Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Studies on Carbonate Ion Transport through Supported Liquid Membrane Using Primene JMT and Tributyl Phosphate

A. G. Gaikwad[a]
[a] CE & PD Division, National Chemical Laboratory, Pune, India

To cite this Article Gaikwad, A. G.(2009) 'Studies on Carbonate Ion Transport through Supported Liquid Membrane Using Primene JMT and Tributyl Phosphate', Separation Science and Technology, 44: 11, 2626 — 2644
To link to this Article: DOI: 10.1080/01496390902886062
URL: http://dx.doi.org/10.1080/01496390902886062

Separation Science and Technology, 44: 2626–2644, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390902886062

Studies on Carbonate Ion Transport through Supported Liquid Membrane Using Primene JMT and Tributyl Phosphate

A. G. Gaikwad
CE & PD Division, National Chemical Laboratory, Pune, India

Abstract: A supported liquid membrane system consisting of source, receiving and membrane phases, in which mixed extractants were used in the membrane phase, was explored for the carbonate ion transport from source to receiving through membrane phase. Primary amine Primene JMT and TBP were used as extractants (carriers) in liquid membrane phase. Different experimental variables such as concentration of carbonate ion, carriers, alkali and hydrogen peroxide, stirring speed, etc have been investigated. Primary amine Primene JMT and TBP mixed carriers show the synergistic effect for the transport of carbonate ions through supported liquid membrane system. The stability of the supported liquid membrane system has been explored for 50 h. The pre-concentration of carbonate ions from dilute solutions were also demonstrated. The effect of different alkalis on the permeability coefficient of transport of carbonate ions through supported liquid membrane system has been investigated. The primary amine in combination with TBP shows more effective for the transport of carbonate ions through supported liquid membrane system in comparison with that of secondary and tertiary amines.

Keywords: Carbonate ion, primary amine primene JMT, supported liquid membrane, synergistic effect, tributyl phosphate (TBP)

Received 23 October 2008; accepted 6 February 2009.

Address correspondence to A. G. Gaikwad, CE & PD Division, National Chemical Laboratory, Pune 411008, India. Tel.: 020-2590-2164; Fax: 020-2590-2612. E-mail: ag.gaikwad@ncl.res.in

INTRODUCTION

The liquid membrane technique has been used for the separation and recovery of metal ions. It has several advantages over solvent extraction and ion exchange methods. Among the liquid membrane techniques, bulk, SLM (supported liquid membrane) and emulsion membranes have been systematically investigated. The synergistic extractions of metal ion with the combined ion exchanger and solvation extractants and their mechanisms are well known (1). Extensive research work on amine extractants has been carried out and reported (2–4). Several authors have also reported synergic extraction of metal ion with different combination of extractants (1,5–8). However, the synergistic transport of carbonate ions through supported liquid membrane is lacking. The proposed liquid membrane has wide applications in separation, purification, and enrichment of several anions using commercial solvating and amine extractants.

The thermal power stations, refineries, vehicles, industrial exhausts, causes air pollution due to emission of gases such as NO_x, SO_2, CH_4, CO, CO_2, hydrocarbons, etc. The molecular weight of the gases N_2O, NO_2, SO_2, CH_4, CO, and CO_2 are 44, 46, 64, 16, 28, and 44 g, respectively. The toxic and acidic gases cause air pollution and acid rain under the climatic conditions. Among these gases, methane and CO have low solubility in water. The aqueous solutions of other gases can be made by bubbling them through aqueous solution under atmospheric conditions instead of leaving them to atmosphere. Then, the next step is to separate the anions from each other by ion exchange, solvent extraction, supported membrane, electrodialysis, ion chromatography, precipitation methods. Among these techniques, the liquid membrane technique is simple, easy to operate and economical viable. Here, the transport studies of carbonate ion through supported liquid membrane are reported. The gases CO_2, CO, SO_2, and N_2O have solubility in water 0.04 mol dm^{-3} at 0°C, 9.29×10^{-4} mol dm^{-3} at 0°C, 1.46 mol dm^{-3} at 25°C and 0.025 mol dm^{-3} at 25°C, respectively. Ostwald solubility coefficients for different gases for the toluene have been given in the literature (1). Among the gases, N_2, O_2, H_2, SO_2 and CO_2, SO_2, and CO_2 have higher solubility in water than that of other gases. The studies on pertraction of carbonate, sulfate, and nitrate ions through the supported liquid membrane are also important in order to develop new methods for the separation and pre-concentration. The transport of these ions through supported liquid membrane is controlled by their solubility, reactivity, and diffusion through solvent medium. In order to explore the synergistic effect during the transport of these anions from source to receiving through the liquid membrane phase in the presence of carriers in the liquid membrane phase under the dynamic steady state conditions in which chemical reaction and diffusion processes are in equilibrium, these research studies are undertaken. The carbonate ion solution in the source phase can be prepared by dissolving carbon dioxide in distilled water. The extracted carbonate ions into liquid membrane phase could be stripped out by alkali metal hydroxide in receiving phase. Sodium bicarbonate, calcium carbonate, and cyclic carbonates are the important products in the commercial markets which are formed during the transport of carbonate ion from source to receiving through membrane phase can be used for commercial applications.

The mechanisms of transport of carbonate ions through supported liquid membrane have been illustrated. The comprehensive investigations on removal and pre-concentration of carbonate ions from aqueous source to aqueous receiving solution by supported liquid membrane have been reported here. The carriers used for these research activities are primary amine (Primene JMT) and TBP (tributyl phosphate) in toluene. The systematic research studies include the experimental variables such as concentration of carriers in the diluent toluene, carbonate ion concentration in source solution, alkali concentration in receiving solution and effect of hydrogen peroxide.

