

Studies on Transport of Carbonate Ions through a Supported Liquid Membrane

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The transport of carbonate ions through a supported liquid membrane in the presence and absence of carriers has been explored. The liquid membrane used was the combined liquid cation and anion exchangers in toluene immobilized in the porous polypropylene support. The permeability coefficient (P) of carbonate ions transport from the source to receiving through membrane phase has been estimated. The different experimental variables such as the concentration of carbonate ions in source phase, the concentration of Aliquat-336 (tricapryl(methyl)ammonium carbonate) and PC-88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) in membrane phase, alkali metal hydroxide concentration in receiving phase, and the stirring speed of the source phase and receiving phase have been explored. The stability of liquid membrane phase during the transport of carbonate ions from source phase to receiving phase was tested for 50 h. The enrichment factor for carbonate ion transport from the source to receiving phase was found to be higher at lower concentrations of carbonate ions in comparison with that of at higher concentrations. A model has been developed for the effective transport of carbonate ions through the cross section area of liquid membrane phase from source to receiving phase.

Key words:

Supported liquid membrane, carbonate ions, liquid anion and cation exchangers, alkali metal hydroxide, permeability coefficient

Introduction

The anions have been separated and quantified by different methods such as precipitation, ion exchange, solvent extraction, ion chromatography, electro dialysis, ion selective electrodes, etc. Anions such as halogens, carbonate, sulphate, phosphate, and nitrate cause pollution. Their recovery and separation from each other and samples are also important from the view point of minimizing pollution. The supported liquid membrane system has been used for the separation, recovery and pre-concentration of both the anions and cations. It has several advantages over solvent extraction and ion exchange techniques. The supported liquid membrane is used for the recovery and separation in single stage and continuously. Research into carbonate ion separation and recovery is encouraging us to develop new methods due to the pollution caused by carbon dioxide emissions. However, studies on the separation of anions by liquid membranes are scarce. Therefore, the aim of this paper is to explore the liquid anion and cation exchange membranes for the transport and separation of carbonate ions.

Thermal power stations, refineries, vehicles, industrial exhausts, generate air pollution due to emis-

sions of gases such as NO_x , SO_2 , CH_4 , CO , CO_2 , hydrocarbons, etc. The molecular mass of these gases are N_2O (44), NO_2 (46), SO_2 (64), CH_4 (16), CO (28) and CO_2 (44). The heavy gases cause air pollution and acid rain under the climatic conditions. Among these gases, methane and CO have low solubility in water. By bubbling these pollutant gases stream through aqueous solution can be dissolved instead of released into the atmosphere. The further step is to separate the anions from each other by ion exchange, solvent extraction, supported membrane, electro dialysis, ion chromatography, precipitation methods. Among these techniques, the liquid membrane technique is simple, easy to operate, and economically viable. Therefore, we decided to explore the separation of carbonate ions, which form after dissolving CO_2 in the aqueous solution. The solubility of the gases in water is as follows: CO_2 ($c = 0.04 \text{ mol dm}^{-3}$ at 0°C), CO ($c = 9.29 \cdot 10^{-4} \text{ mol dm}^{-3}$ at 0°C), SO_2 ($c = 1.46 \text{ mol dm}^{-3}$ at 25°C) and N_2O ($c = 0.025 \text{ mol dm}^{-3}$ at 25°C). Ostwald solubility coefficients have been given for different gases for the toluene.¹ Among the gases, N_2 , O_2 , H_2 , SO_2 and CO_2 , SO_2 and CO_2 have higher solubility than other gases. These results indicate that the transportation of these acid ions from source to the receiving through membrane phase could be controlled by diffusion process. The studies on pertraction of carbonate, sulfate and nitrate ions through the supported liquid membrane

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are advantageous because their transports are controlled by their solubility, reactivity and diffusion through a solvent medium. These studies were undertaken in order to investigate the enhanced transport of anions through a liquid membrane with the help of carriers under dynamic and steady-state conditions, in which the chemical reaction and diffusion processes are in equilibrium. Sodium bicarbonate, calcium carbonate, cyclic carbonates and hydrocarbons are the important products prepared from the carbon dioxide and used for commercial applications. Those carbonates formed during these investigations could be used for commercial purposes.

