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Emulsion liquid membrane pertraction of benzimidazole using a room temperature ionic liquid (RTIL) carrier

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ABSTRACT

Room temperature ionic liquids are emerging as alternative solvents which replace the conventional volatile organic solvents. The solvent extraction/liquid membrane process requires substantial amount of solvent as well as stripping of solute from the solvent. In order to reduce the solvent requirement, emulsion liquid membrane technique is proposed for the benzimidazole separation from aqueous solutions using tri-*n*-octyl methyl ammonium chloride ionic liquid carrier. The distribution coefficient of benzimidazole between aqueous solution and ionic liquid in membrane phase was studied to optimize the external phase pH. Effects of emulsification time, speed of emulsification, internal phase reagent concentration, extractant (carrier) concentration, volume ratio of organic phase to aqueous internal phase and concentration of surfactant (span-80) on the membrane stability as well as contact time, stirring speed, feed concentration, external phase pH and volume ratio of the emulsion to the external phase on the pertraction were studied. The organic phase consists of kerosene and *n*-heptane as diluent. At optimized conditions, the emulsion was stable up to 140 min, the breakage of internal phase was <0.5 and 97.5% of benzimidazole was extracted within 12 min with a concentration factor of 5. It was found that benzimidazole concentration in external phase increased due to membrane breakage after 12 min.

1. Introduction

Benzimidazole is a heterocyclic aromatic organic compound. This bicyclic compound consists of the fusion of benzene and imidazole. The structure is shown in Fig. 1. One of the most common methods of synthesis of benzimidazole is that cyclization of the *o*-arylenediamines in which one of the amino groups has been acylated or thioacylated. The starting material is functionalized such a way that an aromatic product can be formed when cyclization takes place. The simplest method of synthesis of 1-H benzimidazole involves condensation of trimethylorthoformate and *o*-phenylenediamine [1,2] in aqueous or aqueous–alcohol mixture at ambient conditions.

$$C_6H_4(NH_2)_2 + HC(OCH_3)_3 \leftrightarrow C_6H_4N(NH)CH + 3CH_3OH \quad (1)$$

Benzimidazole is produced commercially as pesticide and fungicide. Benzimidazole fungicide is extracted using acetone from a variety of fruit and vegetables followed by solid phase extraction (SPE) clean-up of the extracts on two OH bonded sorbents. Co-extracted waxes were removed by careful selection of solvents for reconstitution. As the waxes are insoluble in methanol, the solvent can be used to redissolve an SPE eluate after evaporation from the resultant precipitation of the waxes.

In the present investigation, emulsion liquid membrane was investigated for benzimidazole separation. There were no literatures on emulsion liquid membranes (ELM) pertraction of benzimidazole from dilute aqueous solutions. The objective of this work is to develop a suitable emulsion for the separation and concentration of benzimidazole from dilute aqueous solutions using an ionic liquid as carrier and experiments were carried out to assess the breakage of membrane.

The surfactant span-80 (sorbition monooleate) was used as emulsifying agent for preparation of emulsion. It is a non-ionic surfactant with hydrophobic lypophilic balance (HLB) value of 4.2 and it is suitable for preparation of W/O (water dispersed in oil) emulsion. It provides relatively stable emulsion and easy to de-emulsify the emulsion produced by span-80. It shows less mass transfer resistance compared to many other surfactants like span-20, span-40, span-60 and ECA 4360 (non-ionic polyamine surfactant).

The major steps for separation and purification of benzimidazole are extraction, stripping followed by distillation, drying and crystallization [3]. But the cost involved in the separation of very low quantity of from aqueous solutions is in the order of 50–60% of the total production cost. In recent years, ELM have been widely used to study the ion transport against its concentration gradient by the coupled transport mechanism (up-hill transport). The ion

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Nomenclature

TOMAC	tri-*n*-octyl methyl ammonium chloride
A	symbol for benzimidazole
A_a^-	benzimidazole anion
B	membrane breakage (dimensionless, %)
C	concentration of benzimidazole in aqueous external phase (g/l)
C_t	concentration of tracer (M)
Cl_a^-	chloride ion
D	distribution coefficient (dimensionless)
K	equilibrium constant
M	molarity (g moles/l)
M/E ratio	membrane to external phase volume ratio
QCl_o	carrier with chloride ion
QA_o	carrier with benzimidazole anion complex
V_{aq}	volume of external phase (l)
V_{int}	volume of internal phase (l)

Subscripts

aq	aqueous phase
eq	equilibrium
f	final
int	internal phase
i	initial
org	organic phase

Superscripts

0	at time $t = 0$

transport through an ELM plays an important role in separation and purification because of high transport efficiency, excellent selectivity and economic advantage. A number of successful research works have been carried out involving the transport of precious metal ions [4–8], drugs [9–13], phenols [14–16], fructose [17–19], the treatment of seawater [20], wastewater [21–24] and amino acids [25] through the ELM technique.

Ionic liquids as green solvents have been extensively studied and found that ionic liquids have great potential as solvents with novel functions such as metal extractants as well as replacements for volatile organic solvents [26] for separation processes. However, using a large amount of ionic liquids as solvents in liquid–liquid extraction systems is highly expensive when compared with conventional organic solvents. But, emulsion liquid membrane uses relatively very small amount of ionic liquids as carrier for extraction. Recently Soto et al. [27] studied the distribution of ampicillin and amoxillin between ionic liquid and water and reported that the extraction was influenced by the pH of the solution and the chemical structure of the antibiotics.

The RTIL carrier tri-*n*-octyl methyl ammonium chloride (TOMAC) was used for extraction of benzimidazole. The chemical formula for TOMAC is $(C_8H_{17})_3CH_3N^+Cl^-$. Few studies were reported using TOMAC as a carrier for separation of amino acids [28,29] and extensive study on recovery of metal ions from effluents was reported.

