatic component with the highest concentrations is seen to be toluene which is not only a requisite for oil paint manufacture but is also very often used as a substitute for benzene. This is based on the perception that toluene is less carcinogenic than benzene. Fig. 1 shows the chromatogram for a prepared mixture of BTEX.

Table 1 also shows that the total of aromatics in the samples was 62.0% (v/v). This high result suggests that efforts to recover aromatic solvents (even if it is a fraction of this amount), are worthwhile pursuing on the grounds of high replacement costs and reduction in damage to the environment (due to dumping of paint waste).

3.2. Extraction of TEX from mixtures using fresh ionic liquids for every stage

The two ionic liquids used were compared with regard to extraction ability; to ascertain whether differences in structures made a significant difference to the amounts of aromatic solvents extracted by the two ionic liquids. This test was done over three cycles/stages under identical conditions for both ionic liquids. For the second and third stages, the raffinate phase from the previous extraction was treated with fresh aliquots of ionic liquids. The results are given in Tables 2 and 3 for [EMpy][ESO_4] and [EMIM][ESO_4], respectively.

Table 2
Extraction results using fresh [EMpy][ESO_4] each for stage.

Aromatic components	1st stage % (v/v)		2nd stage % (v/v)		3rd stage % (v/v)		Total % (v/v)
	Extract	Recovery	Extract	Recovery	Extract	Recovery	
Toluene	3.08	15.6	2.65	13.4	2.18	11.0	40
E/benzene	0.74	11.0	0.62	9.3	0.55	8.2	29
p-Xylene	0.84	11.7	0.69	9.6	0.60	8.3	30
m-Xylene	2.00	11.8	1.44	8.5	1.13	6.7	27
o-Xylene	1.03	14.1	0.78	10.7	0.62	8.5	33

Table 3
Results of the three stages of extractions from fresh [EMIM][ESO_4].

Aromatic components	1st stage % (v/v)		2nd stage % (v/v)		3rd stage % (v/v)		Total % (v/v)
	Extract	Recovery	Extract	Recovery	Extract	Recovery	
Toluene	2.37	12.0	1.66	8.4	1.61	8.2	29
E/Benzene	0.51	7.6	0.37	5.5	0.35	5.2	18
p-xylene	0.57	7.9	0.42	5.8	0.39	5.4	19
m-xylene	0.95	5.6	0.97	5.7	0.93	5.5	17
o-xylene	0.66	9.0	0.52	7.1	0.50	6.8	23

Table 4
Results for three-stage extractions using regenerated [EMpy][ESO_4].

Aromatic components	1st stage % (v/v)		2nd stage % (v/v)		3rd stage % (v/v)		Total % (v/v)
	Extract	Recovery	Extract	Recovery	Extract	Recovery	
Toluene	4.4	20.9	3.2	15.5	2.6	12.4	49
E/benzene	0.84	11.0	0.58	7.5	0.48	5.3	25
p-Xylene	0.93	12.1	0.65	8.4	0.52	6.8	28
m-Xylene	2.4	13.5	1.7	9.5	1.3	7.2	30
o-Xylene	1.25	15.2	0.84	10.2	0.62	7.6	33

Table 6
Total recovery for aromatic components in three stages of extractions from spent solvents.

Aromatic components	[EMIM][ESO_4]		[EMpy][ESO_4]	
	Fresh	Regenerated	Fresh	Regenerated
Toluene [% (v/v)]	29	30	40	49
E/benzene [% (v/v)]	18	23	29	25
p-Xylene [% (v/v)]	19	23	30	28
m-Xylene [% (v/v)]	17	18	27	30
o-Xylene [% (v/v)]	23	27	33	33

As seen in the last columns of Tables 2 and 3 the total recoveries for three-stage extractions are in the ranges (27–40) % and (17–29) % for [EMpy][ESO_4] and [EMIM][ESO_4], respectively. It is concluded from this that the ionic liquid 1-ethyl-3-methylpyridinium ethylsulfate, [EMpy][ESO_4] shows higher extracting capacity for aromatic components than 1-ethyl-3-methylimidazolium ethylsulfate, [EMIM][ESO_4]. The pyridini*um*-based ionic liquid showed significant difference in extraction ability from the imidazolium -based one, with respect to all aromatic components recovered. The extraction ability of the former is much higher than that of the latter. This significant difference could be attributed to the number of π-systems in both cations; the pyridinium ion contains six π-electrons in its 6-membered ring whereas in imidazolium ion has four π-electrons lying in its 5-membered ring which gives the former stronger π-systems hence the stronger the interactions between the ionic liquids and aromatic components. The overall results also indicate that, in all experiments performed, the toluene content is higher than the other aromatic components.

