



Emulsion stabilization using ionic liquid [BMIM]⁺[NTf₂]⁻ and performance evaluation on the extraction of chromium

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ABSTRACT

This study focuses on the role of a hydrophobic ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [BMIM]⁺[NTf₂]⁻ in the preparation of emulsion liquid membrane (ELM) phase containing kerosene as solvent, Span 80 as surfactant, NaOH as internal phase and TOMAC (tri-n-octylmethylammonium chloride) a second ionic liquid as carrier. The first time used [BMIM]⁺[NTf₂]⁻ in ELM was found to play the role of a stabilizer. The emulsion prepared using [BMIM]⁺[NTf₂]⁻ has a long period of stability of about 7 h (at 3% (w/w) of [BMIM]⁺[NTf₂]⁻) which otherwise has a brief stability up to only 7 min. The stability of the emulsion increases with the increase in concentration of [BMIM]⁺[NTf₂]⁻ up to 3% (w/w). Nevertheless, with further increase in concentration of [BMIM]⁺[NTf₂]⁻, a reduction in the stability occurs. The extraction experiments were carried out after holding the ELM for 2 h after the preparation and a removal efficiency of approximately 80% was obtained for Cr. The destabilization of the emulsion was studied by observing the change in the interface height. An empirical correlation for the stability of the emulsion has been proposed.

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1. Introduction

Liquid membrane technology is well known for its wide application in extraction processes to separate hydrocarbons [1–3], heavy metals [4–6], amino acids [7,8] and biological compounds [9,10]. The potential advantages of liquid membrane techniques are low capital and operating costs, low energy and extractant consumption, high concentration factors and high fluxes. This technology has an edge over solvent extraction because it requires less energy and operates in a single stage for extraction and stripping. The main types of liquid membrane systems include emulsion liquid membrane, supported liquid membrane and bulk liquid membrane. However, the liquid membrane techniques have not been adopted for large scale industrial processes primarily due to problems in maintaining its stability.

Emulsion liquid membrane (ELM) was invented by Li [11] to separate hydrocarbons and this technique has been utilized for many other applications such as metal extraction [5,6], wastewater treatment [6] and bio-medical separation [9].

Stability of emulsion is a major concern in the effective use of ELM either in laboratory scale or industrial scale. The resistance to rupture of liquid membrane at high shear stress defines the stability of the emulsion liquid membrane. Repeated coalescence of

the internal droplets on the interface, creaming due to density difference, Ostwald Ripening and flocculation cause the instability of the emulsion. Several techniques to overcome the stability problem have been proposed, and these include the use of aliphatic solvent instead of aromatic solvent [12], the increment of the carbon chain length of the aliphatic solvent [13], the increment of the surfactant concentration [14], the increment of membrane viscosity [13,15], the use of co-surfactants [16], non-Newtonian conversion of the membrane phase [17], the use of Janus particles as stabilizers in emulsion polymerization [18] and the use of functionalized silica particles for high internal phase emulsion [19]. All of the remedies have their own tradeoffs and compromises with the overall extraction efficiency.

Room temperature ionic liquids (RTILs) possess unique and exceptional properties such as negligible vapor pressure, inflammability, thermal stability even at high temperatures, highly polar yet non-coordinating solvent and application based adjustable miscibility/immiscibility in chemical processes [20–25]. These properties have made them potentially useful in a wide range of applications in industries as well as in research. Ionic liquids possess a very negligible vapor pressure that has enabled them to be used as a “green solvent” in synthesis [23,24,26–28], separation and purification [29–34], and electrochemical applications [35]. RTILs being stable and in the liquid form at room temperature, are made of organic cation and organic/inorganic anion. The physical and chemical properties of RTILs can be altered by changing the cation or anion or both to facilitate a particular task, hence they are

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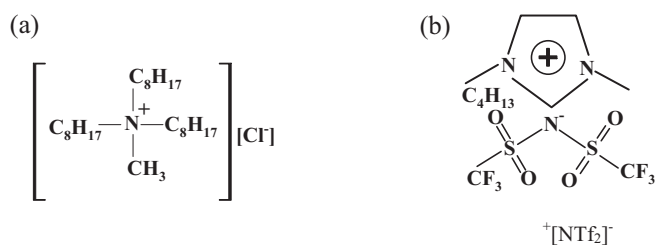


Fig. 1. Structures of TOMAC and [BMIM]⁺[NTf₂]⁻.

sometimes referred as “task specific” ionic liquids [24]. However, very few studies have been reported on the application of ionic liquids in emulsion liquid membrane. Hence, an effort to incorporate ionic liquids with emulsion liquid membrane has been made by investigating the stability and % removal efficiency of emulsion liquid membrane in the presence of ionic liquids. Chromium metal was selected to investigate the removal efficiency of emulsion liquid membrane.

The present study focuses on enhancing the stability of ELM, identification of the role of a hydrophobic ionic liquid [BMIM]⁺[NTf₂]⁻ in it and extraction efficiency of the ELM. Ionic liquid [BMIM]⁺[NTf₂]⁻ was chosen over other ionic liquids due to its hydrophobicity, minimum toxicity, relatively less viscosity and density.

2. Materials and methods

2.1. Chemicals

Ionic liquids [BMIM]⁺[NTf₂]⁻ and TOMAC, with structural formulae illustrated in Fig. 1, were directly obtained from Merck (Germany) and used without any further purification while kerosene of boiling point ranged from 180 °C to 280 °C was received from ACROS (USA). Span 80 (Sorbitan oleate or Sorbitan (Z)-mono-9-octadecenoate) a non-ionic surfactant with a ratio of 4:3 of hydrophilic to lipophilic (HLB), was purchased from Merck (Malaysia). Sodium hydroxide pellets, potassium dichromate and hydrochloric acid were procured from R&M Chemicals (UK). The solution of sodium hydroxide of desired normality was prepared by dissolving appropriate weight of pellets in de-ionized water. Similarly, Cr solution of 500 mg/L was prepared by mixing suitable amount of potassium dichromate in de-ionized water. The prepared Cr solution was diluted with de-ionized water according to the required concentration.