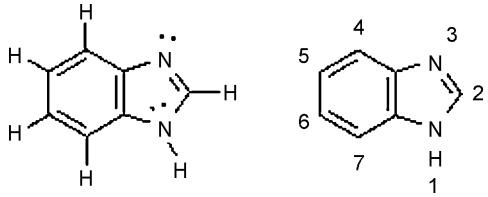

Fig. 1. Structure of benzimidazole.

2. Transport mechanism

In coupled transport mechanism, the carrier complexes with the solute in the external phase-membrane phase interface and exchanges with stripping agent in internal phase interface. The chloride ion present in the TOMAC carrier used to complex the solute. The reaction of dissociated benzmidazole anion (A_a^-) and the carrier (QCl_o) in organic solvent is shown in the following equation:

$$[A_a^-]_{aq} + [QCl_o]_{org} \leftrightarrow [QA_o]_{org} + [Cl_a^-]_{aq} \quad (2)$$

The equilibrium constant of the reversible complexation reaction is shown in the following equation:

$$K = \frac{[QA_o]_{org}[Cl_a^-]_{aq}}{[QCl_o]_{org}[A_a^-]_{aq}} \quad (3)$$

Benzimidazole in aqueous solution exists in an ionic form of different charges depending on the pH of the solution. Benzimidazole is both a moderately weak acid ($pK_a = 5.53$) and a moderately weak base ($pK_a = 11.70$) [30].

When pH of the benzimidazole feed solution is maintained below 5.53, the nitrogen indicated by 3 as shown in Fig. 1 is protonated and becomes cationic form. When pH is maintained above 11.70, the nitrogen marked by 1 as shown in Fig. 1 is deprotonated and becomes anionic form. Hence in the pH range of 5.53–11.7, benzimidazole exists predominantly in neutral form. In this present study, investigation was done to optimize the pH of external phase to get maximum distribution coefficient of benzimidazole between organic-aqueous phase.

The mechanism of the coupled transport may be represented by the scheme shown in Fig. 2 which indicates the transport of benzimidazole anion from feed (external) solution to the receiving (internal) solution facilitated by the carrier in the membrane phase. At the external–membrane phase interface, the carrier binds with benzimidazole anion (A_a^-) to form a complex, QA_o, which is extracted by the membrane. The complex is then transported due to concentration gradient to the membrane-internal phase interface, due to low pH, another interfacial ion-exchange reaction takes place thereby releasing the benzimidazole ion into the internal receiving phase. The carrier returns to the external–membrane phase interface to recombine with benzimidazole anion, the transport being accompanied by counter transport of Cl^- ion. The pH condition of the receiving phase may influence the transport by providing buffer anion of appreciable concentration. In fact, the pH gradient can also provide the driving force for the liquid membrane transport especially under the condition of small Cl^- ion concentration in the receiving phase.

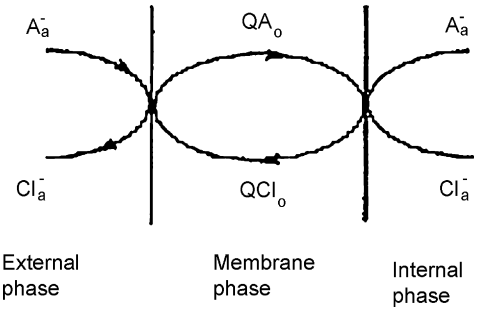

Fig. 2. Schematic diagram of the transport benzimidazole.

3. Materials and methods

3.1. Reagents and solutions

TOMAC was used as an extractant obtained from Sigma. This extractant was dissolved in *n*-heptane–kerosene mixture as a diluent. Kerosene and *n*-heptane were obtained from Fluka Chemika and benzimidazole was obtained from Merck (M). An aqueous solution of HCl (0.1, 0.2, 0.3, 0.4 and 0.5 M) was used as stripping agent. The extractant, diluent and strip agents used were of analytical grade. The external phase (feed) was prepared using benzimidazole at different concentrations of 300 ppm, 450 ppm, 600 ppm and 750 ppm. The organic chemicals for analytical purposes used were of analytical reagents grade and the water used was distilled. To maintain pH in the external phase, acetic acid–acetate buffer was used. To maintain pH of external phase, phosphate buffer was used.

3.2. Emulsion liquid membrane preparation

During the formulation of emulsion liquid membrane, the organic or membrane phase was prepared by dissolving the required concentrations of carrier and surfactant with appropriate diluent. The ELM used in this study was water–oil–water (W/O/W) type of emulsion and formed by mixing organic and aqueous internal phase of HCl solution in the volume ratio of 1:1 Initially, organic or membrane phase which comprised of surfactant, carrier and diluent was stirred at 10,000 rpm for 5 min in a high-speed homogenizer to form a uniform mixture. Then the internal phase was added dropwise and again stirred at about 10,000 rpm for 6 min to form a stable milky white emulsion.

