

Research Article

Extraction of 4-Nitrophenol from Aqueous Solutions using Bulk ionic Liquid Membranes

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Abstract

Room temperature ionic liquids show potential as an alternative to conventional organic membrane solvents mainly due to their properties of low vapour pressure, low volatility and they are often stable. In the present work, the technical feasibilities of room temperature ionic liquids as bulk liquid membranes for 4-nitrophenol removal were investigated experimentally. In this research several hydrophobic ionic liquids were synthesized at laboratory and these ionic liquids (1-Butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide, 1-Hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide, 1-Octyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide, 1-Butyl-1-methylimidazoliumhexafluorophosphate, 1-Hexyl-1-methylimidazoliumhexafluorophosphate, 1-Butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide, and 1-Octyl-3-methyl imidazolium tetra fluoroborate. The distribution coefficients for 4-nitrophenol in these ionic liquids were measured at different pH values and found to be much larger than those in conventional solvents. Through the values of the distribution coefficients and the experiments that were conducted on bulk liquid membrane applying various types of prepared ionic liquids, 1-Butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide was selected as the best ionic liquid which gave the greatest extraction and stripping efficiencies. The effects of several parameters, namely, feed phase pH(4.6-9.92), feed concentration(100-1000 ppm), NaOH concentration(0-0.5M), temperature (20-50°C), feed to membrane volume ratio (200-400ml/80ml ionic liquid) and stirring speeds(75-125 rpm) on the performance of the chosen ionic liquid membrane were also studied. The preliminary study shows that high phenol extraction and stripping efficiencies of 99% and 93% respectively were achieved by ionic liquid membrane with a minimum membrane loss which offers a better choice to organic membrane solvents.

Keywords: Liquid membrane, Ionic liquids, Cation, Anion, Extraction efficiency, stripping efficiency, Distribution coefficient.

1. Introduction

Phenol and its compounds are known to be quite poisonous pollutants. Phenols are frequently produced as wastes from various industries, such as refineries, petrochemical manufacturing, coking operations, coal processing, coal gasification liquefaction processes, pharmaceutical plastics, wood products, paint, and pulp and paper industries. Consequently, phenols must be separated from waste water before discharge to the environment.

Between the accessible treatment techniques, liquid membrane has been evidenced to be one of the most fascinating and efficient method for the extraction of pollutants. Liquid membrane is selective permeability barrier which is separating the feed phase and stripping phase allowing the passage of the target

material between those phases. This process merges those transporting processes which are extraction and stripping processes in a single stage, so supplying lower total cost, simple technically, and without relying on the transport equilibrium restriction (San Román, *et al.*, 2009).

Ionic liquids are defined as a set of low melting point salts that comprise of organic cations and organic/inorganic anions. As a result of their negligible volatility, high thermal stability, high electrical conductivity, they perform as “green solvents” and their characteristics can be controlled in accordance with the purpose of design. These brilliant properties aid them as an option to substitute the volatile organic solvents (Petkovic, *et al.*, 2011).

The choice of a correct solvent is the chief problem in all types of liquid membrane-based separation procedures. The selected solvent should possess a high

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distribution coefficient and at the same time it should have the following properties: insoluble in the aqueous solution, non-viscous and non-volatile. The performance of different solvents must be inspected by evaluation of distribution coefficients (K_d) of the solute in required solvents (Noble and Way, 1987; Mulder, 1996).

The main purpose of this study is to investigate the removal of phenol from aqueous solution using bulk ionic liquid membrane as a separation method. The effects of various process parameters on the extraction process, including: ionic liquid type, pH of feed phase, feed concentration, sodium hydroxide concentration in stripping phase, agitation speeds and temperature were also studied.

2. Experimental

The 4-nitrophenol was provided from Sigma Aldrich, NaOH pellets type Sigma Aldrich, HCl type Sigma Aldrich (conc. =37%w, density=1.2g/ml and formula weight=36.46 g/mole) and the materials that were used in the synthesizing of ionic liquids are given in the Table 1

Table 1: Names of chemicals used in synthesis of ionic liquids

	Name of materials	Formula Weight	Source
1	1-methylimidazole	82.10	Sigma Aldrich
2	N-methylpyrrolidine	85.15	Sigma Aldrich
3	1-bromobutane	137.02	Sigma Aldrich
4	1-bromohexane	165.07	Sigma Aldrich
5	1-bromooctane	193.12	Sigma Aldrich
6	Bis(trifluoromethane)sulfoni-mide lithium salt	287.09	Sigma Aldrich
7	Sodium hexafluorophosphate	167.95	Sigma Aldrich
8	Sodium tetrafluoroborate	109.79	Sigma Aldrich
9	Acetonitrile	41.05	Sigma Aldrich
10	Diethyl ether	74.12	Sigma Aldrich

Preparation of ionic liquids

[Bmim][NTf₂], [Hmim][NTf₂], [Omim][NTf₂], [Bmim][PF₆], [Hmim][PF₆], [Bmpyr][NTf₂] and [Omim][BF₄] were synthesized according to the procedure described in literature (Huddleston, *et al.*, 2001).