2.2. Analytical instruments

An ICP-spectrophotometer (Perkin Elmer, model: Optima 7000 DV) was used for the measurement of the Cr concentration. The emulsion was prepared using a high speed homogenizer (IKA, model: T25 digital Ultra Turrax) and the dispersion of the emulsion in the feed phase was carried out by a stirrer (IKA, model: RW11 Lab Egg). pH values were measured using a CyberScan 510 pH meter while photographs were taken using a digital camera (NIKON, model: DSLR D3000). Surface tension was measured by a tensiometer (Fisher Scientific, model: Tensiomat 21[®]) using a Pt/Ir Du Noüy ring.

2.3. Procedure

2.3.1. Preparation of emulsion and stability analysis

The emulsion was prepared in a 100 mL un baffled beaker by mixing organic solvent and an appropriate amount of non ionic surfactant Span 80. Subsequently, the carrier and ionic liquid (sta-

Table 1
Physical and thermodynamic properties of [BMIM]⁺[NTf₂]⁻ [36].

Property	Temperature (°C)	Value
Density (g/ml)	25	1.43
Viscosity (cP)	25	52
Surface tension (dyne/cm) (Water equilibrated ^a)	25	36.8
Thermal decomposition temperature (°C) (Water equilibrated ^a)		394
Water content (mg/l) (Water equilibrated ^a)	25	3280
Melting point (°C) (Dried ^b)		4

^a Water equilibrated denotes that [BMIM]⁺[NTf₂]⁻ was kept in contact with water.

^b Dried stands for water equilibrated [BMIM]⁺[NTf₂]⁻ that was dried at 70 °C for 4 h on a vacuum line.

bilizer) were added to the mixture. The mixture was homogenized for up to 5 min by the homogenizer at 8400 rpm. NaOH was added drop-wise into the mixture, keeping the whole mixture homogenized for the next 5 min. The ratio of internal to organic phase (I/O) was kept at 1:3 for all the experiments. The surfactant concentration (Span 80) (wherever applicable) was kept 3% (w/w) which is an optimized concentration in order to avoid swelling and to provide sufficient stability. Photographs of the beaker containing the emulsion were taken at regular intervals to analyze its stability. The photographs were analyzed by AUTOCAD to determine the phase separation rate of the emulsion.

2.3.2. Extraction of chromium

The prepared emulsion was poured into another 250 mL beaker containing the Cr solution of 100 mg/L. The ratio of emulsion to feed phase (E/F) was kept at 1:2 for all the extraction experiments. The pH of the feed phase was maintained below 1.5 to establish a pH difference between the internal and external phases, hence maintaining a driving force for Cr to diffuse through the membrane. The whole mixture was gently stirred by a mechanical stirrer, and an agitation speed of 300 rpm was found to be the best to generate fine globules of emulsion with lowest possible breakage. Samples were taken at a regular interval using disposable syringes and the syringes were kept left undisturbed for some time until the emulsion and the feed phase were separated. The feed phase was then taken out, filtered and analyzed using ICP-spectrophotometer.

3. Results and discussion

Physico-chemical properties of this ionic liquid are as shown in Table 1.

3.1. Identification of the role of [BMIM]⁺[NTf₂]⁻ in emulsion without TOMAC

As the first stage of this study, the role of ionic liquid [BMIM]⁺[NTf₂]⁻ is conjectured to behave as one of the following: either as a carrier, surfactant, solvent or stabilizer. In order to substantiate its role, the following experiments were conducted and discussed below.

3.1.1. Consideration of [BMIM]⁺[NTf₂]⁻ as a carrier

In order to identify the role of [BMIM]⁺[NTf₂]⁻ as a carrier, emulsion was prepared by taking kerosene as solvent, Span 80 as surfactant, NaOH (0.1 N) as internal phase and varying amount