3.3. Apparatus

All the experiments were performed at a constant temperature of $30 \pm 0.5\,^{\circ}C$ using a water bath equipped with a temperature controller and an agitator. Extraction experiments were carried out in a cylindrical glass container of 76 mm diameter and 110 mm height. It was charged with the desired ratio of emulsion to external phase (M/E) and stirred well at a particular speed for 20 min. During the contact between aqueous solution and emulsion, solute transport occurred through the membrane phase into the internal phase by coupled transport mechanism. The schematic layout of the ELM extraction process and experimental setup are shown in Figs. 3 and 4. Samples were taken at predetermined time intervals by disposable sanitary syringes and centrifuged in order to separate the emulsion phase from the external phase. External phase benzimidazole concentration was found by UV-visible spectrophotometer (JASCO) in aqueous solutions at concentrations as low as 1.5 ppm with a precision of ±2%. pH measurements were carried out by combined electrode pH meter. After each experiment, emulsion was broken using 25 kHz Ultrasonic Processor (SONOZAP model 4180, Sonaer Inc., USA) and benzimidazole concentration in internal phase was measured. The images of the emulsion were captured using digital colour CCD camera (SANYO VCC 6572P) from magnified samples in high-resolution microscope (magnification power of 1500). The captured emulsion images were analyzed using Bio-Vis software (Expert Vision Labs (P) Ltd., Mumbai) and the sizes of the emulsion drop and internal droplets were measured.

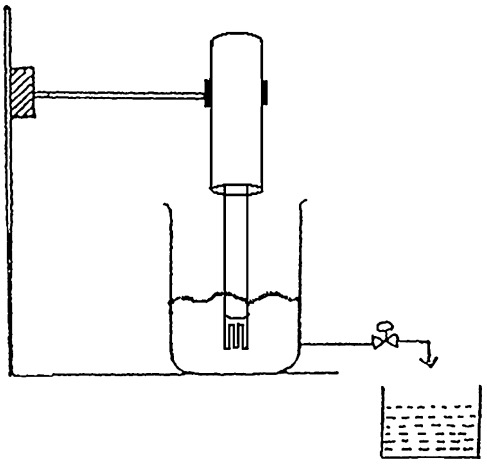

Fig. 4. Experimental setup.

3.4. Extraction equilibrium studies

Experiments to study the effect of pH on distribution coefficient of benzimidazole between organic phase to aqueous phase were conducted using constant temperature rotary shaker. 50 ml of aqueous phase with benzimidazole concentration of 600 ppm and 50 ml of organic phase with 0.5% (v/v) TOMAC were taken in conical flask and agitated for 3 h in the shaker. After reaching equilibrium, the phases were separated and distribution coefficient between membrane and external phase was calculated using the following equation [31]:

$$D = \frac{[QA_o]_{eq} V_{org}}{[A_a^-]_{eq} V_{aq}} \quad (4)$$

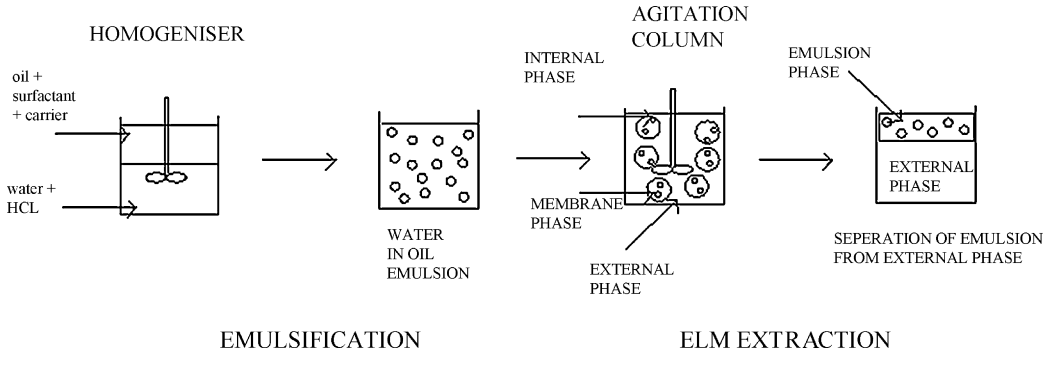

Fig. 3. Schematic diagram of ELM extraction process.

$[QA_o]_{eq}$ was estimated from the following equation:

$$[QA_o]_{eq} V_{org} = V_{aq}\{[A_a^-]_{t=0} - [A_a^-]_{eq}\} \quad (5)$$

3.5. Emulsion breakage study

Emulsion swelling and breakage are undesirable phenomena which are to be minimized for better stability of emulsion. There are two types of emulsion swelling: (1) entrainment swelling and (2) osmotic swelling. Entrainment swelling is caused by the entrainment of the external phase into the internal phase due to the repeated coalescence and re-dispersion of emulsion globules during the dispersion operation, thus always causing an increase in the volume of the internal phase. Entrainment swelling is caused by agitation which is normally neglected because of ELM extractions are carried out at mild agitations only. Osmotic swelling is driven by difference in the osmotic pressure between the external and internal phases. In most ELM systems, osmotic swelling causes an increase in volume of the internal phase because the ionic strength in the internal phase is greater than that in the external phase, leading to the transport of water from the external phase to the internal phase. To avoid osmotic swelling, the pH difference should be kept low between internal and external phase. During the ELM extraction process, the carrier counter transports the solute from external phase to internal phase and Cl^- ions from internal phase to external phase. This leads to change in pH of both internal and external phases. Ultimately the pH difference will be closer. In the present investigation, membrane breakage is predominant than swelling for ELM extraction. In the determination of the membrane breakage, many different methods are employed such as the volume variation method [32,33], internal phase droplet size variation method [34–36], viscosity variation method [37], density variation method [38], tracer method [39] and Carl–Fisher method [40]. In the present study, tracer method was used for measuring the membrane breakage. In this method, tracer was selected based on the previous studies [41]. KCl solution of known concentration was taken as tracer in internal phase of emulsion.