The alkylation of 1-methylimidazole and N-methylpyrrolidine was performed as follows:

A 1-liter, two-necked, round-bottomed flask provided with a heating oil bath (heated by magnetic stirrer and hot plate), an internal thermocouple adapter, and a reflux condenser were utilized for the synthesizing of

ionic liquid as shown in Figure 1. The flask was charged with 81.0 g (\approx 1mole, formula weight =82.10 g/mole) of 1-methylimidazole, 100 mL of acetonitrile (CH₃CN) and 164.424 g (1.20 mole, 20% excess, formula weight =137.02 g/mole) of 1-bromobutane, and brought to a gentle reflux (75- 80°C internal temperature). The solution was heated under reflux for 72 hr and then cooled to room temperature. The following reaction took place:

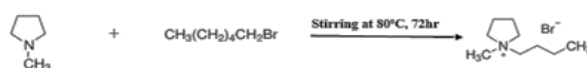


The volatile material was separated from the produced yellow solution under reduced pressure, and the drying step was consisted of two steps:

1. Drying by rotary vacuum evaporator (Figure 2): rotary evaporator is used to remove the large volumes of organic solvents. This procedure is usually used in removing organic solvents from ionic liquid products.
2. High vacuum lines: vacuum lines are used in laboratory, most often for the removal of residual solvents from previously prepared ionic liquids. There are two types of vacuum lines available, the double manifold vacuum line (shown in Figure 3), and the single manifold vacuum line which operates by the same general principle. The product, [Bmim][Br], is slightly yellow and may crystallize at room temperature, depending on the amount of water present in that phase.

The same procedure was used as indicated for [Bmim][Br] with the use of 1-bromohexane(formula weight =166.06 g/mole) instead of 1-bromobutane. 1-bromooctane (formula weight =193.12 g/mole) was used instead of 1-bromobutane to prepare [Omim][Br] and the produced [Omim][Br] was washed with diethyl ether (a volume approximately equal to half of [Omim][Br]). The diethyl ether was decanted followed by adding fresh diethyl ether and this step was repeated two times. Washing with diethyl ether should serve to separate any unreacted material from produced [Omim][Br]. After the third decanting of diethyl ether, any residual diethyl ether was separated by heating the bottom phase to 70°C and agitating while on a vacuum line. The product, [Omim][Br], is slightly yellow and could crystallize at room temperature, depending on the quantity of water existing in that phase.

For the synthesis of 1-butyl-1-methyl pyrrolidinium bromide [Bmpyr][Br], N-methylpyrrolidine (formula weight =85.15 g/mole) was used instead of 1-methylimidazole.



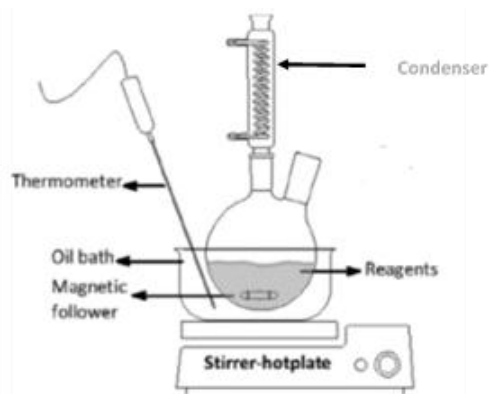


Fig.1 Synthesis arrangement for alkylation process of 1-methylimidazole

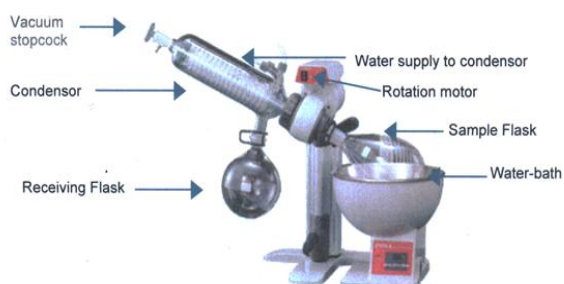


Fig. 2 Rotary vacuum dryer

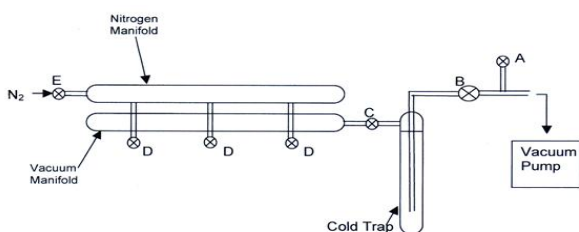
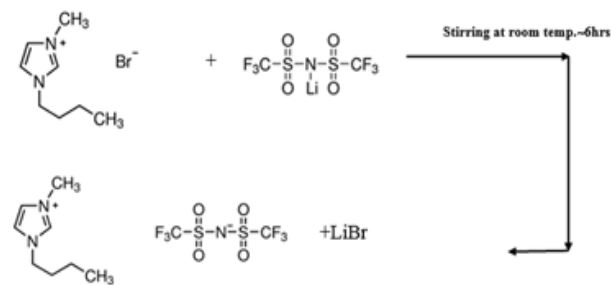


Fig. 3 High vacuum line. A, B, C, D and E are valves.

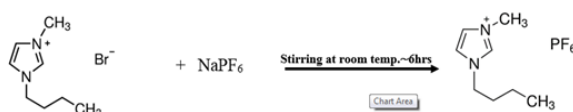
Anion Exchange

The anion of the bromide containing ionic liquids was exchanged according to literature (Shukla, *et al.*, 2011). [Bmim][NTf₂] was synthesised from 0.5 mole (109.56g) of [Bmim][Br] which was dissolved in 200 mL of distilled water followed by the slow adding of Bis(trifluoromethane) sulfonimide lithium salt (LiNTf₂) solution [0.55mole (10% excess mole), 157.89 g in 150 mL distilled water] with stirring at room temperature. After adding of LiNTf₂ solution in [Bmim][Br] solution, the colour of solution was altered to milky white and two layers were separated then the reaction mixture was agitated for 6 hrs. After mixing, two phases were formed, the bottom phase was [Bmim][NTf₂] and the top phase was aqueous lithium bromide (LiBr). The reaction mixture was then transported into a separation funnel and [Bmim][NTf₂] was separated with distilled water. After decanting the top phase, 200 mL of fresh distilled water was thoroughly mixed with the solution. This was repeated two times.