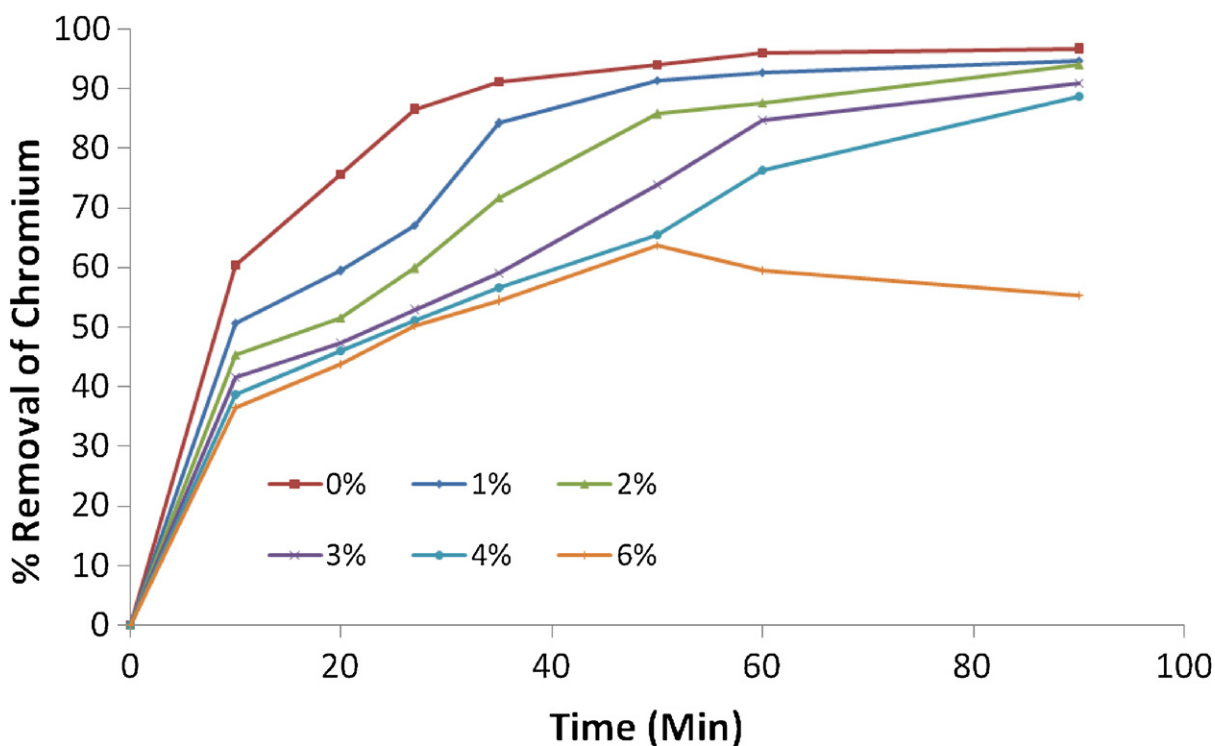


Fig. 2. % removal of Cr with time as a function of $[\text{BMIM}]^+[\text{NTf}_2]^-$ concentration (% w/w) of Cr without any TOMAC. Span 80 = 3% (w/w); I/O = 1:3. Emulsion to feed phase ratio was taken at 1:2.

of $[\text{BMIM}]^+[\text{NTf}_2]^-$. I/O ratio was maintained at 1/3 and Span 80 concentration was kept at the value of 3% (w/w). The initial Cr concentration in the feed phase was 100 mg/L and the pH of the feed was maintained below 1.5. The effect of ionic liquid on the percentage removal of Cr in an emulsion liquid membrane is, as shown in Fig. 2.

Generally, the role of a carrier in emulsion liquid membrane extraction is to enhance the final removal and to increase the rate of extraction. In the absence of TOMAC (carrier), Cr extraction is facilitated by type-I mechanism if $[\text{BMIM}]^+[\text{NTf}_2]^-$ cannot play the role of a carrier. If the ionic liquid was presumed to act as a carrier in the emulsion, then the final % removal of Cr and the rate of % removal of Cr should have increased with the increase in the ionic liquid concentration. On the contrary, an insignificant decrease in the final removal and a significant decrease in the rate of removal can be seen upon increasing the concentration of $[\text{BMIM}]^+[\text{NTf}_2]^-$ from 0 to 2% (w/w), as shown in Fig. 2. Moreover, both the parameters keep on decreasing with the increase in the concentration of ionic liquid up to the value of 4% (w/w). This indicates that the $[\text{BMIM}]^+[\text{NTf}_2]^-$ is not involved in making complex and transporting the metal from the feed phase to the internal phase. Hence, it's a type-I facilitation where no carrier is present.

The decrease in the % removal of chromium with an increase in concentration of $[\text{BMIM}]^+[\text{NTf}_2]^-$ can be explained as the increased mass transfer resistance caused by $[\text{BMIM}]^+[\text{NTf}_2]^-$ during the time of extraction and stripping. It was believed that the diffusion of Cr was hindered by the big size of $[\text{BMIM}]^+[\text{NTf}_2]^-$. Electrostatic and Van der waal's attraction also slowed down the transport of Cr. A sudden decrease in the % extraction of chromium was observed at 6% (w/w) of $[\text{BMIM}]^+[\text{NTf}_2]^-$ after 50 min. This discrepancy can be explained by the aggregated sedimenting tendency of $[\text{BMIM}]^+[\text{NTf}_2]^-$ due to its high density after a long time and at higher concentration of the ionic liquid. From these observations and facts, it can be concluded that $[\text{BMIM}]^+[\text{NTf}_2]^-$ cannot act as a carrier for this operation.

3.1.2. Consideration of $[\text{BMIM}]^+[\text{NTf}_2]^-$ as a surfactant

The role of a surfactant in ELM is to minimize the interfacial energy (interfacial tension) between the organic and the aqueous phase. There is no literature available regarding the use of $[\text{BMIM}]^+[\text{NTf}_2]^-$ as a surfactant, so is for their HLB number. $[\text{BMIM}]^+$ has the properties that can make this ionic liquid to act as a surfactant. Interfacial tension of kerosene and NaOH interface and CMC (Critical Micelle Concentration) of $[\text{BMIM}]^+[\text{NTf}_2]^-$ were experimentally determined.

Emulsion preparation with kerosene as solvent, NaOH as internal reagent and $[\text{BMIM}]^+[\text{NTf}_2]^-$ as surfactant (assumed) was also tried out to check the feasibility of $[\text{BMIM}]^+[\text{NTf}_2]^-$ acting as a surfactant. $[\text{BMIM}]^+[\text{NTf}_2]^-$ is a hydrophobic ionic liquid. It has a density more than kerosene and NaOH. Several combinations of the concentration of organic phase (kerosene); aqueous phase (NaOH) and $[\text{BMIM}]^+[\text{NTf}_2]^-$ were tested. No emulsion was yielded even if the mixture was homogenized at 15,000 rpm. The concentration of $[\text{BMIM}]^+[\text{NTf}_2]^-$ was also varied from in the range of 0.40–7% (w/w) for all of the above combinations of phases but no emulsion was observed.

The failure of micelle formation of $[\text{BMIM}]^+[\text{NTf}_2]^-$ in kerosene can be explained by two possible reasons [37]. The first is the small hydrocarbon tail (butyl) attached to the cationic group of $[\text{BMIM}]^+[\text{NTf}_2]^-$ that does not interact well enough with the kerosene hydrocarbon chain to yield the micelles of the ionic liquids. The other reason that may be attributed is the big size of $[\text{NTf}_2]^-$ anion which is hard to fit the micelle surface region (Stern Layer). Therefore, it can be concluded that $[\text{BMIM}]^+$, the cationic part of $[\text{BMIM}]^+[\text{NTf}_2]^-$ does not behave as a surfactant for the above mentioned solvent and the internal phase.