It is reported that HCO_3^- ions is transported into cells of *Coccochloris* plant in the exchange of OH^- ions in which, as a result of HCO_3^- fixation, occurs during the photosynthesis.^{2,3} Carbonate is a key component present in washing powders and the manufacturers of such products require a simple yet reliable method of quantifying its presence in a given product to ensure that quality control tolerance is maintained. Ion chromatography for the analysis of carbonate has been reported. Effects of bicarbonate on lithium transport in human red cells show the ability of the counter-transport system to establish a lithium gradient across the membrane decrease linearly with bicarbonate concentration in the medium.³ The extraction studies of carbonate anion from aqueous solution with liquid anion-exchanger (quaternary ammonium salts) has been reported.⁵ Studies on transport of carbonate ion by using anion-exchange membranes have been explored.⁶ The reactive separation of carbon dioxide with ionic liquids at the temperature $\theta = 300^\circ\text{C}$ have been investigated.⁷ The liquid carriers in the membrane phase help to convert the CO_2 gas molecules into useful products such as carbonates.⁸ The facilitated or carrier-mediated transport of carbonate ion involves a reversible chemical reaction in combination with a diffusion process.⁹ The carrier-facilitated transport membrane has amine groups for transport of carbonate ions.¹⁰ The polybenzimidazole membranes have the long-term hydrothermal stability up to $\theta = 400^\circ\text{C}$, sulfur tolerance, and durability. Supported membranes have major advantages for reactive separation of carbon dioxide, as an inexpensive and eco-friendly alternative to other techniques for separation of carbonate ions at high temperature.^{11–14} The literature shows that the transport of carbon dioxide or carbonate ions was carried out by facilitated reactive molecules or ions by using alkali metal carbonate or amine groups.

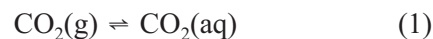
Non-toxic carbon dioxide gas emissions in the atmosphere are the cause of global warming; therefore, it is necessary to develop a method for the sequestration of carbon dioxide. The reaction between

CO_2 and CaO for formation of CaCO_3 requires high energy. The CaO and CO_2 react in an organic liquid in the presence of dispersing agents.¹⁵ $\text{Ca}(\text{HCO}_3)_2$ has more solubility than CaCO_3 in water which is formed by addition of CO_2 in CaCl_2 in the presence of water. Chromatography techniques require a large volume of eluent to separate the carbonate ion with the low equivalent ionic conductivity ions like salts of benzoic acid. Sodium carbonate softens the water by precipitating insoluble calcium or magnesium carbonate. The proposed method of liquid membrane helps to separate, recover and convert the carbonate ions into useful products (changing the stripping solution in the receiving phase).

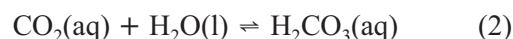
The supported liquid membrane phase consisting of liquid anion exchanger (Aliquat-336, tricapryl(methyl)ammonium carbonate, in toluene) and liquid cation exchanger (PC-88A, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester in toluene) has been explored for the utility of carbonate ion transport. The transport mechanism of carbonate ions through supported liquid membrane has been illustrated. The systematic research studies include the experimental variables such as concentration of carriers in the membrane phase, carbonate ion concentration in the source phase, sodium hydroxide concentration in receiving phase and stirring speed of source and receiving phase.

Theory

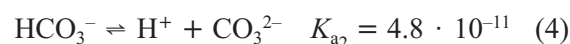
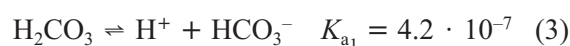
Due to carbon dioxide relatively low solubility and weak acidity in nature it does not strongly favor generation of acidic protons (H^+) from the dissolution in water. At room temperature and atmospheric pressure, the solubility of carbon dioxide is about 90 cm^3 of CO_2 per 100 mL of water. In aqueous solution, the carbon dioxide exists in different forms. First, it simply dissolves.



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



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



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 ex-

cept those of ammonium and Group IA elements. The alkali hydroxide neutralizes the carbonic acid thus forming carbonate and bicarbonate ions.



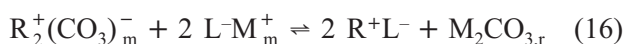
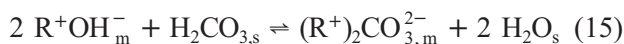
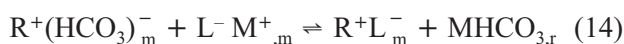
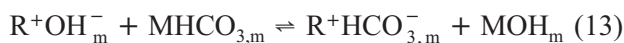
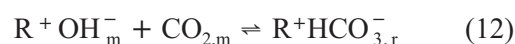
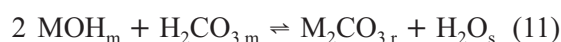
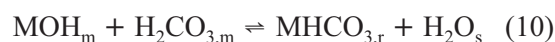
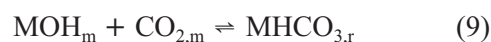
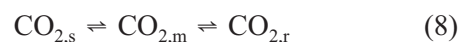
However, the hydration of carbon dioxide is enhanced by the hydrogen peroxide in aqueous solution.¹⁶