THEORY

Due to the relatively low solubility of the carbon dioxide in water and weak dissociation of carbonic acid do not strongly favor the formation of acidic protons (H^+) from the dissolution. At the room temperature and atmospheric pressure, the solubility of carbon dioxide is about $90\,\mathrm{cm}^3$ of CO_2 per 100 mL of water. In the aqueous solution, the carbon dioxide exists in the different forms. First, it simply dissolves.

$$CO_2(g) \leftrightarrow CO_2(aq) \tag{1}$$

Then, the equilibrium is established between the dissolved CO_2 and H_2CO_3, carbonic acid.

$$CO_2(aq) + H_2O(l) \leftrightarrow H_2CO_3(aq) \tag{2}$$

1% of the dissolved CO_2 exists as H_2CO_3. Carbonic acid dissociates in two steps.

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad K_{a1} = 4.2 \times 10^{-7} \tag{3}$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad K_{a2} = 4.8 \times 10^{-11} \tag{4}$$

As carbon dioxide dissolves in the water, the equilibrium is established involving the carbonate ion, CO_3^{2-}. The carbonate anion interacts with cations in water. All the carbonates are insoluble except those of ammonium and Group IA elements. The alkali hydroxide neutralizes the carbonic acid and the carbonate and bicarbonate ions are formed.

$$HCO_3^-(aq) + M^+(aq) \leftrightarrow MHCO_3(aq) \tag{5}$$

$$CO_3^{2-}(aq) + 2M^+(aq) \leftrightarrow M_2CO_3(aq) \tag{6}$$

However, the hydration of carbon dioxide is enhanced by the hydrogen peroxide in aqueous solution (9).

$$2H_2O_2 + 2CO_2 \leftrightarrow 2H_2CO_3 + O_2 \uparrow \tag{7}$$

The solvent extraction is carried out in two steps extraction and stripping for separation or pre-concentration of carbonates ions. A bulk liquid membrane consists of source (s), membrane (m), and receiving (r) phases. In the conventional solvent extraction, the extraction and stripping processes are carried out one after the other. However, during these processes, different modes of occurrence involved are dispersion of one phase into other phase, subsequent to coalescence of dispersed phase and phase separation. This mode of operation frequently leads to solvent loss by emulsion formation. This may cause the loss of costly carriers or chelating agents, and extractant loading. The membrane technique eliminates all such shortcomings. The experimental apparatus is described in Fig. 1. Figure 2 illustrates the transport of carbonate ions from source

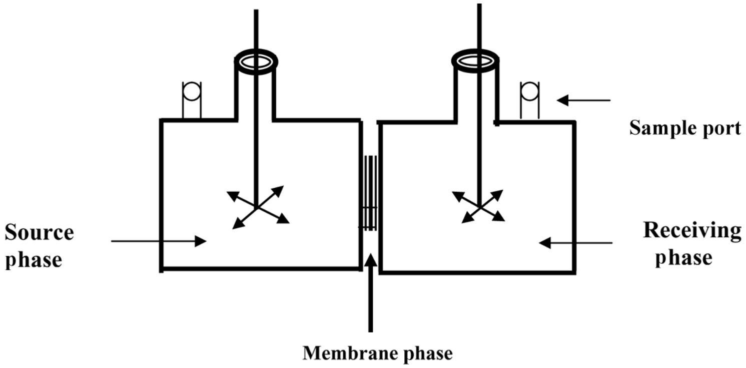


Figure 1. The membrane cell used for the transport of carbonate or bicarbonate ions through supported liquid membrane.

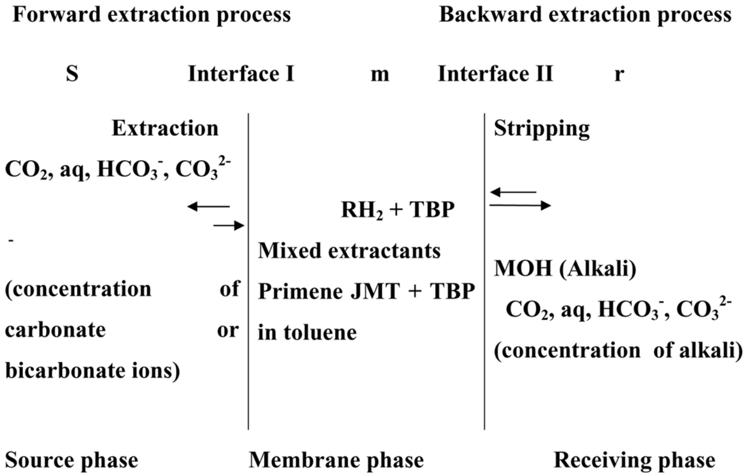


Figure 2. The illustration of carbonate ion transport through supported liquid membrane.

to receiving through liquid membrane phase. This ion transport process of carbonate ion can be represented by two extraction processes, namely, transport of carbonate ion from the aqueous to organic phase as a forward extraction process, and carbonate ion transport from organic phase to the aqueous phase as a backward extraction process. The continuous ion transport of carbonate ions in supported liquid membrane can be simultaneously carried out as extraction and stripping processes.

Permeability is expressed as rate of change of concentration of carbonate or bicarbonate ion with respect to time in a cross section area and volume of source phase

$$J = -V_s \cdot l/A \cdot dc/dt \tag{8}$$

Where, V_s is the volume of the source solution, A the membrane area, and l the membrane thickness. The permeability coefficient of transport of carbonate ions is expressed by equation (9).

$$\mathrm{Ln}(C_t^s/C_0^s) = A/V_s \cdot p/l \cdot t \tag{9}$$

Where, C_0 is the value of C_t at time zero and p is permeability coefficient. To estimate thickness of supported membrane, the geometric thickness of support is multiplied by tortuosity of pores (10,11). The micro-porous polypropylene films thickness was found 3 mm.