3.1.3. Consideration of $[\text{BMIM}]^+[\text{NTf}_2]^-$ as a solvent

Ionic liquids have been proved to be the solvents of future, primarily based on their unique properties over organic solvents. In order to verify the feasibility of ionic liquid $[\text{BMIM}]^+[\text{NTf}_2]^-$ as a

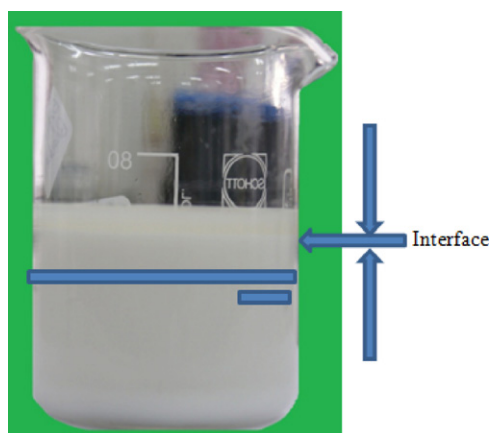


Fig. 3. Emulsion prepared with 3% (w/w) Span 80, TOMAC=0.29% (w/w); [BMIM]⁺[NTf₂]⁻ = 0% (w/w) (after 7 min); scale bar = 1 cm.

solvent for emulsion liquid membrane the emulsion was prepared using [BMIM]⁺[NTf₂]⁻ as a solvent, Span 80 as a surfactant and NaOH as the receiving phase while keeping the proportions of each component the same as it was prepared with kerosene as a solvent in the previous sections.

The concentrations and volumes of [BMIM]⁺[NTf₂]⁻, Span 80 and NaOH and homogenizing speed and time were varied in order to get a stabilized membrane but the stability lasted only for 5 min with the best composition. The density difference between [BMIM]⁺[NTf₂]⁻ and NaOH solution is higher than the difference between kerosene and NaOH therefore, proclivity of sedimenting of the former emulsion is much higher than the latter. Hence, emulsion formed with [BMIM]⁺[NTf₂]⁻ as solvent lasted only for a short duration. The adsorbed amount of Span 80 on the surface of [BMIM]⁺[NTf₂]⁻ was found to be very small and hence interfacial tension was not too reduced to make fine internal droplets of NaOH. The formation of small droplets of Span 80 took place on the surface of ionic liquid upon increasing the Span 80 concentration above 0.3% (w/w). Hence, another reason for the reduced stability may be explained as the insufficient reduction in the interfacial tension of the solvent by Span 80. From the above discussion, it could be concluded that [BMIM]⁺[NTf₂]⁻ cannot be used as a solvent for the above mentioned surfactant and the internal phase to make a stable emulsion liquid membrane.

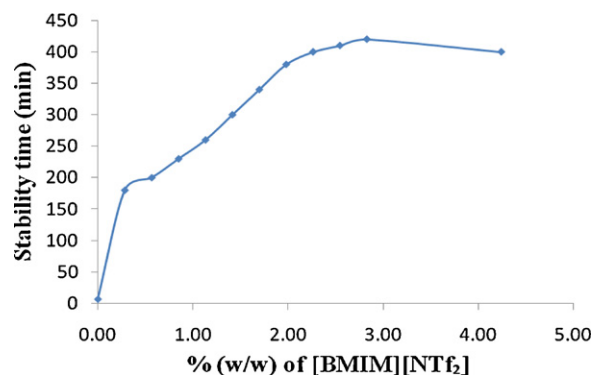


Fig. 5. The effect of the concentration of [BMIM]⁺[NTf₂]⁻ on the stability time of ELM. Span 80 = 3% (w/w); TOMAC = 0.29% (w/w), I/O = 1/3.

3.1.4. [BMIM]⁺[NTf₂]⁻ as a stabilizer when TOMAC is used as a carrier

TOMAC is a very good phase transfer catalyst which is relatively less expensive, easily available and less toxic. Hence, TOMAC was selected as a carrier to study the effect of ionic liquid ([BMIM]⁺[NTf₂]⁻) on the stability of emulsion and subsequent removal efficiency of the same.

The problem with TOMAC when it is used as a carrier in the emulsion liquid membrane with no concentration of [BMIM]⁺[NTf₂]⁻, stability lasted only for 7 min, as shown in Fig. 3 which is not sufficient for the extraction to take place and for subsequent demulsification. From Fig. 4(a), it can be observed clearly that the emulsion was stable for up to 7 h when 3% (w/w) of the ionic liquid [BMIM]⁺[NTf₂]⁻ is added. On the other hand, Fig. 4(b) depicts the separated organic and aqueous phases after 5 h when there is no concentration of [BMIM]⁺[NTf₂]⁻ present in the emulsion. In fact, the phase separation started only after 7 min without [BMIM]⁺[NTf₂]⁻ in the emulsion.

The stability time with the varying concentration of [BMIM]⁺[NTf₂]⁻ is, as shown in Fig. 5. The stability time increases with an increase in the concentration of [BMIM]⁺[NTf₂]⁻ for up to 3% (w/w) of [BMIM]⁺[NTf₂]⁻. After 3% (w/w) of [BMIM]⁺[NTf₂]⁻ onwards, the stability time decreased which consolidated the fact that the [BMIM]⁺[NTf₂]⁻ helped to stabilize the emulsion liquid membrane when it was present up to a certain maximum concentration. If the emulsion liquid membrane contained more than this concentration then emulsion sedimentation took place due to the higher density of ionic liquid. Each experiment was