Emulsion breakage experiment was conducted using equal volume of emulsion and distilled water with optimum pH value (distribution coefficient was maximum at optimum pH). The emulsion and distilled water were agitated for 2 h. External phase was separated from emulsion using separating funnel and the concentration of tracer in external phase was measured. The breakage ratio was found by using the following equation:

$$B(\%) = \frac{V_{aq} C_{t,aq}}{V_{int}^0 C_{t,int}^0} \times 100 \quad (6)$$

where V_{aq} and $C_{t,aq}$ are volumes of external phase and tracer concentration in the external phase after mixing operation. While, V_{int}^0, $C_{t,int}^0$ are initial volume of internal phase and initial concentration of tracer in the internal phase.

3.6. De-emulsification of emulsion

After each ELM extraction experiment, the loaded emulsion was broken using 25 kHz Ultrasonic Processor (SONOZAP model 4180, Sonaer Inc., USA) into internal phase and organic phase. The concentrated internal phase was further purified to get final product. Benzimidazole concentration in internal phase was measured using JASCO UV-vis spectrophotometer. The released organic phase containing the extractant (TOMAC), surfactant (span-80) and diluent (kerosene and *n*-heptane) was reused to prepare fresh emulsion for subsequent ELM extraction experiments.

4. Results and discussion

4.1. Emulsion stability

When the W/O emulsion is dispersed by stirring in the continuous aqueous solution, the emulsion must be sufficiently stable in order to extract the solute ions into the internal aqueous droplets. In ELMs, emulsion globules are stabilized by surfactants and the degree of extraction for a given solute ion into an internal phase is influenced by the stability of emulsions. In this present investigation, the effects of various parameters such as emulsification speed, surfactant concentration, carrier concentration, emulsification time, HCl concentration in internal phase and volume ratio of organic phase to aqueous internal phase (O/A) for preparing stable emulsion were studied in detail and optimum conditions for maximum stability were established. Breakage was also found and the results of above studies were reported and discussed below.

4.1.1. Effect of surfactant concentration

Surfactant plays a vital role in maintaining the stability of emulsion. The amount of surfactant was varied from 1% (v/v) to 5% (v/v) and the results are shown in Fig. 5. It indicates that the increase in amount of surfactant up to 4% (v/v) increased the stability time up to 135 min and further increase in surfactant amount decreased the stability time. As the surfactant amount was increased, interfacial tension between the phases decreased which favours the formation of more fine droplets which produces more stable emulsion. Most of the surfactants tend to form aggregates in bulk of the solution above a particular concentration which is called as critical micelles concentration (CMC). The surfactant aggregates acts as reservoir for water and it promotes transport of water to external phase or internal phase (swelling or breakage) and ultimately it leads to affect the stability of emulsion [42,43].

4.1.2. Effect of emulsification time

The effect of emulsification time on emulsion stability is shown in Fig. 6. Emulsification time was varied from 2 to 10 min. It indicates that the increase in emulsification time up to 6 min increased the stability of emulsion up to 135 min and further increase in time decreased the stability. For insufficient emulsification time (<6 min), the breakage is high because the droplets have larger size, which leads easier coalescence. In contrast, for longer emulsification time, the breakage was increased due to high internal shearing

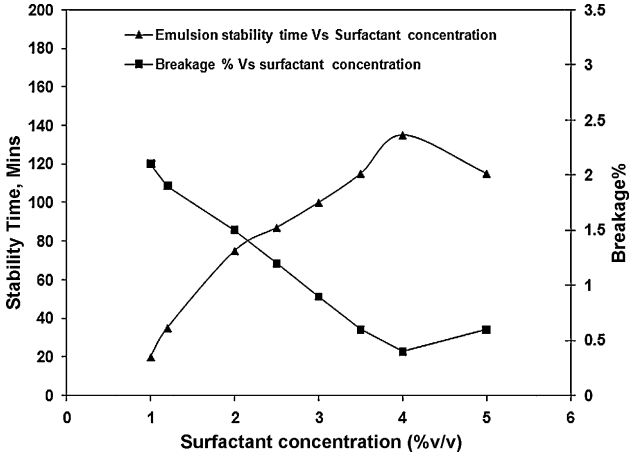

Fig. 5. Effect of surfactant concentration on emulsion stability and emulsion breakage (emulsification time = 6 min, carrier = 0%, emulsification speed = 10,000 rpm, HCl concentration in internal phase = 0.5 M, and O/A ratio = 1).

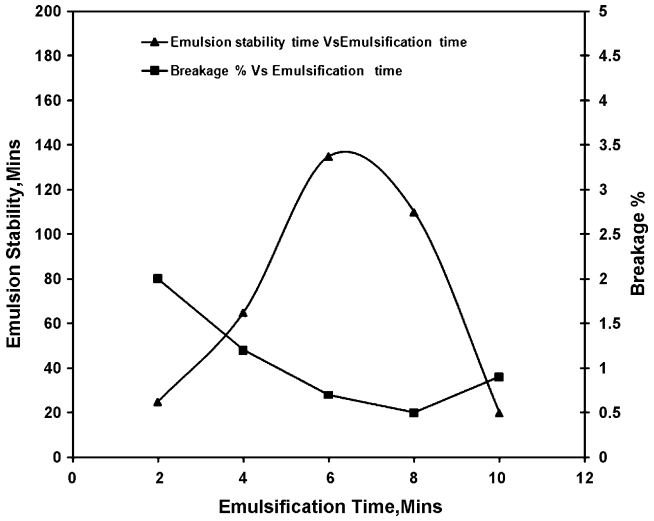

Fig. 6. Effect of emulsification time on emulsion stability time and breakage (surfactant concentration = 4% (v/v), carrier concentration = 0%, emulsification speed = 10,000 rpm, HCl concentration in internal phase = 0.5 M, and O/A ratio = 1).

and cream formation due to prolonged exposure of the emulsion to high speed.