The distribution ratios of carbonic acid and sodium hydroxide for aqueous and toluene determined were 10.75 and 2.10, respectively. The driving forces for the transport of carbonate ions from source to receiving through membrane phase are the solubility of carbonate ions in water and toluene, and difference in concentration gradients in those phases. Tributyl phosphate has a boiling range 100 to 200°C. Primene JMT is also high boiling point primary amine. The overall transport mechanisms of carbon dioxide and carbonate ions are given by following equations.

$$CO_{2,s} \leftrightarrow CO_{2,m,} \leftrightarrow CO_{2,r} \tag{10}$$

$$MOH_{,m} + CO_{2,m} \leftrightarrow MHCO_{3,r} \tag{11}$$

$$MOH_{,m} + H_2CO_{3,m} \leftrightarrow MHCO_{3,r} + H_2O_{,s} \tag{12}$$

$$2MOH_{,m} + H_2CO_{3,m} \leftrightarrow M_2CO_{3,r} + H_2O_{,s} \tag{13}$$

The solvating solvents such as TBP, TOPO, TTA, β-diketone, etc. form oxonium salt with acids such as HCl, HNO_3, H_2SO_4, H_3PO_4, $HClO_4$, H_2CO_3 etc., and acts as liquid anion exchanger. The formed liquid anion exchangers are used to carry the anions or anionic complexes from interface I to II. The use of mixed primary or secondary or tertiary amine and solvating extractants in membrane phase enhances the carbonate ion transport. The backbone of primary amine Primene JMT (RNH_2) for simplicity is represented by R. The formation of liquid anion exchangers of TBP and Primene JMT with carbonic acid is given by following equations.

$$RH_{2,m} + H^+HCO^-_{3,m} \leftrightarrow RH_2 \rightarrow H^+HCO^-_{3,m} \tag{14}$$

$$TBP_m + H_2CO_{3,s} \leftrightarrow TBP \rightarrow H^+HCO^-_{3\,m} \qquad \text{(oxonium salt)} \tag{15}$$

The formed liquid anion exchangers transport bicarbonate anions from interface I to interface II as presented by following equations.

$$RH_2 \rightarrow H^+HCO^-_{3,m} + MOH_{,r} \leftrightarrow RH_{2,m} + M^+HCO^-_{3,r} \tag{16}$$

$$\mathrm{TBP} \rightarrow \mathrm{H^{+}HCO^{-}_{3,m}} + \mathrm{MOH_{,r}} \leftrightarrow \mathrm{TBP_{,m}} + \mathrm{M^{+}HCO^{-}_{3,r}} \tag{17}$$

The solvating solvents also form the solvating complex with carbonate ion at interface I. The formations of solvating complexes are given by the Equations (18) and (19).

$$\mathrm{H_2CO_{3t,s}} + \mathrm{yTBP_m} \leftrightarrow \mathrm{H_2CO_3} \cdot \mathrm{yTBP_m} \tag{18}$$

$$\mathrm{H_2CO_{3,s}} + \mathrm{nR} \leftrightarrow \mathrm{H_2CO_3} \cdot \mathrm{nR_m} \tag{19}$$

The synergistic complexes formations are also taken place at interface I. Those complexes formations are given by the following equations.

$$\mathrm{RH_2} \rightarrow \mathrm{H^{+}HCO^{-}_{3,m}} + \mathrm{yTBP_{,m}} \leftrightarrow \mathrm{RH_2} \rightarrow \mathrm{H^{+}HCO_3^{-}} \cdot \mathrm{yTBP_{,m}} \tag{20}$$

$$\mathrm{TBP} \rightarrow \mathrm{H^{+}HCO^{-}_{3,m}} + \mathrm{nRH_{2,m}} \leftrightarrow \mathrm{TBP} \rightarrow \mathrm{H^{+}HCO_3^{-}} \cdot \mathrm{nRH_{2,m}} \tag{21}$$

Here y and n stands for TBP and amine molecules for solvation of carbonate ion. The formed all these complexes diffuse from interface I to interface II. These complexes were dissociated at interface II. The carbonate ions $\mathrm{HCO^{1-}_{3,\,r}}$ or $\mathrm{CO^{2-}_{3,\,r}}$ are released to receiving phase. The liquid anion exchangers and solvating solvent are diffused back to interface I for repeatedly transport of carbonate ions.

$$\begin{aligned}\mathrm{RH_2} \rightarrow \mathrm{H^{+}HCO_3^{-}} \cdot \mathrm{yTBP_{,m}} + \mathrm{MOH} &\leftrightarrow \mathrm{RH_{2\,m}} + \mathrm{yTBP_{,m}} \\ &+ \mathrm{M^{+}HCO^{-}_{3,r}} + \mathrm{H_2O}\end{aligned} \tag{22}$$

$$\begin{aligned}\mathrm{TBP} \rightarrow \mathrm{H^{+}HCO_3^{-}} \cdot \mathrm{nRH_{2,m}} + \mathrm{MOH} &\leftrightarrow \mathrm{TBP^{-}_{,m}} + \mathrm{nRH_{2,m}} \\ &+ \mathrm{M^{+}HCO^{-}_{3,r}} + \mathrm{H_2O}\end{aligned} \tag{23}$$

The transport of carbonate ions with secondary and tertiary amines can be expressed in the similar way as given in the above equations (14) to (23), just using bulky groups R_1, R_2, and R_3 for the hydrogen atoms in the secondary and tertiary amines, respectively. Their mechanisms of transport of carbonate ions (where R_1, R_2, R_3, and R_4 are different long chain groups) are given as follows.

$$\mathrm{R_1R_2NH} + \mathrm{H^{+}HCO_3^{-}} \leftrightarrow \mathrm{R_1R_2\ NH_2^{+}\ HCO_3^{-}} \tag{24}$$

$$\mathrm{R_1R_2R_3N} + \mathrm{H^{+}HCO_3^{-}} \leftrightarrow \mathrm{R_1R_2R_3\ NH^{+}\ HCO_3^{-}} \tag{25}$$

$$\mathrm{R_1R_2R_3R_4N^{+}} + \mathrm{H^{+}HCO_3^{-}} \leftrightarrow \mathrm{R_1R_2R_3R_4\ N^{+}\ HCO_3^{-}} + \mathrm{H^{+}} \tag{26}$$