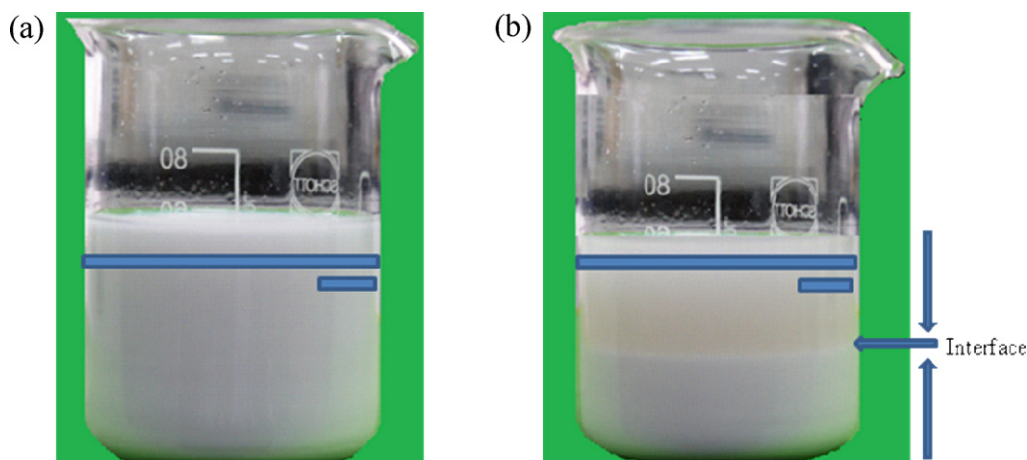


Fig. 4. (a) Emulsion prepared with [BMIM]⁺[NTf₂]⁻ = 3% (w/w); TOMAC = 0.29% (w/w) (after 7 h), (b) Emulsion prepared with [BMIM]⁺[NTf₂]⁻ = 0% (w/w); TOMAC = 0.29% (w/w) (after 5 h); scale bar = 1 cm.

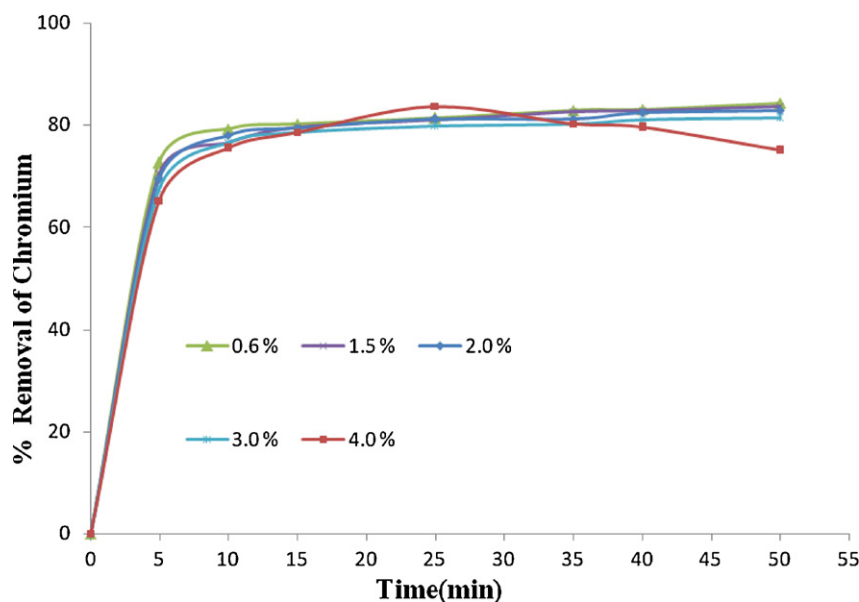


Fig. 6. % removal of Cr with time as a function of $[BMIM]^+[NTf_2]^-$ concentration (% w/w) with TOMAC. TOMAC = 0.29% (w/w); Span 80 = 3% (w/w); I/O = 1:3; E/F = 1:2.

conducted twice and the results for the stability time were reproducible with minor difference between two corresponding values.

The increased stability of the emulsion liquid membrane by addition of $[BMIM]^+[NTf_2]^-$ may be explained by Coulombic interactions of the charges on the ions of ionic liquids $[BMIM]^+[NTf_2]^-$ and TOMAC. The other interactions present in the emulsion are between other chemical complex groups such as Span 80 and TOMAC; TOMAC and NaOH; $[BMIM]^+[NTf_2]^-$ and NaOH. These strong interactions help to avoid the coalescence of the internal droplets but they also cause the hindrance to Cr–TOMAC complex diffusion through the membrane.

Apart from strong interactions between ions, there is a possibility of hydrogen bonding present between $[BMIM]^+[NTf_2]^-$ and $[OH]^-$ group of NaOH. The hydrogen bonding may cause a strong protection surrounding the internal droplets to avoid coalescence. $[BMIM]^+[NTf_2]^-$ is capable of developing a polymeric structure with large cavities [38] when it is used for different kinds of reactions. These polymeric structures of ionic liquid may also help to understand the cause for the enhanced stability. The polymeric structure of ionic liquid $[BMIM]^+[NTf_2]^-$ may behave like polymeric surfactant of the A–B, A–B–A or $(BA)_n$ graft type to generate a repulsive barrier to prevent the collapse of the emulsion liquid membrane.

3.1.5. The removal efficiency of the emulsion liquid membrane stabilized by ionic liquid $[BMIM]^+[NTf_2]^-$ with TOMAC

The prepared emulsion was kept for 2 h to verify its stability then it was poured into an un baffled beaker containing Cr feed phase. The emulsion was prepared with varied concentration of $[BMIM]^+[NTf_2]^-$. The samples were taken at regular intervals.

The effect of ionic liquid $[BMIM]^+[NTf_2]^-$ on the removal efficiency of the emulsion liquid membrane having TOMAC as a carrier is, as shown in Fig. 6. TOMAC concentration was kept at a constant value of 0.29% (w/w) for all the experiments. On the contrary, the percentage removal of the emulsion liquid membrane prepared with TOMAC and $[BMIM]^+[NTf_2]^-$ decreases due to the hindrance caused by both of the compounds. From Fig. 6, the time taken for 70% of the removal of chromium is only 5 min.

3.1.6. Effect of $[BMIM]^+[NTf_2]^-$ concentration on phase separation rate of the stabilized emulsion

The emulsion was prepared by taking kerosene as solvent, Span 80 as surfactant, NaOH (0.1 N) as internal phase, TOMAC as carrier and varying amount of $[BMIM]^+[NTf_2]^-$. I/O ratio was maintained at 1/3 and Span 80 concentration was kept 3% (w/w). TOMAC concentration was kept at a constant value of 0.29% (w/w). The stabilized membranes started to separate into organic and aqueous phases after their maximum time of stability which is dependent on the concentration of $[BMIM]^+[NTf_2]^-$. Creaming and coalescence are the main causes for emulsion sedimentation for the current composition of emulsion. The sedimentation of the emulsion due to Ostwald ripening is insignificant, since aqueous NaOH and kerosene are almost insoluble in each other.