4.1.3. Effect of emulsification speed

Experiments were conducted at different emulsification speeds from 2000 to 12,000 rpm. Fig. 7 shows the effect of emulsification speed on the stability of emulsion. The emulsion breakage decreased with the increase of the agitation speed up to a particular speed. An efficient emulsification gives good dispersion of the internal phase to membrane phase. The fact that these droplets become smaller and will take much more time to coalesce. This is conducive to good stability of the emulsion. In addition, the size of the internal phase droplets is smaller at greater agitation intensity, creating a larger surface area for extraction and hence obtaining higher recovery. It is clearly indicated that only at the speed of around 10,000 rpm, stable emulsion was formed and further increase in speed the cream formation was observed. At low speeds de-emulsification takes place quickly. The emulsion drop size varies from 0.1 to 2 mm and the internal drop size varies from 5 to 20 μm range.

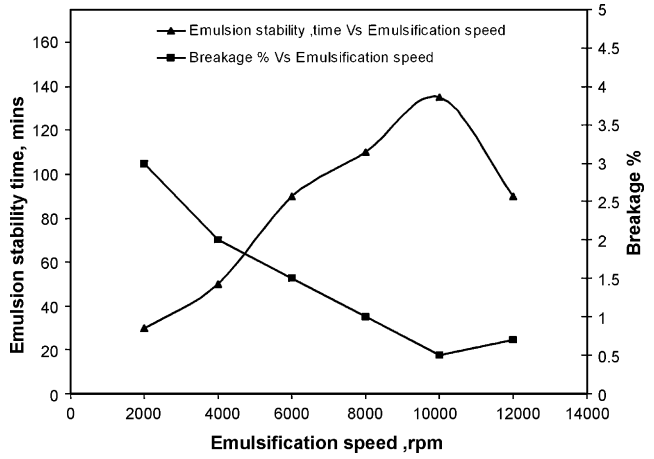

Fig. 7. Effect of emulsification speed on emulsion stability and breakage (emulsification time = 6 min, carrier concentration = 0%, surfactant concentration = 4%, HCl concentration in internal phase = 0.5 M, and O/A ratio = 1).

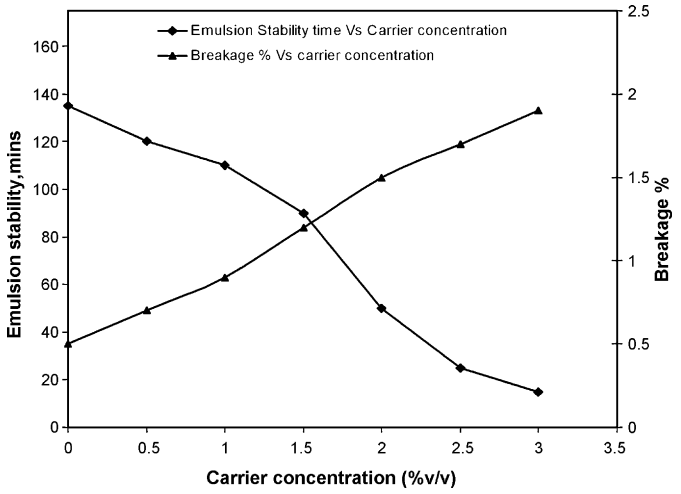

Fig. 8. Effect of carrier concentration on emulsion stability and breakage (surfactant concentration = 4% (v/v), emulsification time = 6 min, emulsification speed = 10,000 rpm, HCl concentration in internal phase = 0.5 M, and O/A ratio = 1).

4.1.4. Effect of carrier concentration

With the above-optimized results of surfactant concentration 4% (v/v), emulsification time of 6 min, and at speed 10,000 rpm, the amount of carrier was varied from 0.5% (v/v) to 3% (v/v) and the results obtained are shown in Fig. 8. The ranges of the carrier concentration to obtain the maximum stability are 0.5–1.0% (v/v). From the results, it could be observed that increasing the amount of carrier has two effects: the viscosity of membrane phase, which limits the extraction rate, decreases by increasing the carrier concentration and hence the carrier acts as thinner for the membrane phase. At the same time, increasing the carrier concentration over a certain limit decreases the stability of the emulsion [44–48].

4.1.5. Effect of internal phase concentration

Experiments were conducted under the same conditions as mentioned previously by varying the concentrations of the internal phase such as 0.2, 0.4, 0.5 and 1.0 M of HCl solution. Fig. 9 shows the effect of internal phase concentration on emulsion stability. When the HCl concentration was increased, the stability of the emulsion decreased. This may be due to the reduction in the properties of the surfactant by acidity in the internal phase that consequently led to a destabilization of the emulsion. HCl concentration of 0–0.4 M

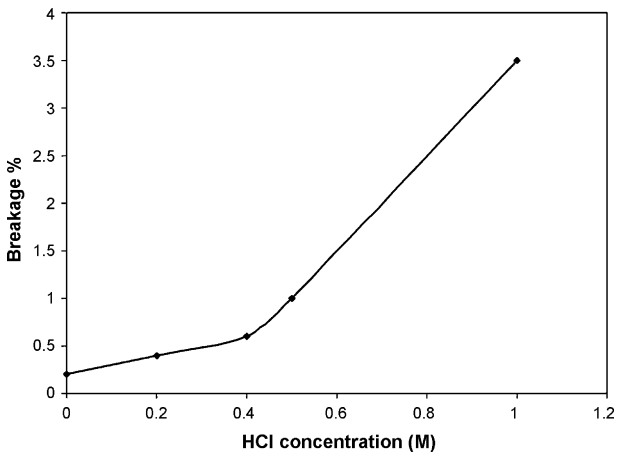

Fig. 9. Effect of HCl concentration in internal phase on emulsion breakage (surfactant concentration = 4% (v/v), carrier concentration = 0.5%, emulsification time = 6 min, emulsification speed = 10,000 rpm, and O/A ratio = 1).