For the synthesis of [Hmim][NTf₂], [Omim][NTf₂], and [Bpyr][NTf₂] the same procedure was used as for [Bmim][NTf₂].

The above procedure reported for synthesis of [Bmim][NTf₂] was followed for synthesizing [Bmim][PF₆] also. Here instead of LiNTf₂, NaPF₆ was added to [Bmim][Br] solution.



For synthesizing [Omim][BF₄] NaBF₄ was added to [Omim][Br] solution instead of LiNTf₂.



Determination of distribution coefficient

The experiment was carried out at (21±1 °C). A 1000 ppm of 4-nitrophenol solution was prepared by dissolving theoretical amount of crystal phenol in distilled water. The mixture of extraction consists 2.0 mL of such a solution and 1.0 gram of pure ionic liquid. The stoppered glass was used as a container of contacting materials. The mixture of extraction was vigorously stirred for 30 min. An UV spectrophotometer (Perkin Elmer Lambda 950) was used to measure the concentrations of phenol at 317.6 nm. The concentration of phenol in organic phases can be determined by material balance. The distribution ratio (K_d) of the phenol between an organic phase and aqueous solutions was defined by Equation 1:

$$K_d = \frac{C_{IL}}{C_w} \quad (1)$$

Where C_{IL} and C_w refer to equilibrium concentration of the solute in organic phase and in aqueous phase, respectively.

Bulk ionic liquid membrane experiment:

A borosilicate glass cell with dimension of 12cm length, 6 cm width and 12 cm height was used to perform the experiments. The cell consists of two equal compartments; the partition wall was 0.2 cm thickness

at the middle of cell. This wall rises from the bottom by a distance of 8 cm in order to permit the transfer of 4-nitrophenol from one section to another. A volume of 80 mL of ionic liquid was weighed and transported into the cell above the bottom clearance. The phenol solution of 300 ppm concentration, represent feed phase, whilst, the NaOH solution of 0.5M concentration represent stripping phase. The volume of each phase was 200 mL. Figure 4 shows the arrangement of the cell and solutions.

The feed and stripping phases were agitated by mechanical stirrers with stainless steel propeller stirrer; 4-bladed of 3.5 cm diameter at 200 rpm. Whereas magnetic stirrer with a magnetic bar was used to agitate the membrane phase. Two samples of (1 ml) were taken from feed and stripping phase every 30 minutes for 5 h. A micropipette type Gilson, was used to take the samples. The obtained samples were scanned by UV-VIS spectrometer in order to compute the extraction and stripping efficiencies.

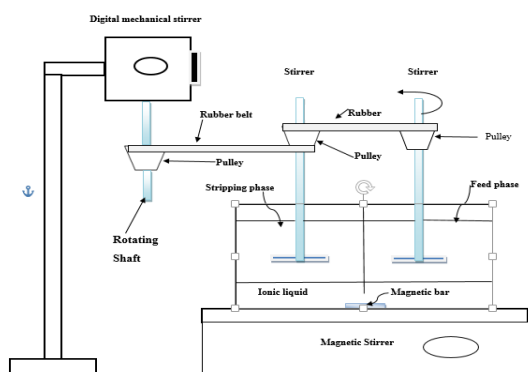


Fig.4 Figure 4: Extraction unit of 4-nitrophenol compounds

The performance of bulk liquid membrane is evaluated by computing the both extraction and stripping efficiencies. The concentration of phenolic compound in each phase were measured for this purpose. The calculation of extraction and stripping efficiencies were achieved by using Equations 2 and 3, respectively.

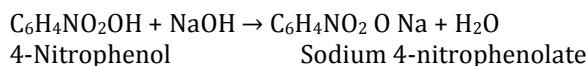
$$E\% = \frac{C_o - C_F}{C_o} \times 100 \quad (2)$$

$$S\% = \frac{C_S}{C_o - C_F} \times 100 \quad (3)$$

Where: E & S are extraction and stripping efficiency respectively, C_o is the Initial concentration of phenol in the feed in ppm, C_F is concentration of feed samples after extraction and C_S is 4-nitrophenol concentration in stripping samples after extraction.

Notes:

The amount of sodium phenolate which was measured in the stripping phase was converted to phenol according to mole balance:



3. Results and discussion

Distribution coefficient of synthesized ionic liquids:

Experimental data of distribution coefficients for 4-nitrophenol is listed in Table 2 as a function of pH of feed phase. As can be seen from this table, K_d values of the 4-nitrophenol are extremely high under the condition of pH smaller than 7, and then these values drops sharply for pH greater than 7. The characteristic of 4-nitrophenol change in different pH medium may causes this manner. The value of (pK_a) of 4-nitrophenol in water is 7.2. Analytical chemistry calculations indicated that in acidic medium, 4-nitrophenol occurred in molecular form (Laitinen & Harris, 1975). Whereas, the anionic portion increases with the increasing of pH of aqueous phase and reaches the half at pH equals the value of pK_a . For that reason, in acidic conditions it is suitable to consider the interactions among ionic liquid and molecules of the 4-nitrophenol are in charge of the high distribution coefficients. The molecular dynamic simulations confirmed that ionic liquids are powerfully dissolved by solvents which can form the hydrogen bonding. Basically the mechanism of dissolving including the formation of hydrogen bonds with the anions (Hanke, *et al.*, 2002). According to this result, the interactions of hydroxyl hydrogen of the 4-nitrophenol with hydrogen bonding of $[\text{PF}_6]^-$ or $[\text{BF}_4]^-$ will be predictable. A portion of these interactions diminished in the case of basic solution as result of the reduction of molecules of phenol. Finally a low distribution coefficients observed in the medium of basic solution.