EXPERIMENTAL SECTION

Reagents and Apparatus

The solvating extractant TBP (tri-butyl phosphate) and Aliquat 336 (Tricaprylylmethylammonium chloride/Trioctylmethylammonium chloride) (Aldrich Chemicals CO, USA), and Amberlite LA 1 (N-dodecenyl (trialkylmethy1) amine), Alamine 336 (tri-octyl/decyl amine) and Primary amine (RNH_2) – Primene JMT (Mol. wt. 361, Roam and Haas Co.), were used. LiOH, NaOH, KOH, and NH_3 (Aldrich Chemicals CO, USA) (99.99% with purity) were used. TBP and Primene JMT solutions in toluene were prepared by mechanically shaking for 1 hour at with an equal volume of aqueous solution containing carbonic acid. After equilibration, the aqueous and organic phases were separated by centrifugation. The suitable concentrations of the extractants were used to impregnate on the microporous polypropylene membrane supports. The thickness 10^{-2} cm in between two microporous supports was observed. The different concentrations of organic solutions were prepared by diluting a desired amount of extractant with toluene. Carbonate ion solutions were prepared by dissolving a suitable flow rate of carbon dioxide in distilled water. The dilute solutions of carbonate, sulphate, and nitrate ions were prepared from the stock solutions. The low concentrations of carbonate, sulphate, and nitrate ions were determined by ion-selective electrodes. The higher concentration of carbonate ion in the solution was estimated by acid-base titration. The experimental apparatus used in this investigation to measure the permeability coefficient (P) is described in Fig. 1. A supported liquid membrane with an interfacial area $11.94\,cm^2$ was used. The variation of carbonate ion concentration with respect to time was estimated from the samples drawn from the source and receiving solutions at interval of time with acid-base titration.

Preparation of Supported Liquid Membrane

A membrane 2500 (Celenease Co., USA), which is a microporous polypropylene membrane of thickness 2.5×10^{-3} cm, average pore size $0.04\,\mu m$, porosity 45% was used as the supporting membrane for the immobilization of mixed extractants in toluene. The membrane supports were immobilized with carriers by soaking it in different concentrations of amine and solvating extractants solution for 2 h. The impregnation of carriers over the polymer porous support was carried out by the repeated treatments. The amount of impregnated carriers on porous support was determined by weight in difference method. The quantity of amine and solvating extractants solutions immobilized in the microporous support was 0.35 ml.

Procedure

A source solution with a suitable carbonate ion concentration in 35 ml volume in the big compartment of the cell, and the receiving phase with 25 ml and appropriate concentration of alkali in the small compartment of the cell were used. The source and receiving solutions separated by supported liquid membrane were in contact with each other without leakage. The samples of the source and receiving solutions were withdrawn with pipette and analyzed for carbonate ions with acid-base titrations.

RESULTS AND DISCUSSIONS

Concentration Variation with Time

Figure 3 shows the carbonate ion concentration variation with respect to time in source phase. The permeability coefficient values were calculated from such plots by using membrane cross section area 11.94 cm^2 and source phase volume 35 ml. The calculated permeability coefficient values

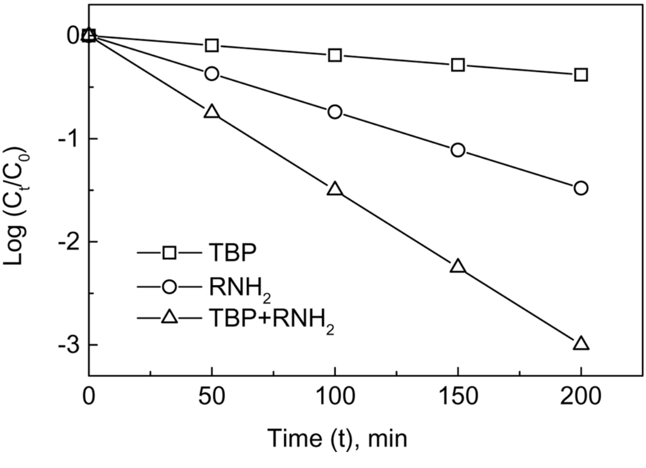


Figure 3. The variation of log C_t/C_0 with respect to time, carbonate ion = 0.04 M, Primene JMT = 0.1 M, TBP = 0.1 M, NaOH,$_r$ = 0.2 M, V_s = 35 ml, V_m = 0.35 ml, V_r = 25 ml and A = 11.94 cm^2.

were used to interpret the data of transport of carbonate ion through supported liquid membrane system at different experimental variables.

Effect of Stirring Speed

The effect of the stirring speed in bulk solution on the diffusion of carbonate ions through bulk solution is also important factor in order to minimize the diffusion layer at the interfaces. The source and receiving phases were independently stirred over the range 40 to 140 rpm (Fig. 4). The permeability coefficient increases for the range 40 to 110 rpm, which indicates the thickness of diffusion layer, decreases. However, the P values nearly remain constant during the stirring of both the phases with the range of 110 to 140 rpm. This region represents for the achievement of minimum diffusion layer thickness at the interfaces. Further, research studies were done at 120 rpm.