The stabilized membrane was held for the next 3 h after it started to destabilize to analyze the stability with respect to the concentration of $[BMIM]^+[NTf_2]^-$. The calculation of the phase separation was done by noting the height of the interface from the bottom of the beaker at a regular interval. The normalized height of the emulsion is a ratio of the height of the interface from the ground level and the total height of the emulsion. Therefore, it's a dimensionless quantity. The stabilized membrane stability time and their phase separation with respect to time are shown in Fig. 7. It can be observed from Fig. 7 that an increment in the concentration of $[BMIM]^+[NTf_2]^-$ to 3% (w/w) increases the final (after 3 h) interface height of the destabilized emulsion. It implies that the sedimentation rate decreases upon increasing the concentration of $[BMIM]^+[NTf_2]^-$ up to 3% (w/w). The decreased sedimentation rate may be explained by the effective electrostatic interactions between the two ionic liquids, $[BMIM]^+[NTf_2]^-$ and TOMAC, over the density of ionic liquids and NaOH. Fig. 7 illustrates that an increment in the concentration of $[BMIM]^+[NTf_2]^-$ above 3% (w/w) decreases the interface height of the destabilized emulsion. It means that the sedimentation rate of the destabilized emulsion increases upon increasing the concentration of $[BMIM]^+[NTf_2]^-$ above 3% (w/w). The increased sedimentation could be understood by the dominance of the density of $[BMIM]^+[NTf_2]^-$ and NaOH over electrostatic interactions between ionic liquids $[BMIM]^+[NTf_2]^-$ and TOMAC. However, the complete phase separation of the stabilized membrane into its original phases took place only after 2–3 days.

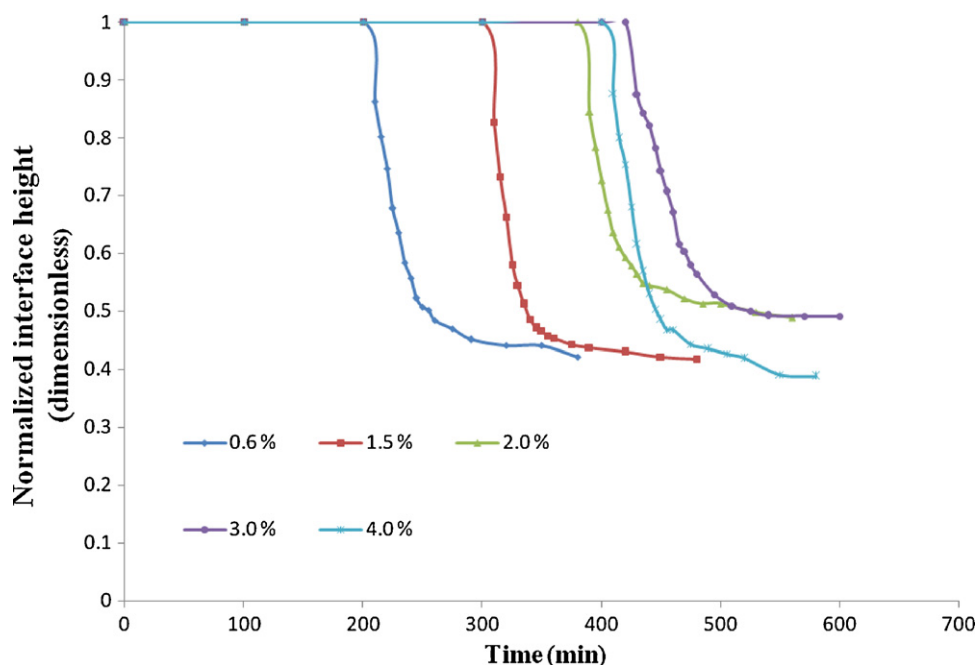


Fig. 7. The effect of ionic liquid concentration (% w/w) [BMIM]⁺[NTf₂]⁻ on the phase separation of the stabilized membrane. TOMAC=0.29% (w/w); Span 80=3% (w/w); I/O=1:3.

The experimental data of stability time and initial rate of sedimentation of the emulsion prepared with TOMAC=0.29% (w/w); Span 80=3% (w/w); I/O=1:3 has been given in Table 2.

The stability time of the emulsion as a function of [BMIM]⁺[NTf₂]⁻ concentration (% w/w) (x_1) and initial rate of sedimentation (x_2) is correlated to be as

$$t_{s, \text{pred}} = ax_1^b + x_2^c + 7 \quad (1)$$

where a , b and c are parameters.

The term 7 min in the above correlation takes care of stabilized time when concentration of [BMIM]⁺[NTf₂]⁻ is equal to zero in emulsion liquid membrane containing TOMAC as carrier, NaOH as stripping phase and kerosene as solvent. The parameters are estimated using data in Table 1, by nonlinear parameter estimation scheme with the help of MATLAB 7.0.4 software and the predicted stabilized time relationship is given as

$$t_{s, \text{pred}} = 1446.6x_1^{0.54549}x_2^{0.38057} + 7 \quad (2)$$

The stability time of the emulsion is dependent more on the concentration of [BMIM]⁺[NTf₂]⁻ than the initial rate of sedimentation of the emulsion, as observed from Eq. (2). The comparison between the predicted values and experimental values has been reported in Table 3. The low values of deviations as summarized in Table 3 imply the accuracy of the correlation.

The predicted and experimental stabilized times are in good agreement within $\pm 9\%$ deviation as shown in Fig. 8. However, the

Table 2

Experimental data on stabilized time with ionic liquid concentration [BMIM]⁺[NTf₂]⁻ and initial rate of sedimentation height with TOMAC=0.29% (w/w); Span 80=3% (w/w); I/O=1:3.