A conventional solvent extraction was carried out in two steps as extraction and stripping one after the other for the separation or pre-concentration of cation or anions. However, during the solvent extraction, different modes of occurrence involved are dispersion of one phase as drops in another 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. A liquid membrane process, which consists of source (s), membrane (m) and receiving (r) phases, is a combined process of extraction and stripping. The dispersion free membrane technique eliminates all such shortcomings. Fig. 1 illustrates the transport of carbonate or bicarbonate ions from source to receiving through liquid membrane phase. Two extraction processes can represent this ion transport process of carbonate or bicarbonate. Namely, transport of carbonate or bicarbonate ions from the aqueous to the organic phase as a forward extraction process (extraction),

and carbonate or carbonate ions transport from the organic phase to the aqueous phase as a backward extraction process (stripping).

The transportation of carbon dioxide from source to receiving through membrane phase by molecular diffusion mechanism is also considered. The facilitated and diffusion transport of molecular carbon dioxide and carbonate ions from source to receiving through membrane phase in the presence of alkali was taken into account. The liquid anion exchanger was used to carry the carbonate or bicarbonate anion from interface I to II. The liquid cation exchanger is used to provide the metal or ammonium cation to react with carbonate or bicarbonate anion. Then carbonate or bicarbonate anions are transported into the receiving phase. The overall transport mechanisms of carbon dioxide and carbonate ions are given by the following equations:



Forward extraction process

s Interface I m

extraction
 $\text{CO}_2, \text{aq}, \text{HCO}_3^-, \text{CO}_3^{2-}$
 ← →
 (concentration of
 carbonate or
 bicarbonate ions)

$\text{R}^+ \text{L}^-$
 mixed extractants
 Aliquat-336+PC-88A
 in toluene

source phase

membrane phase

Backward extraction process

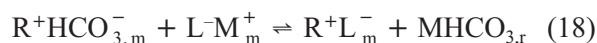
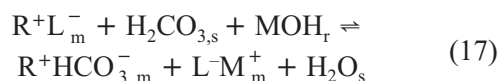
m Interface II r

stripping
 ← →
 NaOH,
 $\text{CO}_2, \text{aq}, \text{HCO}_3^-, \text{CO}_3^{2-}$
 (concentration of alkali)

receiving phase

Fig. 1 – Presentation of carbonate ion transport through supported liquid membrane

Combined liquid anion and cation exchangers react with carbonate or bicarbonate and metal ion from source and receiving phases at interface I and interface II, respectively.



The formed $R^+HCO_3^-$ and L^-M^+ liquid anion-exchanger bicarbonate-ion pair and liquid cation-exchanger metal-ion pair react and form metal bicarbonate. The formed metal bicarbonate is transported to the receiving phase. Thus, repeatedly, reactions (17) and (18) are preceded. The molecular diffusion of carbon dioxide from source to receiving through membrane phase is shown by reaction (8). Reactions (9) and (12) show the facilitated reactive molecular carbon dioxide transport from source to receiving through membrane phase. The reactions (10), (11), (13), (14), (15), (16), (17) and (18) show the facilitated reactive carbonate or bicarbonate ions transport from source to receiving through membrane phase.

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

$$J = -V_s/A \cdot dc/dt \quad (19)$$

Where, V_s is the volume of the feed of source solution and A the membrane area. From the integration form of the above equation, the permeability coefficient of transport of carbonate ions is expressed by the equation (20).

$$\ln(c_t^s/c_0^s) = A/V_s \cdot P/l \cdot t \quad (20)$$

Where, c_0 is the value of c_t at time zero and P is permeability coefficient and l the membrane thickness. To estimate thickness of supported membrane, the geometric thickness of support is multiplied by tortuosity of pores.^{16,17} The microporous polypropylene films thickness was found to be 6.2 mm.

Experimental

Reagents and apparatus

The liquid anion exchanger Aliquat-336 (tricapryl(methyl)ammonium chloride) (Aldrich Chemicals CO, USA), and the liquid cation exchanger PC-88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) (Daihachi Chemical Industry, Japan) were used. The chemicals used were obtained from Merck and Aldrich Chemicals CO.