The results indicate that the permeability coefficient varies at different concentrations of carriers are used in the membrane phase (Fig. 4). In the absence of carriers in the membrane phase, there is also transport of carbonate ions from source to receiving through membrane phase. However, the transport of carbonate ions through the supported liquid membrane shows that the transport of carbonate ion enhances with the use of carriers in the membrane phase. There is also synergistic effect in

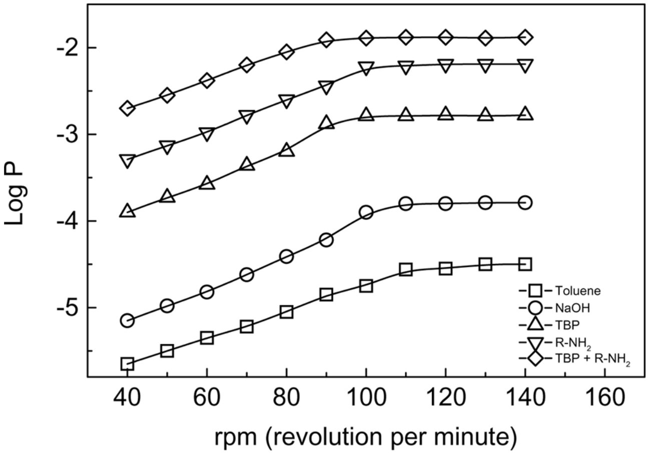


Figure 4. The effect of stirring speed of source and receiving phases on permeability coefficient (P), Carbonate ion = 0.04 M, Primene JMT = 0.1 M, TBP = 0.1 M, NaOH,$_r$ = 0.2 M, V_s = 35 ml, V_m = 0.35 ml, V_r = 25 ml and A = 11.94 cm^2.

the transport of carbonate ions through supported liquid membrane by using combined carriers Primene JMT and TBP in the membrane phase. The further research studies are reported for the in divisional Primene JMT, TBP, and combined Primene JMT + TBP carriers in the membrane phase.

Effect of Carbonate Ion Concentration

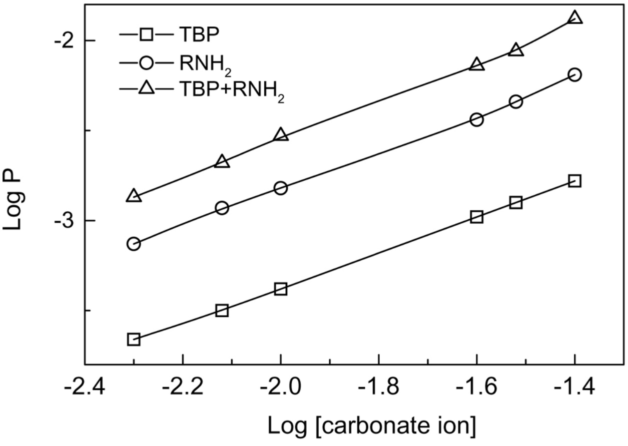
In order to explore the significant effect of carbonate ion concentration on the permeability coefficient during the permeation of carbonate ions, the experiments were carried out at different initial concentrations of carbonate ions in the source solution. The relation between P and carbonate ion concentration in the source solution has been illustrated in the Fig. 5a. The increase in P value along with an increase in the carbonate concentration was observed for 0 to 0. 04 M range.

Effect of Alkali Concentration

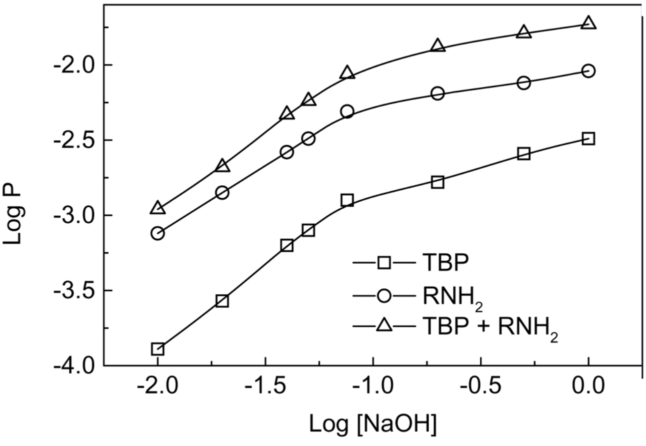
The extraction of carbonate ion at the interface I depend on the difference in gradient concentration of carbonate ion in source, membrane, and receiving phase; affinity of extractants towards carbonate ion at interface I; and releasing ability of extractants for carbonate ion at interface II in the presence of alkali in the receiving phase. In order to strip out the carbonate ion from the membrane phase, it is necessary to use alkali in the receiving phase and make it competitive to extractants during the stripping process. Thus, with the increase in alkali concentration in the receiving solution, the distribution ratio of carbonate ion decreases at the stripping side. However, the effect of alkali concentration in the receiving phase on stripping out the carbonate ion from membrane phase was studied in the alkali concentration range from 0 to 1 M (Fig. 5b). The P value decrease along with a decrease in the alkali concentration of the receiving solution.

Effect of the Carrier Concentration

The carrier plays a significant role during the permeation of carbonate ion in the supported liquid membrane in viewpoint of its economically viability, effective transport, stability, industrial applications, etc. It is therefore significant to investigate the effect of the Primene JMT concentration on the permeation of carbonate ion through supported



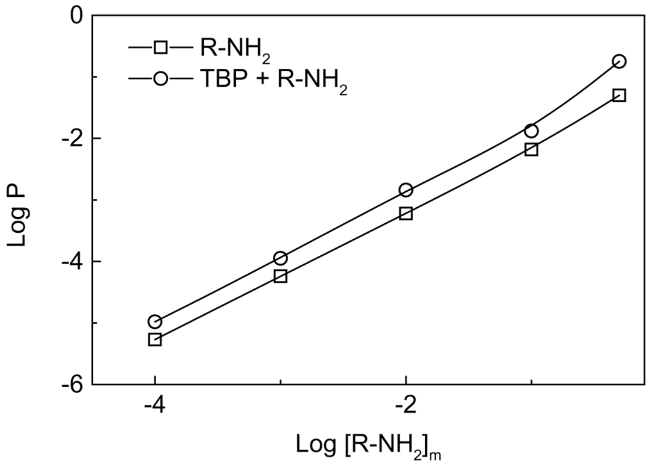
(a)