Concentration of [BMIM] ⁺ [NTf ₂] ⁻ (w/w)	Initial rate of sedimentation time (min ⁻¹)	Experimental stability (min)
0.6	0.0150	220
1.5	0.0120	330
2.0	0.0100	400
3.0	0.0086	425
4.0	0.0067	465

Table 3

Comparison between experimental stability time and predicted and stability time.

Concentration of [BMIM] ⁺ [NTf ₂] ⁻	$t_{s, \text{exp}}$ (min)	$t_{s, \text{pred}}$ (min)	% deviation
0.6	220	221.4	0.6
1.5	330	335.3	1.6
2.0	400	365.9	8.5
3.0	425	430.5	1.3
4.0	465	457.7	1.5

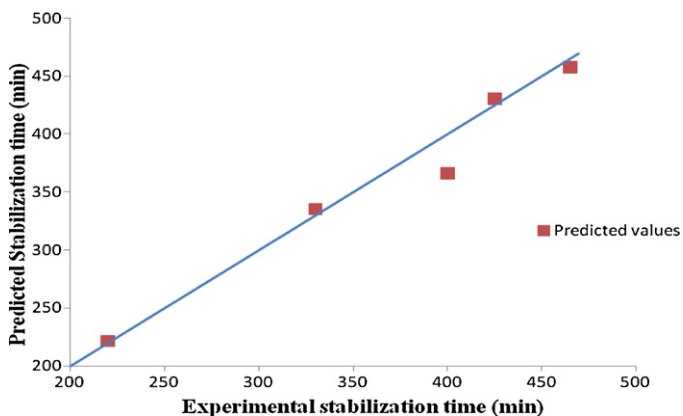


Fig. 8. Experimental stability time versus predicted stability time.

correlation is only applicable for lower range of the ionic liquid concentrations. It does not hold the accuracy for the higher concentrations of ionic liquid [BMIM]⁺[NTf₂]⁻.

4. Conclusion

The present work focuses on the stability aspects of emulsion liquid membrane and in this context, the experimental investigation identifies the use of hydrophobic ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [BMIM]⁺[NTf₂]⁻ as a stabilizer with the preparation of the emul-

sion liquid membrane containing TOMAC as a carrier. The enhanced stability of the emulsion liquid membrane caused by the addition of $[\text{BMIM}]^+[\text{NTf}_2]^-$ could be explained by the strong interactions such as coulombic, dipolar and ionic interactions among the ionic liquids and NaOH. It was observed that the stability of the emulsion liquid membrane could be enhanced for a duration of up to 7 h. Experiments had proved that the stability of the emulsion liquid membrane can be enhanced for a duration of up to 7 h. 80% removal of chromium could be achieved even after keeping the emulsion for 2 h before the extraction experiments were carried out. The sedimentation rate of the stabilized membrane for the next 3 h after its maximum stability time was found to be decreasing with the increase in concentration of $[\text{BMIM}]^+[\text{NTf}_2]^-$ up to 3% (w/w). It starts to increase with further increase in the concentration of $[\text{BMIM}]^+[\text{NTf}_2]^-$. An empirical correlation relating stability time of emulsion as a function of $[\text{BMIM}]^+[\text{NTf}_2]^-$ concentration (% w/w) and initial rate of sedimentation of the emulsion is proposed and the predicted stability times are in good agreement with the experimental stability times. Ultimately, this paper reflects the potential use of “task specific” ionic liquids as a stabilizer in the field of emulsion liquid membrane.

List of symbols

a, b, c	constant
E/F	emulsion to feed phase ratio
I/O	internal to organic phase ratio
$t_{s, \text{exp}}$	experimental stability time of the emulsion (min)
$t_{s, \text{pred}}$	predicted stability time of the emulsion (min)
x_1	concentration of $[\text{BMIM}]^+[\text{NTf}_2]^-$ (% w/w)
x_2	initial rate of sedimentation of the emulsion (min^{-1})