Carbonate ion solutions were prepared by bubbling suitable flow rate of carbon dioxide gas through aqueous solution under atmospheric pressure. The content of carbonate ions in the aqueous solution was confirmed by acid base titration. The solubility of carbon dioxide in aqueous phase was enhanced by addition of hydrogen peroxide.¹⁸ The experimental set up used for this supported liquid membrane system was similar as described earlier and as shown in Fig. 2.¹⁹ An interfacial area of membrane was $A = 11.94 \text{ cm}^2$. The carbonate ion concentrations with respect to time in source and receiving phase were determined by withdrawing samples and acid-base titrations. The reproducibility of the experiment was checked by comparing the mean results of two reproducible runs.

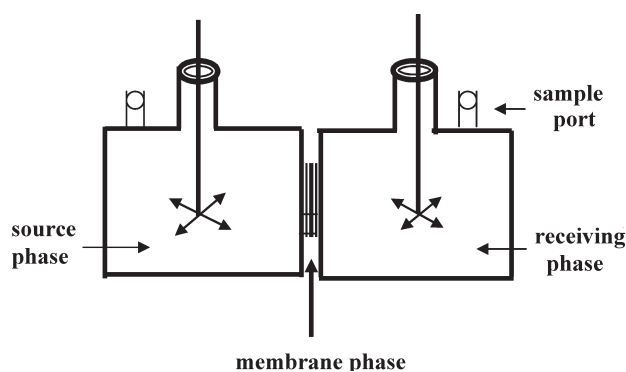


Fig. 2 – Set up of membrane cell used for the transport of carbonate or bicarbonate ions through supported liquid membrane

Preparation of supported liquid membrane

A membrane Celgard 2500, (Hoechst Celanese Corporation), which is a microporous polypropylene membrane of thickness $l = 2.5 \cdot 10^{-3} \text{ cm}$, average pore diameter $d = 0.04 \text{ mm}$, porosity 45 % was used as the support for the immobilization of liquid membrane phase in toluene. The liquid ion exchangers (anionic and cationic) were converted into bicarbonate/carbonate and sodium form by repeatedly shaking with sodium bicarbonate and sodium hydroxide solutions. The suitable concentrations of the liquid ion exchangers were impregnated on microporous polypropylene membrane supports. The thickness 10^{-2} cm was observed in between two microporous supports. Different concentrations of liquid ion exchangers were prepared by diluting a desired amount with toluene. The liquid membranes were immobilized by soaking different concentrations of liquid anion and cation exchangers for 2 h. The immobilized liquid anion and cation exchangers in the microporous supports were determined and found to be 0.029 mL cm^{-2} by weighing the membrane supports before and after immobilization.

Procedure

A 35 mL source phase with carbonate ion and 25 mL receiving phase with sodium hydroxide concentrations were taken in two different compartments of membrane cell. These two compartments of source and receiving solutions were in contact with each other through a supported liquid membrane without leakage. The source and receiving phases were stirred independently without disturbing the membrane phase. The samples of the source and receiving solutions at interval of time were taken out and analyzed for the quantification of carbonate ion with acid base titration.

Results and discussions

Estimation of permeability coefficient (P)

Fig. 3 shows the variation of carbonate ion concentration in source phase with respect to time. From these plots, the values of P were calculated from their slope and substituting the values of feed volume and area of membrane. The values of permeability coefficient (P) were used for the interpretation of data.

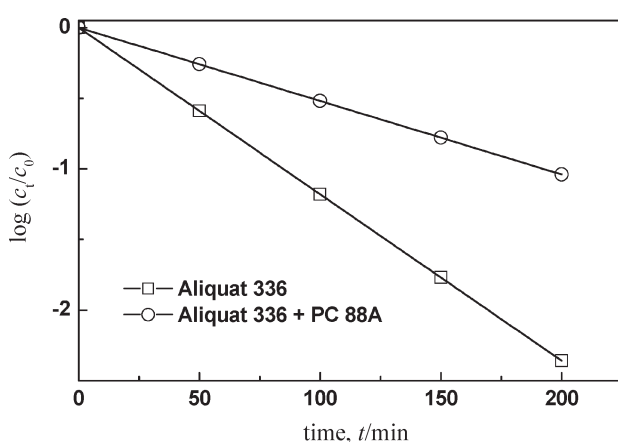


Fig. 3 – Plot of $\log c_t/c_0$ vs. time, carbonate ion $c = 0.04 \text{ mol dm}^{-3}$, Aliquat-336 $c = 0.01 \text{ mol dm}^{-3}$, PC-88A $c = 0.01 \text{ mol dm}^{-3}$, NaOH, $c = 0.5 \text{ mol dm}^{-3}$, $V_s = 35 \text{ mL}$, $V_m = 0.35 \text{ mL}$, $V_r = 25 \text{ mL}$ and $A = 11.94 \text{ cm}^2$