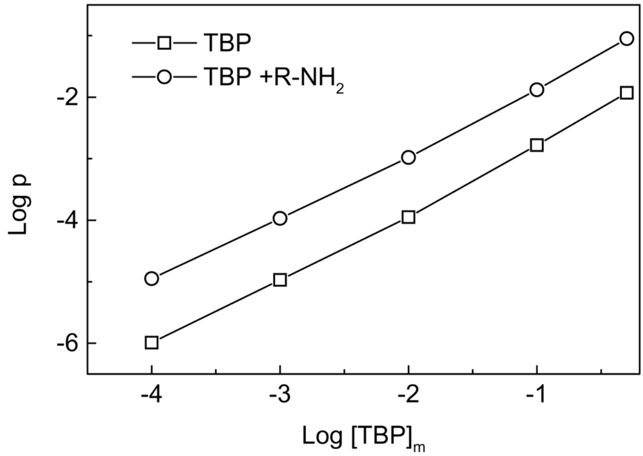
(b)

Figure 5. (a) The variation of P with respect to carbonate ion concentration of the source solution, Primene JMT = 0.1 M, TBP = 0.1 M, NaOH,$_r$ = 0.2 M, V_s = 35 ml, V_m = 0.35 ml , V_r = 25 ml and A = 11.94 cm^2. (b) The relation of P with respect to sodium hydroxide concentration of receiving solution, Carbonate ion = 0.04 M, Primene JMT = 0.1 M, TBP = 0.1 M, V_s = 35 ml, V_m = 0.35 ml, V_r = 25 ml and A = 11.94 cm^2.

liquid membrane system. The variation of concentration of Primene JMT was carried out over the range from 10^{-4} to 0.5 M. The permeability co-efficient of carbonate ion was observed in the increase in order with an increase in the Primene JMT concentration over the



(a)



(b)

Figure 6. The effect of variation of carrier concentration on permeability coefficient (P), (a) Carbonate ion = 0.04 M, TBP = 0.1 M, $NaOH_{,r}$ = 0.2 M, V_s = 35 ml, V_m = 0.35 ml, V_r = 25 ml, A = 11.94 cm^2 and Primene JMT variation, (b) Carbonate ion = 0.04 M, TBP = 0.1 M, $NaOH_{,r}$ = 0.2 M, V_s = 35 ml, V_m = 0.35 ml, V_r = 25 ml, A = 11.94 cm^2 and TBP variation.

studied range (Fig. 6a). The variation of concentration of TBP was investigated over the range from 10^{-4} to 0.5 M. The permeability co-efficient of carbonate ion increases along with an increase in the

TBP concentration over 10^{-4} to 0.5 M range (Fig. 6b). It could be possible to explore its utility for the effective separation and pre-concentration of carbonate ion at optimum concentration of Primene JMT and TBP. These optimum concentrations of carriers in low volume membrane phase make the supported liquid membrane system economically inexpensive, efficient, and effective in comparison with that of liquid extraction system.

Effect of Different Alkalis

During the investigations of permeation of carbonate or bicarbonate ions in supported liquid membrane system, different alkalis, ammonia, LiOH, NaOH, and KOH have been used in order to assess their effect on the ion transport of carbonate or bicarbonate. The concentration of these alkalis used was 0.2 M. The results shows that KOH is more competitive towards carbonate or bicarbonate ion transport with comparison that of other alkalis by using these carriers (Fig. 7).

Permeability of Different Anions

The different anions such as sulfate, nitrate, and carbonate were used for the anion transport studies from source to receiving through membrane

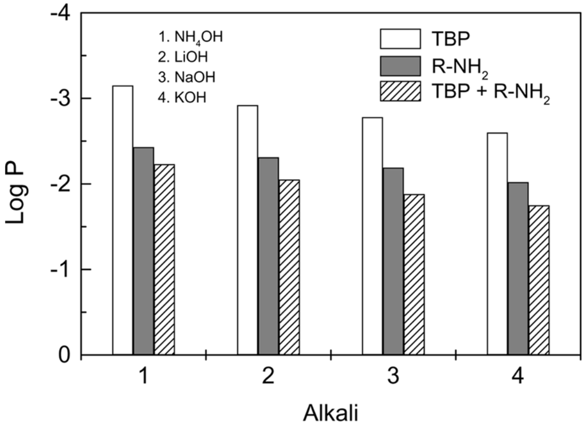


Figure 7. The effect of alkali on permeability coefficients, Carbonate ion = 0.04 M, Primene JMT = 0.1 M, TBP = 0.1 M, $MOH_{,r}$ = 0.2 M, V_s = 35 ml, V_m = 0.35 ml, V_r = 25 ml and A = 11.94 cm^2.

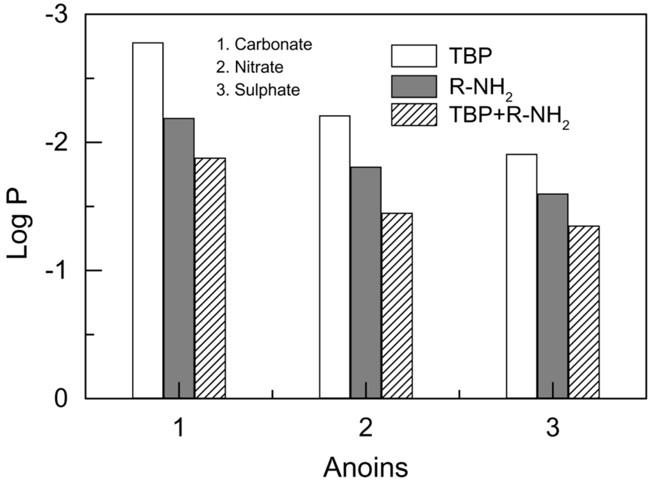


Figure 8. The variation of permeability coefficients with respect to anions, carbonate or sulphate or nitrate ion = 0.04 M, Primene JMT = 0.1 M, TBP = 0.1 M, NaOH,$_r$ = 0.2 M, V_s = 35 ml, V_m = 0.35 ml, V_r = 25 ml and A = 11.94 cm^2.

phase. The concentration of the different anions in the source phase is an important factor for the competitive transport of carbonate or bicarbonate anion from the mixture of sulphate, carbonate, and nitrate. The sulphate, carbonate or bicarbonate, and nitrate anions in terms of acidic form are used in the source phase at the same concentration of 0.04 M, in a separate experiment. The evaluated permeability coefficients for these anions are given in Fig. 8.