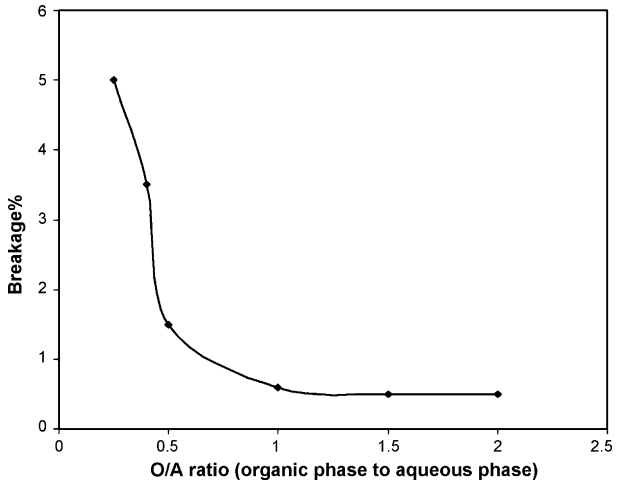

Fig. 10. Effect of volume ratio of organic phase to internal phase (O/A) on the stability of the emulsion (surfactant = 4% (v/v), carrier concentration = 0.5% (v/v), emulsification time = 6 min, emulsification speed = 10,000 rpm, and HCl concentration in internal phase = 0.5 M).

range was chosen for ELM extraction study based on the breakage results.

4.1.6. Effect of volume ratio of the organic phase to the aqueous internal phase (O/A)

With the above optimized emulsification conditions, the volume ratios of the membrane phase to internal phase were varied between 0.25 and 2.0. Fig. 10 shows the effect of variation of this ratio on the stability of the emulsion. It is evident that the increase of volume ratio of the organic phase to aqueous internal phase leads to an increase in the stability of the emulsion. The results may be explained on the basis of the fact that increasing the internal phase volume makes the emulsion unstable and there is leakage of the internal phase into the continuous phase and eventually leakage occurs. This may be due to increase in drop diameter and insufficient membrane phase to hold all the internal phase [49]. Volume ratio (O/A) of 1 was chosen as optimum for maximum emulsion stability.

4.2. ELM extraction

The effects of various parameters such as agitation time for extraction, agitation speed, membrane phase to external phase (M/E) ratio, carrier concentration, pH of the external phase and benzimidazole concentration in the external phase on extraction performance were studied in detail and optimum conditions for maximum percentage recovery of benzimidazole were established. The results of above studies are reported and discussed below.

4.2.1. Effect of pH on distribution coefficient

In order to establish the optimal pH values for both the feed and receiving aqueous phase for the ELM system, the results of equilibrium studies were used as the guideline. Fig. 11 shows the variation of distribution coefficient with pH of benzimidazole between aqueous external phase and organic (membrane) phase. The distribution coefficient increases up to an external pH of 13 and becomes constant. This is due to deprotonation of nitrogen 1 shown in Fig. 1. Lower values of distribution coefficient at low pH may be realized by incomplete dissociation of the benzimidazole as anion (pH below 11). Since the maximum value of distribution coefficient is achieved in the pH range of 12–13. The optimum pH for extraction

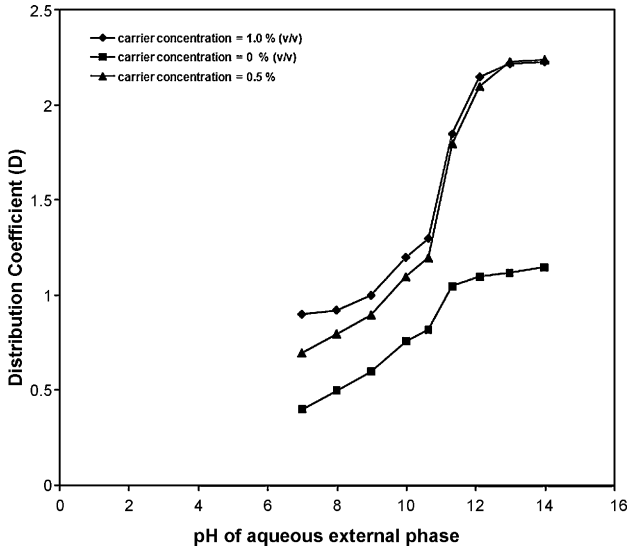

Fig. 11. Effect of pH of aqueous external phase and carrier concentration on distribution coefficient of benzimidazole between organic phase to aqueous phase (surfactant concentration in organic phase = 4% (v/v), and benzimidazole in feed = 600 ppm).

was chosen as 13. The internal phase pH was initially kept as 6 to keep emulsion swelling under control.

4.2.2. Effect of contact time for extraction

Experimental studies were carried out for different benzimidazole concentrations in external phase varying with contact time for extraction. The results were presented in Fig. 12. The percentage extraction of solute is defined as the ratio of difference between initial and final solute concentration to that of initial concentration.

$$\text{extraction of solute}\,(\%) = \frac{C_{\text{aq,i}} - C_{\text{aq,f}}}{C_{\text{aq,i}}} \times 100 \quad (7)$$

It was observed from the figure that as the time for extraction was increased, the concentration of benzimidazole decreased and 97.5% of benzimidazole removed within 12 min. After 15 min, slight increase in benzimidazole in external phase due to membrane breakage.