Effect of the stirring speed

The effect of the stirring speed in bulk solutions on the diffusion of carbonate or bicarbonate anion through bulk solution is also an important factor in order to minimize the diffusion layer at the interfaces. The source and receiving phases were independently stirred at speeds ranging from $n = 40$ to 130 min^{-1} (Fig. 4). The permeability coefficient increases for the range $n = 40$ to 110 min^{-1} , which indicates that the thickness of the diffusion layer decreases. However, the P values nearly re-

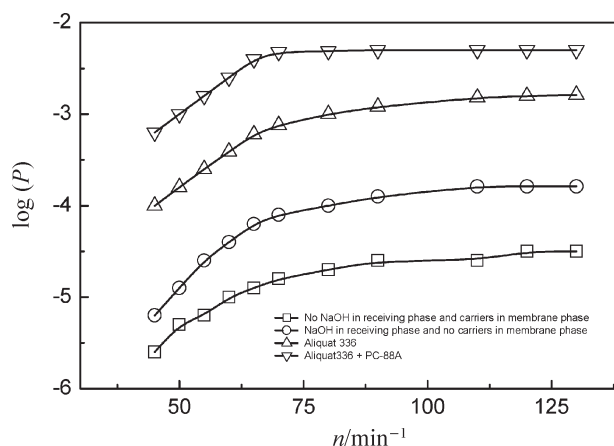


Fig. 4 – Effect of stirring speed of source and receiving phases on permeability coefficient (P) of carbonate ion, carbonate ion $c = 0.04 \text{ mol dm}^{-3}$, Aliquat-336 $c = 0.01 \text{ mol dm}^{-3}$, PC-88A $c = 0.01 \text{ mol dm}^{-3}$, NaOH, $c = 0.5 \text{ mol dm}^{-3}$, $V_s = 35 \text{ mL}$, $V_m = 0.35 \text{ mL}$, $V_r = 25 \text{ mL}$ and $A = 11.94 \text{ cm}^2$

main constant during the stirring of both phases in the range from $n = 110$ to 130 min^{-1} . This region represents the achievement of minimum diffusion layer thickness at the interfaces of the membrane phase. Further, research studies were done at $n = 110 \text{ min}^{-1}$.

Transport of carbonate ions through liquid membrane in absence and presence of carriers

Determined the distribution ratios of carbonic acid and sodium hydroxide solutions between distilled water and toluene were 10.75 and 2.10, respectively. The transport of carbonate ions from source to receiving phase through membrane phase took place due to their solubility in toluene and difference in gradient concentration in those phases. The results show that there is a transport of carbonate ions in the presence of the hydroxide ions in the membrane phase from source to receiving phase. However, the enhanced facilitated pertraction of carbonate ions from source to receiving through membrane phase by using the liquid ion exchangers as the carriers have been investigated. The obtained results were encouraging and presented in Fig. 4.

Effect of carbonate ion concentration

The permeation studies of carbonate or bicarbonate anions were carried out with the variation of their concentration in the source solution. The relation between P and carbonate ion concentration in the source solution is illustrated in Fig. 5a. Increased P values along with an increase in the carbonate ion concentration were observed for the concentration range, $c = 0$ to 0.04 mol dm^{-3} .