Pre-Concentration of Carbonate Ion

0.1 M Primene JMT + 0.1 M TBP in toluene were used for pre-concentration of carbonate ions. The effect of variation of the initial carbonate ion concentration in the source solution was explored from the range 10^{-7} to 10^{-2} M. The dilute solutions of carbonate ions were prepared from the stock solutions. The variation in the enrichment factor (EF is a ratio of carbonate ion concentration at time in the receiving to source phase) value with respect to initial carbonate ion concentration in source solution has been illustrated in Fig. 9a. The EF value decreases with increase in the initial carbonate ion concentration in the source phase. Thus, effective and efficient pre-concentration of carbonate ion can be carried out from dilute solutions.

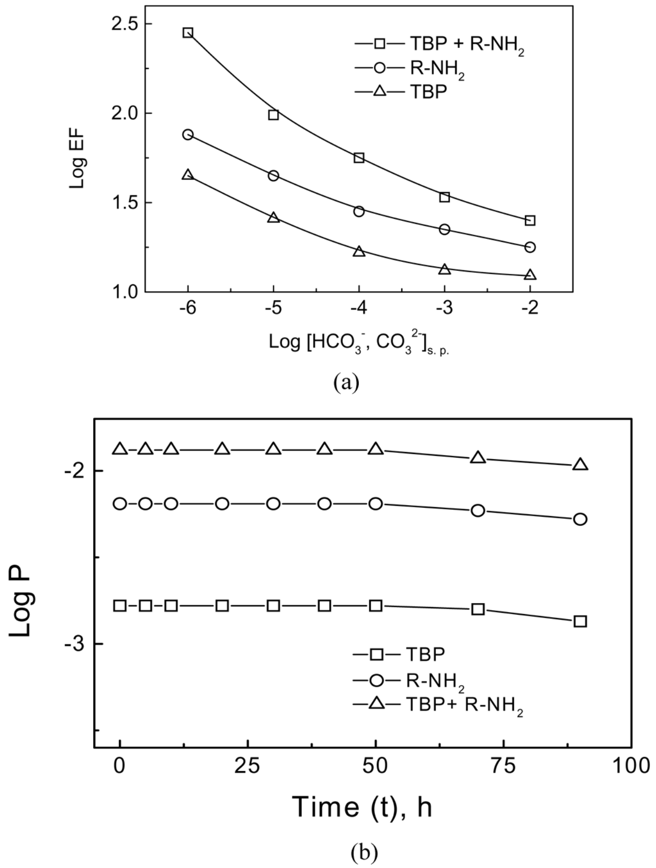


Figure 9. (a) The pre-concentration of carbonate ion from source to receiving solution, Primene JMT = 0.1 M, TBP = 0.1 M, $NaOH_{,r}$ = 0.2 M, V_s = 35 ml, V_m = 0.35 ml, V_r = 25 ml and A = 11.94 cm^2. (b) The stability of supported liquid membrane with respect to time, Carbonate ion = 0.04 M, Primene JMT = 0.1 M, TBP = 0.1 M, $NaOH_{,r}$ = 0.2 M, V_s = 35 ml, V_m = 0.35 ml, V_r = 25 ml and A = 11.94 cm^2.

Stability of Liquid Membrane

In general, the stability of the supported liquid membrane is not up to the mark besides the many years of study by many researchers, the supported liquid membrane has not been commercialized because the carrier phase in the polymer matrix is not stable and will be lost with time. In this paper, the polymeric membrane support used was polypropylene with an average pore size 0.04 um. The supported liquid membrane was prepared by merely soaking the membrane in an amine and solvating solvent solution.

In this case, the amine solution in the pores could gradually be lost to the source phase and/or the receiving phase with time. Since the loss of the extractants is the major problem with the supported liquid membrane, the membrane stability is studied. The stability of polypropylene support has been checked under the experiments conditions. The supported liquid membrane has been continuously used for 50 h (Fig. 9b). During these hours of experiments, the P value remains unaffected. However, the durability of microporous polypropylene support has been found to be satisfactory. The effective and synergistic transport of carbonate ions have been observed with Primene JMT + TBP system. However, beyond 50 h operation time, the impregnated amine and solvating extractants slowly get dissolved in source and/or receiving phase. Therefore, after 50 h, the membrane life decreases with the increase in the operation time.

Effect of Hydrogen Peroxide

The hydrogen peroxide acts as a good hydrating agent (9) for carbon dioxide. Therefore, the effect of hydrogen peroxide on the permeability coefficient of carbonate or bicarbonate ions was explored. The concentration of hydrogen peroxide in source phase was varied from 0 to 0.01 M. The results show that the permeability coefficient (P) of carbonate or bicarbonate ion increases for this concentration range (Fig. 10).

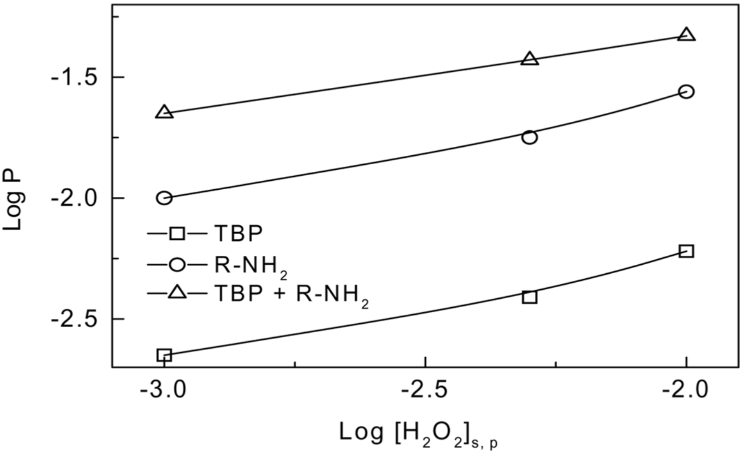


Figure 10. Variation of permeability coefficient of carbonate ion with respect to hydrogen peroxide concentration in source phase, Carbonate ion = 0.04 M, Primene JMT = 0.1 M, TBP = 0.1 M, NaOH$_{,r}$ = 0.2 M, V_s = 35 ml, V_m = 0.35 ml, V_r = 25 ml and A = 11.94 cm^2.