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References

- [1] C.M. Das, G. Rungta, S.D. Arya, S. De, Removal of dyes and their mixtures from aqueous solution using liquid emulsion membrane, *J. Hazard. Mater.* 159 (2008) 365–371.
- [2] C.C. Lin, R.L. Long, Removal of nitric acid by emulsion liquid membrane: experimental results and model prediction, *J. Membr. Sci.* 134 (1997) 33–45.
- [3] P. Venkateswaran, K. Palanivelu, Recovery of phenol from aqueous solution by supported liquid membrane using vegetable oils as liquid membrane, *J. Hazard. Mater.* 131 (2006) 146–152.
- [4] S. Chowta, P.K. Mohapatra, B.S. Tomar, K.M. Michael, A. Dakshinamoorthy, V.K. Manchanda, Recovery of americium(III) from low acid solutions using an emulsion liquid membrane containing PC-88A as the carrier extractant, *Desalination Water Treat.* 12 (2009) 62–67.
- [5] R.A. Kumbasar, I. Sahin, Separation and concentration of cobalt from ammoniacal solutions containing cobalt and nickel by emulsion liquid membranes using 5,7-dibromo-8-hydroxyquinoline (DBHQ), *J. Membr. Sci.* 325 (2008) 712–718.
- [6] H.R. Mortaheb, H. Kosuge, B. Mokhtarani, M.H. Amini, H.R. Banihashemi, Study on removal of cadmium from wastewater by emulsion liquid membrane, *J. Hazard. Mater.* 165 (2009) 630–636.
- [7] H. Itoh, M.P. Thien, T.A. Hatton, D.I.C. Wang, Water transport mechanism in liquid emulsion membrane process for the separation of amino acids, *J. Membr. Sci.* 51 (1990) 309–322.
- [8] M. Matsumoto, T. Ohtake, M. Hirata, T. Hano, Extraction rates of amino acids by an emulsion liquid membrane with tri-*n*-octylmethylammonium chloride, *J. Chem. Technol. Biotechnol.* 73 (1998) 237–242.
- [9] T. Kaghazchi, A. Kargari, R. Yegani, A. Zare, Emulsion liquid membrane pertraction of L-lysine from dilute aqueous solutions by D2EHPA mobile carrier, *Desalination* 190 (2006) 161–171.
- [10] J.-Q. Shen, W.-P. Yin, Y.-X. Zhao, L.-J. Yu, Extraction of alanine using emulsion liquid membranes featuring a cationic carrier, *J. Membr. Sci.* 120 (1996) 45–53.
- [11] N.N. Li, Separating Hydrocarbons with Liquid Membranes, U.S. Patent 3,410,794 (1968).
- [12] F. Nakashio, M. Goto, M. Matsumoto, J. Irie, K. Kondo, Role of surfactants in the behavior of emulsion liquid membranes—development of new surfactants, *J. Membr. Sci.* 38 (1988) 249–260.
- [13] T. Kinugasa, K. Watanabe, H. Takeuchi, Effect of organic solvents on stability of liquid surfactant membranes, *J. Chem. Eng. Japan* 22 (1989) 593–597.
- [14] E.C. Hsu, N.N. Li, Membrane recovery in liquid membrane separation processes, *Sep. Sci. Technol.* 20 (2–3) (1985) 115–130.
- [15] R.E. Terry, N.N. Li, W.S. Ho, Extraction of phenolic compounds and organic acids by liquid membranes, *J. Membr. Sci.* 10 (1982) 305–323.
- [16] Y.S. Mok, K.H. Lee, W.K. Lee, Control of swelling in liquid emulsion membranes employed for lactic acid separation, *J. Chem. Tech. Biotechnol.* 65 (1996) 309–316.
- [17] A.H.P. Skelland, X. Meng, Non-Newtonian conversion solves problems of stability, permeability, and swelling in emulsion liquid membranes, *J. Membr. Sci.* 158 (1999) 1–15.
- [18] H.E. Muller, A. Walther, M. Hoffmann, Emulsion polymerization using janus particles as stabilizers, *Angew. Chem. Int. Ed.* 47 (2008) 711–714.
- [19] A. Bismarck, V.O. Ikem, A. Menner, High internal phase emulsions stabilized solely by functionalized silica particles, *Angew. Chem. Int. Ed.* 47 (2008) 8277–8279.
- [20] J.D. Holbrey, K.R. Seddon, Ionic liquids, *Clean Prod. Processes* 1 (1999) 223–237.
- [21] M.J. Earle, K.R. Seddon, Ionic liquids. Green solvents for the future, *Pure Appl. Chem.* 72 (7) (2000) 1391–1398.
- [22] K. Mikami, *Green Reaction Media in Organic Synthesis*, first ed., Blackwell, UK, 2005.
- [23] T. Welton, Room-temperature ionic liquids. Solvents for synthesis and catalysis, *Chem. Rev.* 99 (1999) 2071–2083.
- [24] P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Second ed., WILEY-VCH, Weinheim, 2008.
- [25] M. Freemantle, New horizons for ionic liquids, *Chem. Eng. News* 79 (2001) 21–25.
- [26] C.J. Adam, M.J. Earle, G. Robert, K.R. Seddon, Friedel–Crafts reactions in room temperature ionic liquids, *Chem. Commun.* 19 (1998) 2097–2098.
- [27] P.J. Dyson, D.J. Ellis, D.C. Parker, T. Welton, Arene hydrogenation in a room-temperature ionic liquid using a ruthenium cluster catalyst, *Chem. Commun.* 1 (1999) 25–26.
- [28] C.E. Song, E.J. Roh, Practical method to recycle a chiral (salen) Mn epoxidation catalyst by using an ionic liquid, *Chem. Commun.* 10 (2000) 837–838.
- [29] A.E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J.H. Davis Jr., R.D. Rogers, Task-specific ionic liquids for the extraction of metal ions from aqueous solutions, *Chem. Commun.* 1 (2001) 135–136.
- [30] A.P. de los Rios, F.J. Hernandez-Fernandez, L.J. Lozano, S.S. Sanchez, J.I. Moreno, C. Godínez, Removal of metal ions from aqueous solutions by extraction with ionic liquids, *J. Chem. Eng. Data* 55 (2010) 605–608.
- [31] A.E. Visser, R.P. Swatloski, W.M. Reichert, S.T. Griffin, R.D. Rogers, Traditional extractants in nontraditional solvents: group 1 and 2 extraction by crown ethers in room-temperature ionic liquids, *Ind. Eng. Chem. Res.* 39 (10) (2000) 3596–3604.
- [32] S. Dai, Y.H. Ju, C.E. Barnes, Solvent extraction of strontium nitrate by a crown ether using room temperature ionic liquids, *J. Chem. Soc. Dalton Trans.* (1999) 1201–1202.
- [33] L.C. Branco, J.G. Crespo, C.A.M. Afonso, High selective transport of organic compounds by using supported liquid membranes based on ionic liquids, *Angew. Chem. Int. Ed.* 41 (2002) 2771–2773.
- [34] A.G. Fadeev, M.M. Meagher, Opportunities for ionic liquids in recovery of bio-fuels, *Chem. Commun.* 3 (2001) 295–296.
- [35] I.W. Sun, C.L. Hussey, Electrochemistry of niobium chloride and oxide chloride complexes in the basic aluminum chloride-1-methyl-3-ethylimidazolium chloride room-temperature ionic liquid, *Inorg. Chem.* 28 (1989) 2731–2737.
- [36] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation, *Green Chem.* 3 (2001) 156–164.
- [37] M. Blesic, M.H. Marques, N.V. Plechkova, K.R. Seddon, L.P.N. Rebelo, A. Lopes, Self-aggregation of ionic liquids: micelle formation in aqueous solution, *Green Chem.* 9 (2007) 481–490.
- [38] H. Weingrtnr, Understanding ionic liquids at the molecular level: facts, problems, and controversies, *Angew. Chem. Int. Ed.* 47 (2008) 654–670.