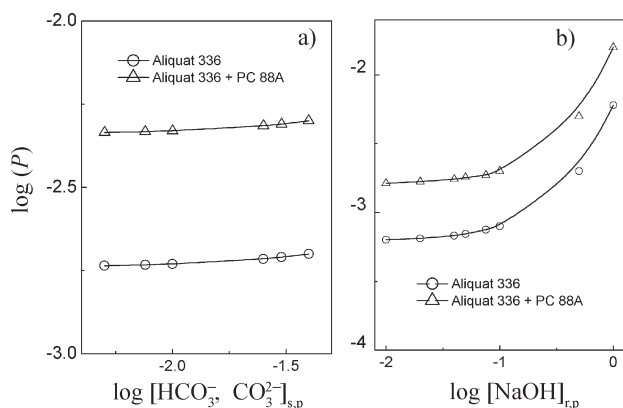


Fig. 5 – (a) Relation between P and carbonate ion concentration of the source solution, Aliquat-336 $c = 0.01 \text{ mol dm}^{-3}$, PC-88A $c = 0.01 \text{ mol dm}^{-3}$, $\text{NaOH}_r, c = 0.5 \text{ mol dm}^{-3}$, $V_s = 35 \text{ mL}$, $V_m = 0.35 \text{ mL}$, $V_r = 25 \text{ mL}$ and $A = 11.94 \text{ cm}^2$, (b) Relation between P and sodium hydroxide concentration of receiving solution, carbonate ion $c = 0.04 \text{ mol dm}^{-3}$, Aliquat-336 $c = 0.01 \text{ mol dm}^{-3}$, PC-88A $c = 0.01 \text{ mol dm}^{-3}$, $V_s = 35 \text{ mL}$, $V_m = 0.35 \text{ mL}$, $V_r = 25 \text{ mL}$ and $A = 11.94 \text{ cm}^2$

Effect of sodium hydroxide concentration

The presence of sodium and hydroxide ions in the membrane phase may be due to the mechanisms of distribution and extraction depending on their behavior in toluene. The pertraction of carbonate ions from source to receiving through membrane phase depends on the sodium hydroxide concentration in the receiving phase. Therefore, it is necessary to explore the sodium hydroxide concentration variation in the receiving phase and check its competitiveness to liquid ion exchangers in the stripping process of carbonate or bicarbonate ions. With the increase in sodium hydroxide concentration in receiving solution, the distribution ratio of carbonate or bicarbonate ion decreases at the stripping side. The sodium hydroxide concentration in the receiving solution varied from $c = 0$ to 1 mol dm^{-3} (Fig. 5b). The permeability coefficient (P) of carbonate or bicarbonate ions increases with the increase in sodium hydroxide concentration in the receiving solution.

Effect of carrier concentration

The liquid anion exchanger extracts and transport carbonate or bicarbonate ions from source to receiving through membrane phase. The liquid cation exchanger extracts sodium ions from receiving into the liquid membrane phase and provides to carbonate ions. It is, therefore, significant to investigate the effect of Aliquat-336 and PC-88A concentration on the permeation of carbonate or bicarbonate ion. The enhanced facilitated pertraction of carbonate or bicarbonate ions from source to receiving through membrane phase were investigated. The variation of concentration of Aliquat-336 and PC-88A was carried out over the range from

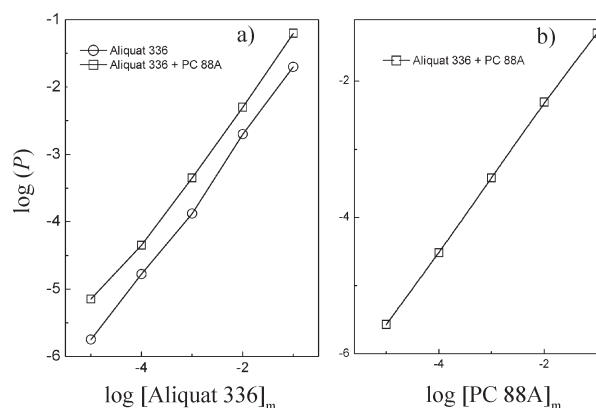


Fig. 6 – Effect of concentration of carrier on permeability coefficient (P) of carbonate ion, (a) Carbonate ion $c = 0.04 \text{ mol dm}^{-3}$, PC-88A $c = 0.01 \text{ mol dm}^{-3}$, $\text{NaOH}_r, c = 0.5 \text{ mol dm}^{-3}$, $V_s = 35 \text{ mL}$, $V_m = 0.35 \text{ mL}$, $V_r = 25 \text{ mL}$, $A = 11.94 \text{ cm}^2$ and Aliquat-336 variation, (b) Carbonate ion $c = 0.04 \text{ mol dm}^{-3}$, PC-88A $c = 0.01 \text{ mol dm}^{-3}$, $\text{NaOH}_r, c = 0.5 \text{ mol dm}^{-3}$, $V_s = 35 \text{ mL}$, $V_m = 0.35 \text{ mL}$, $V_r = 25 \text{ mL}$, $A = 11.94 \text{ cm}^2$ and PC-88A variation

$c = 10^{-5}$ to 0.1 mol dm^{-3} , the permeability coefficient of carbonate or bicarbonate ion increases with increase in concentration of Aliquat-336 and PC-88A (Fig. 6a, b).