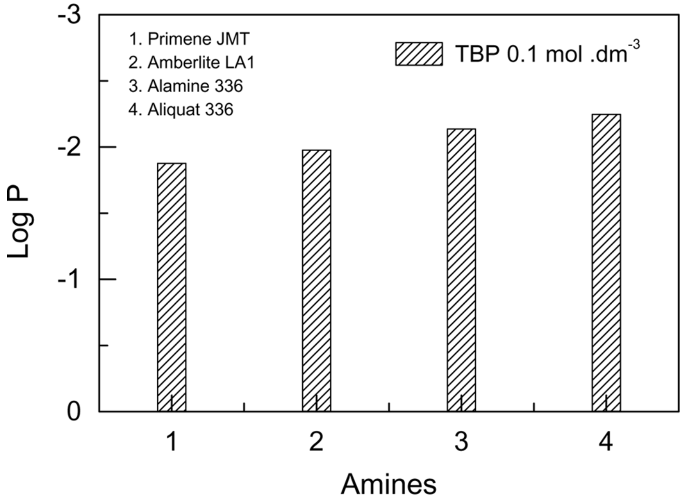


Figure 11. The effect of amine extractant in the transport of carbonate ions, carbonate ion = 0.04 M, Amine (Primene JMT, Amberlite LA1, Alamine 336 and Aliquat-336) = 0.1 M, TBP = 0.1 M, $NaOH_{,r} = 0.2$ M, $V_s = 35$ ml, $V_m = 0.35$ ml, $V_r = 25$ ml and $A = 11.94\,cm^2$.

Hydrogen peroxide is a nonpolluting agent and it enhances the hydration of carbon dioxide. Thus, use of hydrogen peroxide in the source phase has added advantages for the transport of carbonate ion from the source to receiving through the membrane phase.

Permeability Coefficients for Different Amine Extractants

Figure 11 shows the effect of primary (Primene JMT), secondary (Amberlite LA1), tertiary (Alamine 336), and quaternary (Aliquat 336) amine in the presence of TBP on the transport of carbonate ions from source to receiving through the membrane phase. The results indicate that primary amine (Primene JMT) in the presence of TBP effectively transports carbonate ions from source to receiving through the membrane phase in comparison with that of other amines under the same experimental conditions.

CONCLUSIONS

The investigations on the transport of carbonate ions from source to receiving through supported liquid membrane phase show the synergistic effect in the presence of mixed extractants Primene JMT and TBP in toluene the membrane phase. The carbonate ion concentration in the source phase, the carrier concentration membrane phase, and alkali concentration in the receiving phase have been optimized. The effect of use of hydrogen peroxide in the source phase, hydrogen peroxide increases the carbonate ion concentration in the source phases, on the transport of carbonate ions from source to receiving through the membrane phase shows an added advantage. The mixed extractants Primene JMT and TBP have been found to be efficient for the pre-concentration of the carbonate ions from dilute solutions. The primary amine (Primene JMT) in the presence of TBP effectively transports carbonate ions from source to receiving through the membrane phase in comparison with that of other amines such as secondary, tertiary, and quaternary under the same experimental conditions.

REFERENCES

1. Sekine, T.; Hasegawa, Y. (1977) *Solvent Extraction Chemistry, Fundamentals and Applications*; Marcel Dekker: New York, p. 108.
2. Sto, K. (1996) Solvent extraction of technetium (IV) by primary amine in heptane solution from aqueous alkaline solution. *J. Radioanal. Nucl. Chem.*, *203*: 97–107.
3. Saha, S.; Chakma, A. (1995) Selective CO_2 separation from CO_2/C_2H_6 mixtures by immobilized diethanolamine/PEG membranes. *J. Membr. Sci.*, *98*: 157–171.
4. Klinowski, J.; Russer, A. (1970). Electric conductivity of liquid ion exchangers. *J. Chem. Soc. (B)*, 1156–1158.
5. Branco, L.C.; Crespo, J.G.; Afonso, C.A.M. (2002) Highly selective transport of organic compounds by using supported liquid membranes based on ionic liquids. *Angew. Chem. Int. Ed.*, *41*: 2771.
6. Alguacil, F.J.; Martinez, S. (2001) Solvent extraction of Zn (II) by Cyanex 923 and its application to a solid-supported liquid membrane system. *J. Chem. Technol. & Biotechnol.*, *76*: 298.
7. Danesi, P.R. (1984–85) Separation of metal species by supported liquid membrane. *Sepn. Sci. and Technol.*, *19*: 857.
8. Boyadzhiev, L. (1990) Liquid pertraction or liquid membranes—State of the art. *Sepn. Sci. and Technol.*, *25*: 187.
9. Moore, H.H.; Hudson, R.L. (2000) IR detection of H_2O_2 at 80 K in ion-irradiated laboratory ices relvent to Eropa. *Icarus*, *145*: 282–288.
10. Prasad, R.; Sirkar, K.K. (1988) Dispersion-free solvent extraction with microporous hollow-fiber modules. *AICHE Journal*, *34*: 177.
11. Prasad, R.; Sirkar, K.K. (1987) Microporous membrane solvent extraction. *Sepn. Sci., Technol.*, *22*: 619.