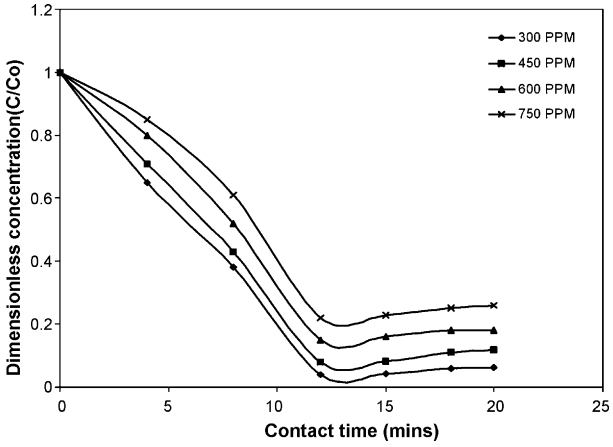

Fig. 12. Effect of contact time on dimensionless concentration profile of benzimidazole in external phase for various feed concentrations (agitation speed = 200 rpm, pH of external phase = 13, pH of internal phase = 6, carrier = 0.5%, M/E ratio = 1:1, and HCl concentration in internal phase = 0.3 M).

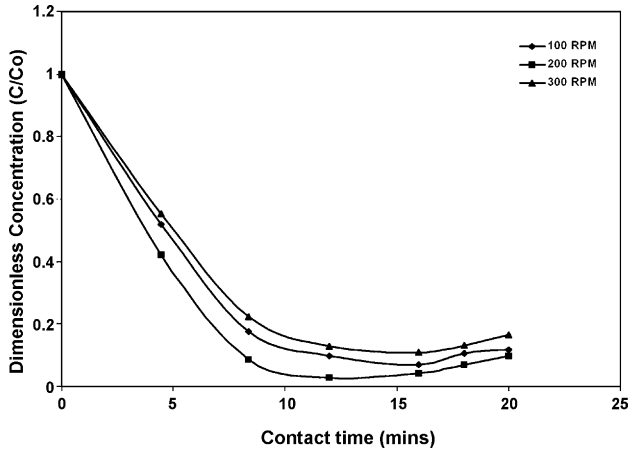

Fig. 13. Effect of agitation speed on dimensionless concentration profile of benzimidazole in external phase (pH of external phase = 13, pH of internal phase = 6, M/E ratio = 1:1, carrier = 0.5%, feed concentration = 300 ppm, and HCl concentration in internal phase = 0.3 M).

4.2.3. Effect of agitation speed

The effect of agitation speed on performance of extraction was studied and the results obtained are shown in Fig. 13. It was observe that as the speeds were increased from 100 to 300 rpm, the percentage extraction from external phase increased and decreased at a specified M/E ratio. The similar results had been found for various M/E ratios and feed concentrations. The speed of 200 rpm was found to be the most effective to remove the maximum percentage of solute for all M/E ratios and feed concentrations. The reason for the drop in percentage solute extracted from external phase beyond 200 rpm was due to either de-emulsification induced by higher shear of the impeller or due to leakage from internal phase [50].

4.2.4. Effect of emulsion to external phase ratio (M/E ratio)

With the above optimized results of time for extraction of 12 min and at a speed of 200 rpm, the M/E ratio was varied from 0.75:1 to 1:3 for different feed concentrations. The results are given in Fig. 14. It was found that at M/E ratio of 1:1, the percentage recovery of solute in external phase was high and further increase in M/E ratio decreased the percentage extraction. This drop may be due to

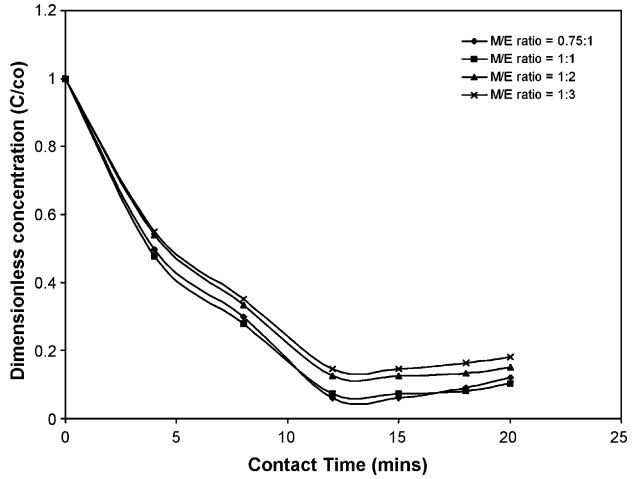

Fig. 14. Effect of M/E ratio on dimensionless concentration profile of benzimidazole in external phase (agitation speed = 200 rpm, feed concentration = 300 ppm, pH of external phase = 13, pH of internal phase = 6, carrier = 0.5%, and HCl concentration in internal phase = 0.3 M).

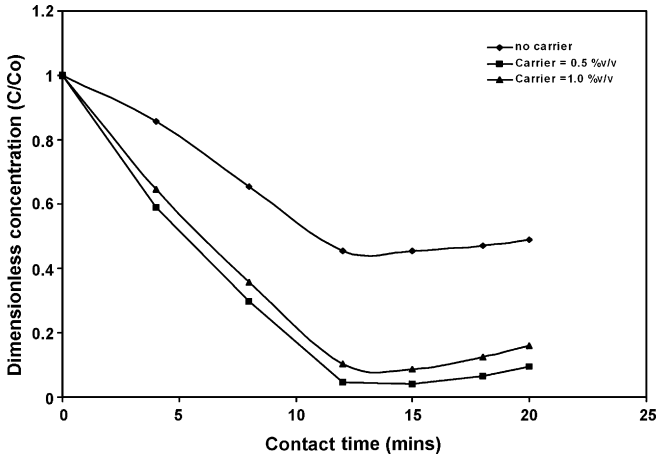

Fig. 15. Effect of carrier concentration on dimensionless concentration profile of benzimidazole in external phase (feed concentration = 300 ppm, agitation speed = 200 rpm, M/E ratio = 1:1, pH of external phase = 13, pH of internal phase = 6, and HCl concentration in internal phase = 0.3 M).

the decrease in area of contact between the emulsion and external phase, as the volume of external phase was increased.