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 were used in order to assess their effect on the ion transport of carbonate or bicarbonate. The concentration of these alkalis used was $c = 0.5 \text{ mol dm}^{-3}$. The results show that KOH is more competitive towards carbonate or bicarbonate ion transport in comparison with other alkalis by using these carriers (Fig. 7).

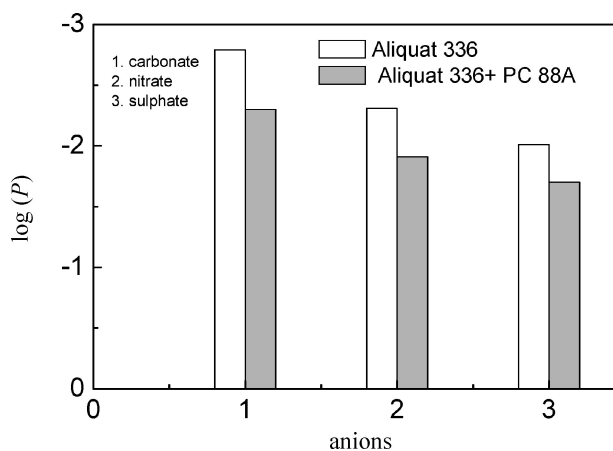


Fig. 7 – Permeability coefficients for different anions, carbonate or sulphate or nitrate ion $c = 0.04 \text{ mol dm}^{-3}$, Aliquat-336 $c = 0.01 \text{ mol dm}^{-3}$, PC-88A $c = 0.01 \text{ mol dm}^{-3}$, $\text{NaOH}_r, c = 0.5 \text{ mol dm}^{-3}$, $V_s = 35 \text{ mL}$, $V_m = 0.35 \text{ mL}$, $V_r = 25 \text{ mL}$ and $A = 11.94 \text{ cm}^2$

Permeability of different anions

Different anions such as sulfate, nitrate and carbonate were used for the anion transport studies from source to receiving through membrane 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 were used in the source phase at same concentration of $c = 0.04 \text{ mol dm}^{-3}$, in separate experiment. The evaluated permeability coefficients for these anions are given in Fig. 8.

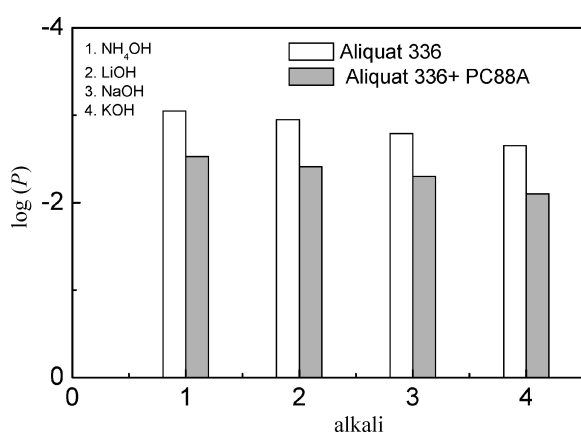


Fig. 8 – Log of permeability coefficients for different alkalis, carbonate ion $c = 0.04 \text{ mol dm}^{-3}$, Aliquat-336 $c = 0.01 \text{ mol dm}^{-3}$, PC-88A $c = 0.01 \text{ mol dm}^{-3}$, NaOH, $c = 0.5 \text{ mol dm}^{-3}$, $V_s = 35 \text{ mL}$, $V_m = 0.35 \text{ mL}$, $V_r = 25 \text{ mL}$ and $A = 11.94 \text{ cm}^2$

Pre-concentration of carbonate ions

0.01 mol dm^{-3} Aliquat-336 and PC-88A in toluene was immobilized on porous supports. The effect of variation of initial carbonate ion concentration in source solution was explored from $c = 10^{-7}$ to $10^{-1} \text{ mol dm}^{-3}$. The enrichment factor was defined as the concentration ratio of carbonate or bicarbonate ions of receiving to source phase (EF). Variation in the enrichment factor value with respect to initial carbonate ions concentration in source solution is illustrated in Fig. 9a. The EF value decreases with increase in the initial carbonate or bicarbonate ion concentration in the source solution. Thus, the effective and efficient pre-concentration of carbonate or bicarbonate ions can be carried out from dilute solutions.

Stability of liquid membrane

The stability of polypropylene support was checked for the transport of carbonate or bicarbonate ions from source to receiving through membrane phase. The supported liquid membrane system was continuously been used for 50 h (Fig. 9b). In these studies, the P value remains unaffected.