As can be seen from Table 2, the distribution coefficients of 4-nitrophenol in the acidic medium obey the following order: $[\text{BF}_4]^- > [\text{NTf}_2]^- > [\text{PF}_6]^-$, and this arrangement is caused by the difference in strength of hydrogen bonding between $[\text{BF}_4]^-$, $[\text{NTf}_2]^-$ or $[\text{PF}_6]^-$ and the 4-nitrophenol. The calculation of chemical quantum (Tsunekawa, *et al.*, 2003) showed that effective negative charge of $[\text{BF}_4]^-$ is much stronger than both $[\text{NTf}_2]^-$ and $[\text{PF}_6]^-$. The hydrogen bonding among $[\text{BF}_4]^-$ and 4-nitrophenol is so stronger that this 4-nitrophenol possess an elevated distribution coefficient.

Table 2: Distribution coefficients of the 4-nitrophenol between ionic liquids and aqueous solution as a function of pH of aqueous phase (22 ± 1 °C)

	Ionic liquid	Distribution coefficient (K_d)		
		pH= 2.93	pH= 6.04	pH= 8.35
1	[Bmim][NTf ₂]	35.3	35.1	0.47
2	[Hmim][NTf ₂]	33.4	33.1	0.39

3	[Omim][NTf ₂]	30.2	30	0.35
4	[Bmim][PF ₆]	33.4	33	0.34
5	[Hmim][PF ₆]	32.2	31.9	0.45
6	[Bmpyr][NTf ₂]	29.5	29.1	0.43
7	[Omim][BF ₄]	158	-	-
8	Benzene	-	6.2	-
9	Cyclohexane	-	3.5	-
10	Dichloromethane	-	8.1	-

Tables 2 displays a comparison for the distribution coefficients of the 4-nitrophenol and conventional solvents such as benzene, cyclohexane and dichloromethane. In neutral medium, the distribution coefficients of the conventional solvent are much lower than those of ionic liquids. So, the ionic liquids possess many applications in separation processes of the phenols from waste water.

Depending on the results that have been obtained by measuring the distribution coefficient of different ionic liquids, the following ionic liquids were chosen as membrane solvents in this study: [Bmim][NTf₂], [Hmim][NTf₂], [Omim][NTf₂], [Bmim][PF₆], [Hmim][PF₆], [Bmpyr][NTf₂] and [Omim][BF₄]. These ionic liquids exhibit a powerful solvation and possess a high distribution coefficient. [Omim][BF₄] has the highest value of distribution coefficient: 158 at pH ≈ 2.93 for 4-nitrophenol. Unfortunately, [Omim][BF₄] was found to be unsuitable solvent in liquid membrane extraction, because it has a density close to the density of water (1.12 g/cm³), which makes [Omim][BF₄] mixed with aqueous solution at a slow rotation speed not exceeding 50 rpm.

Figure 5 shows that [Bmim][NTf₂] was the best ionic liquid because of its high extraction efficiency, this can be attributed to the high distribution coefficient compared with other ionic liquids as indicated in Table 2.

As can be seen from Figure 5, extraction efficiency of the ionic liquids follows the order: [Bmim][NTf₂] > [Hmim][NTf₂] > [Omim][NTf₂]; [Bmim][PF₆] > [Hmim][PF₆]. It can be concluded from these results that, the increasing of the length of alkyl chain on the cation of the ionic liquids, leads to the decreasing of extraction efficiency. In addition to, the efficiency values are elevated in the case of using [NTf₂]⁻ anion compared with that of [PF₆]⁻ anion. The current work is in agreement with the work done by Y.S. Ng (Ng, *et al.*, 2011), in that the hydrophobic behaviour of ionic liquids was not effective in the deciding the 4-nitrophenol extraction efficiency. Whilst, the work of Fan, *et al.*, 2008 confirmed that phenol extraction efficiency increased with the increasing of hydrophobic part in ionic liquid as result of increasing strength of hydrogen bond.

The results of present work can be clarified according to the Einstein-Stokes equation:

$$D = \frac{kT}{c\pi\eta r} \quad (4)$$

Where D is the diffusion coefficient, k is the Boltzmann's constant, T is absolute temperature, c is a constant (4 to 6), η is viscosity of liquid and r is effective hydrodynamic or Stokes radius. According to this equation, the diffusion coefficient (D) is inversely proportional to the viscosity of the liquid and the viscosity of ionic liquid increases with increasing chain length. For instance, the viscosity of [Bmim][NTf₂], [Hmim][NTf₂] and [Omim][NTf₂] are: 0.03144, 0.05964 and 0.09104 Pa.s at 20.2 °C respectively. The decreasing of diffusion coefficient caused a drop in the extraction efficiency which is mainly dependent on diffusion process.

On the other side of apparatus where stripping processes took place, Figure 6 indicated that the stripping process is done effectively by applying NaOH solution. Although a different values of stripping efficiencies were obtained, [Bmim][NTf₂] was possessed the greater efficiency compared with other ionic liquids. This result of possessing [Bmim][NTf₂] to the highest value of stripping efficiency was due to its lower viscosity compared with other ionic liquids. The viscosity of ionic liquid play a vital role in overriding stripping rate because of low viscosity membrane diminishes the membrane thickness.