4.2.5. Effect of carrier concentration

Extraction studies were carried out at 12 min of agitation time, agitation speed of 200 rpm and M/E ratio of 1:1, the carrier concentrations were varied from 0% (v/v) to 3% (v/v). The results obtained are shown in Fig. 15. From the results, it could be observed that increasing the amount of carrier has two effects: the viscosity of membrane phase, which limits the extraction rate, decreases by increasing the carrier concentration and hence the carrier acts as thinner for the membrane phase. At the same time, increasing the carrier concentration decreases the stability of the emulsion. On the other hand, an increase in concentration of the carrier in the membrane phase up to 0.5% increases the extraction rate and with 0%, the enhancement was insignificant. Above 1.0% (v/v), the percentage recovery was decreased. This may be due to release of solute from internal phase to the external phase by membrane breakage. The optimum carrier concentration for this system was found to be about 0.5% (v/v).Effect of feed concentration

The feed concentrations were varied as 300, 450, 600 and 750 ppm. Experimental studies were with other optimized parameters of contact time for extraction of 12 min, agitation speed of 200 rpm, M/E ratio of 1:1 and the carrier concentration of 0.5% (v/v) with different feed concentrations and the results were shown in Fig. 12. It was observed that the increase in feed concentrations decreased the percentage of extraction. This is due to saturation of internal phase and this confirms that ELM technique is more effective for pertraction of benzimidazole from dilute aqueous solutions and replacing the liquid–liquid extraction and stripping in one single stage with minimizing the solvent requirement.

4.2.7. Effect of HCl concentration in the internal aqueous phase

Different types of acid solutions have been reported as stripping solutions for liquid membrane processes with sulfuric acid solutions [51–53] and hydrochloric acid solutions [54–56] for extracting amino acids using ELM were reported. Hydrochloric acid was better stripping agent than sulfuric acid [57]. In this work, with the other optimized variables, the effects of HCl concentration in internal phase (0.1, 0.2, 0.3 and 0.4 M) on the extraction efficiency were investigated. The results are shown in Fig. 16. It indicates that the stripping efficiency increased with an increase in HCl concentration up to 0.3 M, above which extraction performance decreased.

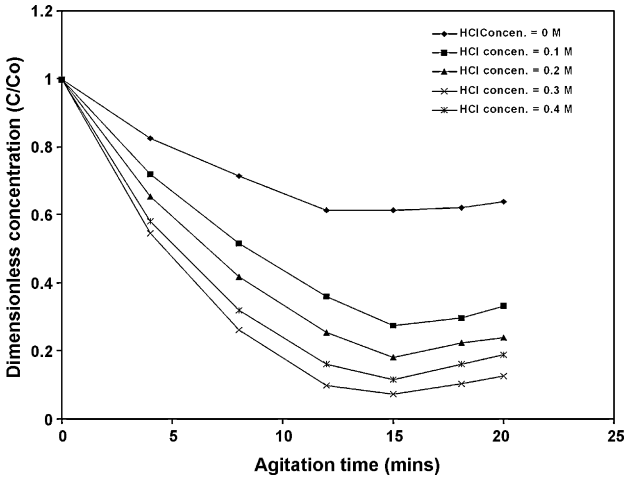

Fig. 16. Effect of HCl concentration in internal phase on dimensionless concentration profile of benzimidazole in external phase (feed concentration = 300 ppm, agitation speed = 200 rpm, pH of external phase = 13, pH of internal phase = 6, carrier = 0.5% (v/v), and M/E ratio = 1:1).

This may be due to the release of solute into the external phase attributed by membrane breakage which was studied and shown in Fig. 9. According to the results, 0.3 M HCl is considered as suitable stripping solution concentration.

5. Conclusion

The ELM pertraction of benzimidazole from aqueous solutions by a W/O/W emulsion was investigated using a room temperature ionic liquid (RTIL). System parameters were optimized with a view to maintain the emulsion stability. It was found that TOMAC is a suitable carrier for benzimidazole in emulsion liquid membrane transport system. The ELM pertraction technique is more effective than the conventional liquid–liquid extraction method and the following results were found:

- Under the ranges studied, the distribution coefficient of benzimidazole increased with increasing pH at a fixed amount of TOMAC concentration (Fig. 11) up to pH of 13.
- The optimum conditions for better stability of emulsion are surfactant concentration 4% (v/v), emulsification speed = 10,000 rpm, emulsification time = 6 min, carrier concentration = 0%, HCl concentration = 0%, volume ratio of organic phase to aqueous phase = 1.
- The suitable ELM pertraction operating parameters would be an aqueous external pH of 13, span-80 concentration of 4% (v/v), an aqueous internal HCl concentration of 0.3 M, internal phase pH of 6.0, volume ratio of external to emulsion of 1:1 and that of organic to internal phase (O/A) ratio of 1:1, TOMAC concentration of 0.5% (v/v) and an agitation speed of 200 rpm for maximum solute recovery.
- By proper selection of the extraction parameters, the system is capable of extracting more than 97.5% of the benzimidazole present in the dilute aqueous solutions within 12 min. After 12 min, there was decrease in extraction of benzimidazole due to breakage of emulsion which causes extracted solute released into the external phase.

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