3.3. Extraction of TEX using regenerated ionic liquids

To test the efficacy of regenerated solvents, the same experiments, as described in Section 3.3 for fresh solvents was repeated with regenerated solvents. The results are shown in Tables 4 and 5.

It is clear from the results in Tables 3 and 4 that the regenerated solvents give recoveries in the same range as that obtained by using fresh ionic liquids for each stage of the extraction process. This is a very important result for the potential of these ionic liquids to be used in industrial applications. It implies that the extraction can be done repeatedly with a limited amount of ionic liquids. Since the cost of ionic liquids are generally very high this result holds good promise for industrial application of ionic liquids for recovery and reuse of ionic liquids.

It is evident from the results in Table 6 that for all the aromatic components listed; the pyridinium-based ionic liquid gives substantially higher extraction percentages than the imidazolium counterpart. There is another aspect of the results in Table 6 which is worthy of consideration, namely, the order of extraction of individual aromatic components. As can be seen in Table 6, there is a general increase in the percentages extracted in the following order for both ionic liquids: *m-xylene* < *ethyl benzene* < *p-xylene* < *o-xylene* < *toluene*. This observation can be explained in terms of steric hindrance and effects of attached groups on the π-systems of the substituted benzenes. Furthermore, it appears that the longer the alkyl chains which are attached to the aromatic rings, the more difficult it is for the molecules to organise themselves in a sandwich structure. This is in line with the observation made by Meindersma et al., [25] that alkyl substitution on the aromatic ring affects the molecular interaction in the preferred functional groups. Further support for the perceived enhanced TEX interactions with the ionic liquids may be deduced from the views of Poole, [26] and Holbrey et al., [27]. The former suggests that hydrogen bonding between TEX and the ionic liquid may give rise to stronger interactions, whereas the latter proposes that ionic liquids and aromatic solutes organise themselves in a sandwich structure in which the ionic liquid cation and the aromatic solutes interact in an alternating structure through π-π interactions with the ionic liquid anion, arranged around this complex. In a similar context, Deetlefs et al., [28] noted that the presence of benzene significantly alters the structure of an imidazolium ionic liquid through cation - cation interaction.

Table 5
Results of the three stages of extractions using regenerated [EMIM][ESO_4].

Aromatic components	1st stage % (v/v)		2nd stage % (v/v)		3rd stage % (v/v)		Total % (v/v)
	Extract	Recovery	Extract	Recovery	Extract	Recovery	
Toluene	2.16	10.9	1.94	9.8	1.78	9.0	30
E/benzene	0.51	7.6	0.50	7.5	0.49	7.3	23
p-Xylene	0.60	8.3	0.54	7.5	0.52	7.2	23
m-Xylene	0.94	5.5	1.08	6.4	1.04	6.1	18
o-Xylene	0.70	9.6	0.64	8.8	0.59	8.1	27

4. Conclusions

- ➢ The pyridinium-based ionic liquid has higher extraction ability than the imidazolium based one.
- ➢ The ionic liquids can be recovered with their properties intact after they have been used in an extraction procedure.
- ➢ It is relatively easy to recover the ionic liquids from the extraction phases.
- ➢ The ionic liquids appear to retain their extraction abilities after repeated use.
- ➢ As ionic liquids are considered to be ‘green solvents’ their use in reclaiming valuable organic solvents is good for the protection of the environment from pollution.
- ➢ Since the ionic liquids can be relatively easily regenerated, there appears to be a high potential for their use in industrial scale extraction of aromatic solvents.

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