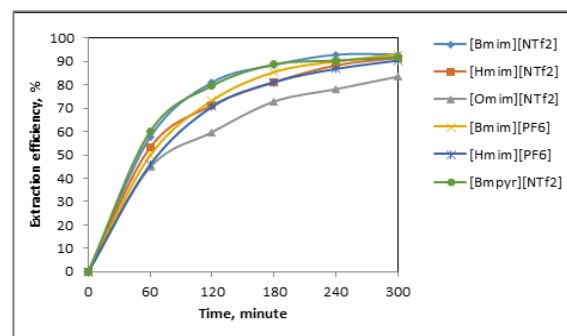


Fig.5 Extraction efficiency of 4-Nitrophenol by bulk ionic liquid membrane (Feed phase pH: ≈ 4.6; Feed concentration: 300 ppm; NaOH concentration: 0.5 M; Aqueous and membrane stirring speed=100 rpm; Temperature=22°C).

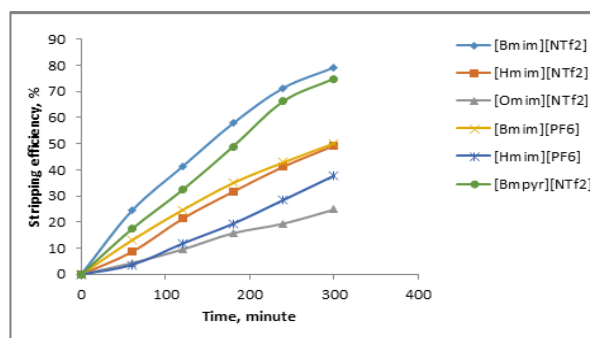


Fig.6 Stripping efficiency of 4-Nitrophenol by bulk ionic liquid membrane (Feed phase pH: ≈ 4.6; Feed concentration: 300 ppm; NaOH concentration: 0.5 M; Aqueous and membrane stirring speed=100 rpm; Temperature=22°C)

Factors affecting the performance of the best ionic liquid membrane ([Bmim][NTf2])

1. Aqueous stirring speed of feed phase and stripping phase

Figures 7 and 8 confirm that the increase of aqueous stirring speed from 75 to 125 rpm increases the extraction and stripping efficiency. Higher aqueous stirring speed results in increasing of extraction and stripping rate through supplying a better mixing and reducing the boundary layer thickness between the membrane phase and aqueous phase.

In the present work, the value of aqueous stirring speed (75-125 rpm) was lower than that used in other previous studies (100-300 rpm) such as (Ng, *et al.*, 2011) and (Lakshmi, *et al.*, 2013). In spite of this difference in rotation speed, the obtained extraction efficiencies were satisfactory.

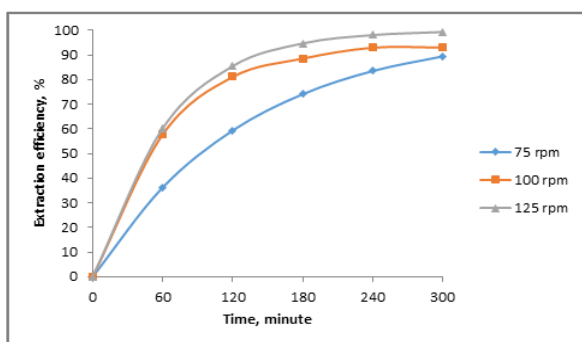


Fig.7 Effect of aqueous stirring speed on the extraction efficiency of 4-nitrophenol by bulk ionic liquid membrane (Feed phase pH: \approx 4.6; Feed concentration: 300 ppm; NaOH concentration: 0.5 M; Membrane stirring speed=100 rpm; Temperature=22°C).

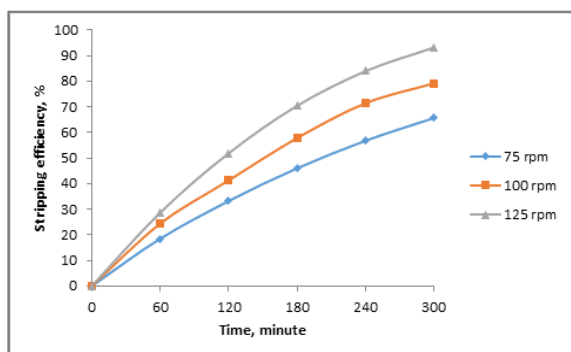


Fig.8 Effect of aqueous stirring speed on the stripping efficiency of 4-nitrophenol by bulk ionic liquid membrane (Feed phase pH: \approx 4.6; Feed concentration: 300 ppm; NaOH concentration: 0.5 M; Membrane stirring speed=100 rpm; Temperature=22°C).

2. Membrane stirring speed

Through Figure 9 and 10, it can be concluded that the speed of rotation of membrane affected the extraction and stripping efficiency of the membrane, but to a

lesser extent compared with the effect of variation of aqueous stirring speed. The existence of membrane stirring enhanced the performance of liquid membrane, while in the case of the absence of membrane agitation; it was found that the extraction and stripping efficiencies were affected significantly. However, this enhancement became lower as the membrane stirring speed was increased from 100 to 130 rpm, where the extraction and stripping efficiencies were very close.

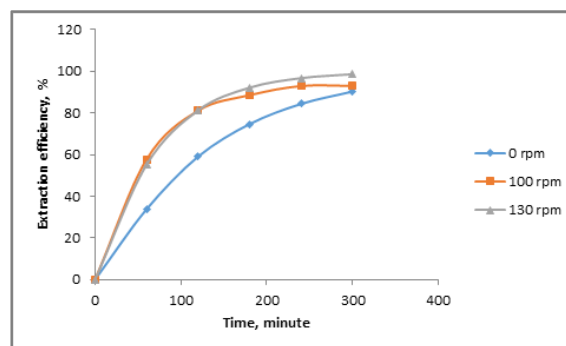


Fig.9 Effect of membrane stirring speed on the extraction efficiency of 4-nitrophenol by bulk ionic liquid membrane (Feed phase pH: \approx 4.6; Feed concentration: 300 ppm; NaOH concentration: 0.5 M; Aqueous stirring speed=100 rpm; Temperature=22°C).

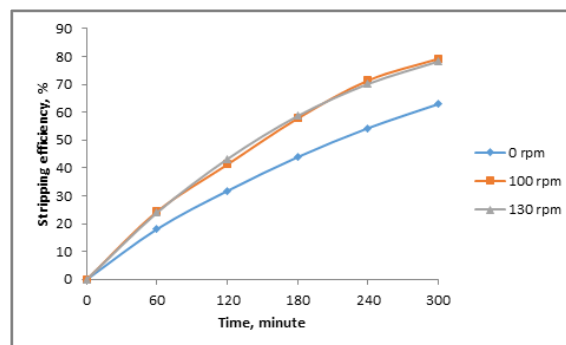


Fig.10 Effect of membrane stirring speed on the stripping efficiency of 4-nitrophenol by bulk ionic liquid membrane (Feed phase pH: \approx 4.6; Feed concentration: 300 ppm; NaOH concentration: 0.5 M; Aqueous stirring speed=100 rpm; Temperature=22°C).

3. Feed concentration

Figure 11 and 12 indicate that the feed concentration has less influence on the extraction efficiency. The final extraction efficiency remained approximately constant for all phenols as the feed concentration was increased from 100 to 1000 ppm. This may be resulted from the high dissolving capacity or high distribution coefficient of phenol in the ionic liquids. Furthermore, the simultaneous stripping process in liquid membrane system also prolonged the time required for membrane saturation.

A similar trend was observed for the stripping efficiency as the feed concentration was increased from 100 to 1000 ppm, and as shown in Figure 12. This manner can be attributed to that the stripping rate was fast enough at low feed concentrations (100-1000) to avoid the built-up of phenol concentration in the membrane-stripping interface due to the low available amount of phenol in the membrane phase. In the work of Lakshmi, *et al.*, 2013, higher feed concentration (2000-6000 ppm) was used. They observed higher stripping efficiency due to accumulation of phenol in membrane. With the aid of magnetic stirring in the membrane phase, significant amount of accumulated phenol in the membrane phase was distributed to a further distance in the stripping compartment. This eventually increased the effective contact area between membrane-stripping interface. Thus, the stripping rate and efficiency were increased as the feed concentration was increased from 2000 to 6000 ppm.

4. NaOH concentration

Figure 13 clarifies that the concentration of NaOH has small effect on the extraction efficiency of bulk ionic liquid membrane. Final extraction efficiency remained approximately unchanged for NaOH concentration range of 0 - 0.5 M. Figure 14 confirms that the variation of NaOH concentration had significant influence on the stripping efficiency of the system. When the concentration exceeded the value of 0.05, the extraction efficiency approximately remained the same. Hypothetically, after the diffusion process, phenol reacts with NaOH in the stripping phase to procedure 4-sodiumnitrophenolate, and the activity of molecular phenol in the stripping phase is repressed. In other words, the activity of unreacted molecular phenol delayed the stripping process by reducing the concentration gradient between the membrane and stripping phase under low NaOH concentration, thus dropping the stripping rate and efficiency. This is supported by the works of Lakshmi (Lakshmi, *et al.*, 2013), (Ng, *et al.*, 2011) and (Li, *et al.*, 2005).

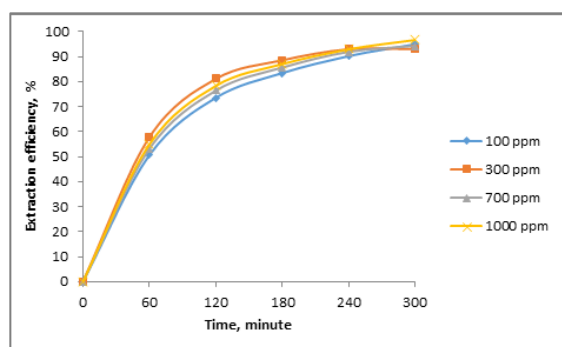


Fig.11: Extraction efficiency of 4-nitrophenol by bulk ionic liquid membrane at different feed concentrations (Feed phase pH: ≈ 4.6 ; NaOH concentration: 0.5 M; Aqueous and membrane stirring speed=100 rpm; Temperature=22°C).

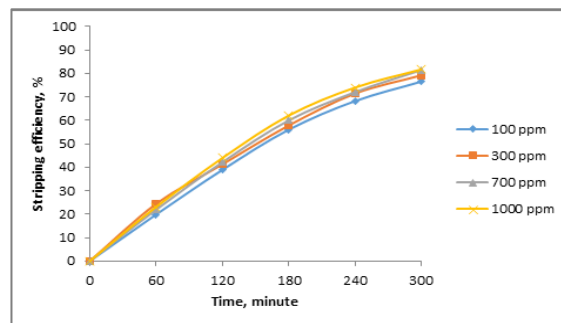


Fig.12 Stripping efficiency of 4-nitrophenol by bulk ionic liquid membrane at different feed concentrations (Feed phase pH: ≈ 4.6 ; NaOH concentration: 0.5 M; Aqueous and membrane stirring speed=100 rpm; Temperature=22°C).

5. Feed phase pH

Figure 15 shows that the extraction efficiency of 4-nitrophenol by [Bmim][NTf₂] based liquid membrane remains approximately constant when the feed phase pH is held below the value of pK_a. However, there was a drastic reduction in the extraction efficiency when pH of feed solution approached the value of pK_a or became greater than the value of pK_a. For example, the extraction efficiency of 4-nitrophenol remains approximately constant at 93% when the feed phase pH is held below 4.6 and becomes 65.76 and 3.20 % at pH equals 7.07 and 9.92 respectively. The results of the current study appear to be consistent with the work of Fan, *et al.*, 2008 and Khachatryan, *et al.*, 2005. The reduction in the efficiency of extraction of 4-nitrophenol is a consequence of the formation of hydrogen bonding between the molecular phenols with the anion of the ionic liquid. The weak bonding results in lowering the value of distribution coefficient (K_d), furthermore 4-nitrophenol that was used in the present work is a weak acid, and ionized as phenolate ion under high pH condition (\geq pK_a value). This fact of possessing 4-nitrophenol a lower distribution coefficient at high value pH leads to reduction of extraction efficiency of 4-nitrophenol.

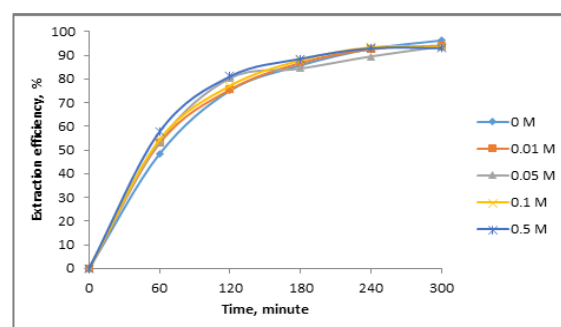


Fig.13 Extraction efficiency of 4-nitrophenol by bulk ionic liquid membrane at different NaOH concentrations (Feed phase pH: ≈ 4.6 ; Feed concentration: 300 ppm; Aqueous and membrane stirring speed=100 rpm; Temperature=22°C).

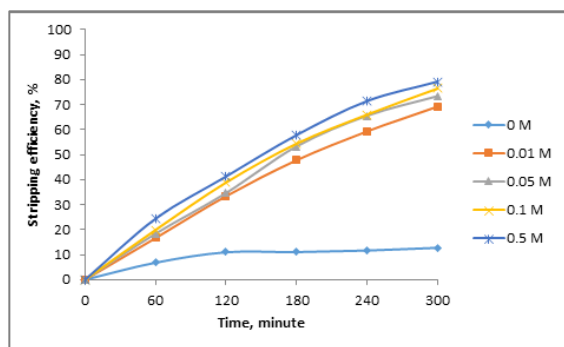


Fig.14 Stripping efficiency of 4-nitrophenol by bulk ionic liquid membrane at different NaOH concentrations (Feed phase pH: \approx 4.6; Feed concentration: 300 ppm; Aqueous and membrane stirring speed=100 rpm; Temperature=22°C).

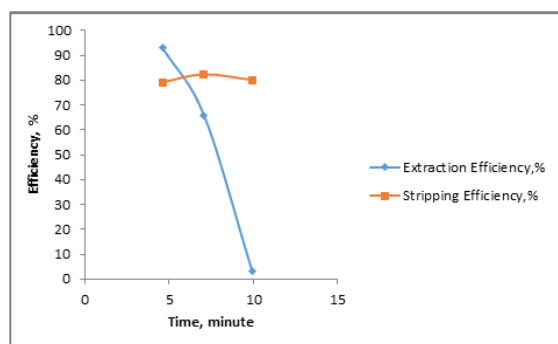


Fig.15 Effect of feed phase pH on the performance of bulk ionic liquid membrane of 4-nitrophenol (Feed concentration: 300 ppm; Aqueous and membrane stirring speed=100 rpm; Temperature=22°C)

Besides that, Figure 15 shows that the stripping efficiency is less affected by the feed phase pH, for example the stripping efficiency of 4-nitrophenol is recorded in the range of 79.188– 80.11 % for pH range of 4.6– 9.92. The low extraction efficiency for phenolate ion by [Bmim][NTf₂] guaranteed a stable one way transport process was achieved in high pH stripping phase, so that the stripping efficiency was not affected by increasing of pH value.

6. The ratio of feed solution to ionic liquid

In this study two ratios of feed solution to [Bmim][NTf₂] ionic liquid were used (200 ml feed: 80 ml ionic liquid and 400 ml feed: 80 ml ionic liquid).

Figure 16 and 17 display the effect of phase volume ratios on values of extraction and stripping efficiency. It can be seen that values of extraction and stripping efficiency decrease slightly with increasing phase volume ratio from 200 ml feed: 80 ml ionic liquid to 400 ml feed: 80 ml ionic liquid. This low reduction in both extraction and stripping efficiency due to the powerful solvation ability of ionic liquid when used as a solvent in liquid membrane. The same behaviour was observed by Fan, *et al.*, 2008, who extracted phenol from the aqueous solution by [C6mim][PF₆] and found

that the distribution coefficient of 4-nitrophenol changed slightly when the ratio of aqueous solution to ionic liquid increased from 1: 1 to 5: 1. Therefore, the extraction and stripping efficiency will not be affected because it mainly depends on the distribution coefficient

7. Temperature of extraction

To examine the effect of temperature on the extraction and stripping efficiency of the 4-nitrophenol, the extraction experiments of 4-nitrophenol by [Bmim][NTf₂] were carried out at 22, 30, 40 and 50 °C. Figures 18 and 19 show the temperature dependence of the extraction and stripping efficiency of the 4-nitrophenol and these efficiencies are enhanced with the increase in temperature. This enhancement in efficiencies can be interpreted by the improving of the diffusion of species which transported through liquid membrane, due to the reduction of the membrane viscosity. It was previously demonstrated that diffusion coefficient (D) is inversely proportional to the viscosity of the liquid and the increase of diffusion coefficient lead to rising of both extraction and stripping efficiencies which are mainly dependent on diffusion process.

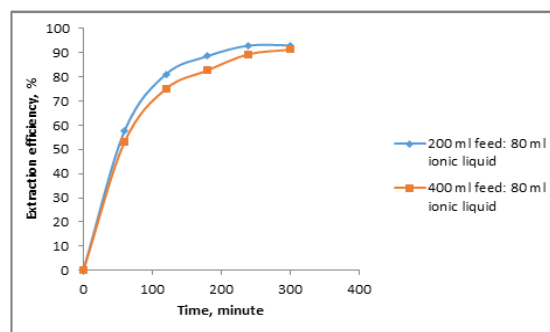


Fig.16 Extraction efficiency of 4-nitrophenol by bulk ionic liquid membrane at different phase volume ratios (Feed phase pH: \approx 6.5; Feed concentration: 300 ppm; NaOH concentration: 0.5 M; Aqueous and membrane stirring speed=100 rpm; Temperature=22°C).

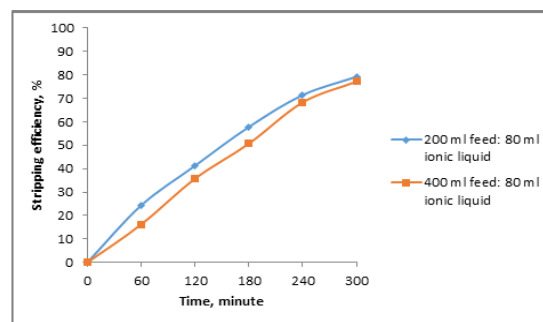


Fig.17 Stripping efficiency of 4-nitrophenol by bulk ionic liquid membrane at different phase volume ratios (Feed phase pH: \approx 6.5; Feed concentration: 300 ppm; NaOH concentration: 0.5 M; Aqueous and membrane stirring speed=100 rpm; Temperature=22°C).

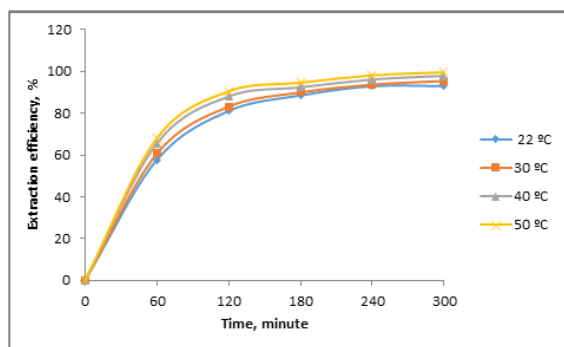


Fig.18 Extraction efficiency of phenol by bulk ionic liquid membrane at different temperatures (Feed phase pH: ≈ 4.6 ; Feed concentration: 300 ppm; NaOH concentration: 0.5 M; Aqueous and membrane stirring speed=100 rpm).

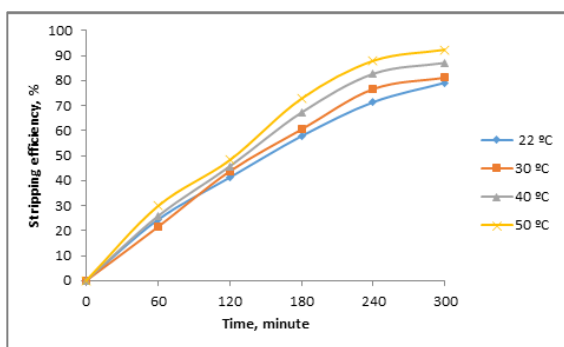


Fig.19 Stripping efficiency of 4-nitrophenol by bulk ionic liquid membrane at different temperatures (Feed phase pH: ≈ 4.6 ; Feed concentration: 300 ppm; NaOH concentration: 0.5 M; Aqueous and membrane stirring speed=100 rpm)

Conclusions

1. Through studying of the distribution ratios of 4-nitrophenol between ionic liquids and aqueous solution at different pH values, the results indicated that distribution ratios of 4-nitrophenol were highly affected by pH of aqueous phase and nature of ionic liquids. The results confirmed that ionic liquids have potential application in practical liquid-liquid extraction process of phenol from aqueous solution due to having higher distribution ratios compared with organic solvents.
2. Through experiments that were conducted to choose the best ionic liquid, The results showed that [Bmim][NTf₂] gave the greatest 4-nitrophenol extraction and stripping efficiencies compared to other used ionic liquid. Also, it was found that the hydrophobicity of the ionic liquids did not have significant effect on the results of extraction and stripping efficiencies.
3. The performance of the best ionic liquid ([Bmim][NTf₂]) as bulk liquid membrane was improved by increasing both aqueous and membrane stirring speeds. Extraction and stripping efficiencies

remained unaffected when feed concentration was increased from 100 to 1000 ppm.

4. The variation of NaOH concentration had no effect on the extraction efficiency of bulk ionic liquid membrane and on the contrary it had significant influence on the stripping efficiency.

5. The feed pH did not affect the extraction efficiency of 4-nitrophenol for pH less than pK_a . However, the extraction efficiency was reduced strongly when pH of feed solution $\geq pK_a$. In contrast, the stripping efficiency was not affected by increasing the pH value.

6. Both extraction and stripping efficiencies decreased slightly with increasing phase volume ratio from 200 ml feed: 80 ml ionic liquid to 400 ml feed: 80 ml ionic liquid.

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