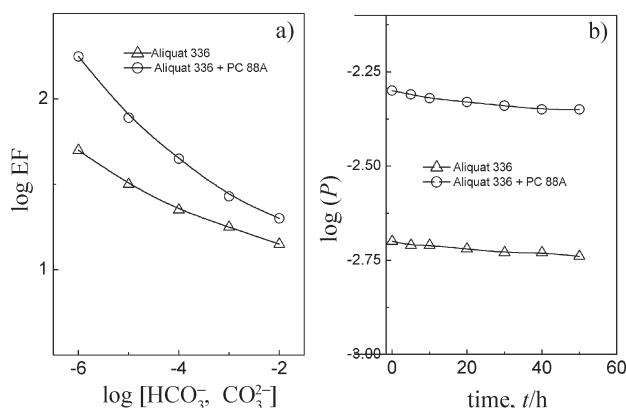


Fig. 9 – (a) Representation of pre-concentration of carbonate ion from source to receiving solution, carbonate ion $c = 0.04 \text{ mol dm}^{-3}$, Aliquat-336 $c = 0.01 \text{ mol dm}^{-3}$, PC-88A $c = 0.01 \text{ mol dm}^{-3}$, NaOH, $c = 0.5 \text{ mol dm}^{-3}$, $V_s = 35 \text{ mL}$, $V_m = 0.35 \text{ mL}$, $V_r = 25 \text{ mL}$ and $A = 11.94 \text{ cm}^2$, (b) Presentation of stability of supported liquid membrane, carbonate ion $c = 0.04 \text{ mol dm}^{-3}$, Aliquat-336 $c = 0.01 \text{ mol dm}^{-3}$, PC-88A $c = 0.01 \text{ mol dm}^{-3}$, NaOH, $c = 0.5 \text{ mol dm}^{-3}$, $V_s = 35 \text{ mL}$, $V_m = 0.35 \text{ mL}$, $V_r = 25 \text{ mL}$ and $A = 11.94 \text{ cm}^2$

The small decreased P value could be due to loss of liquid ion exchangers. The stability of liquid membrane system is quite good. The durability of micro-porous polypropylene support was satisfactory.

Effect of hydrogen peroxide on permeability coefficient

The hydrogen peroxide acts as good hydrating agent¹⁸ for carbon dioxide. Therefore, it is worthwhile to explore the effect of hydrogen peroxide on the permeability coefficient of carbonate or bicarbonate ions. The concentration of hydrogen peroxide in the source phase was varied from $c = 0$ to 0.01 mol dm^{-3} . The results show that the permeability coefficient (P) of carbonate or bicarbonate ion increases for this concentration range (Fig. 10). Hy-

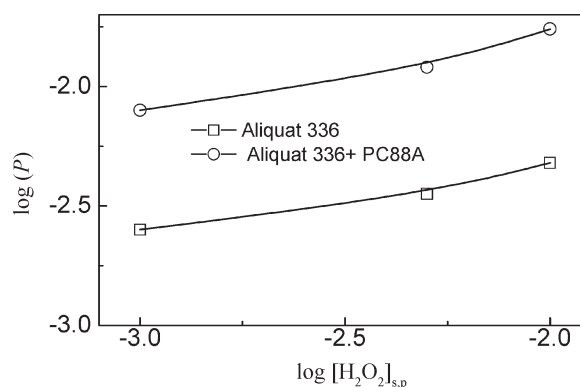


Fig. 10 – Effect of hydrogen peroxide concentration on the transport of carbonate ion from source to receiving through membrane phase, carbonate ion $c = 0.04 \text{ mol dm}^{-3}$, Aliquat-336 $c = 0.01 \text{ mol dm}^{-3}$, PC-88A $c = 0.01 \text{ mol dm}^{-3}$, NaOH, $c = 0.5 \text{ mol dm}^{-3}$, $V_s = 35 \text{ mL}$, $V_m = 0.35 \text{ mL}$, $V_r = 25 \text{ mL}$ and $A = 11.94 \text{ cm}^2$

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

The model for the transport of carbonate ions

The model plots of ratio of carbonate ion concentration with respect to time to initial carbonate ion concentration at time zero (c_t/c_0) of source phase vs. time for different cross-section area values are shown in Fig. 11. The cross-section area of membrane and volume of source phase are used in the calculation of permeability coefficient of carbonate or bicarbonate ions. The membrane area and source phase volume are involved in the cell constant in order to design and setup the supported liquid membrane system. The variation of carbonate ion concentration in the source phase with respect to time shows that the cross-section area of membrane is very important while designing the supported liquid membrane cell.

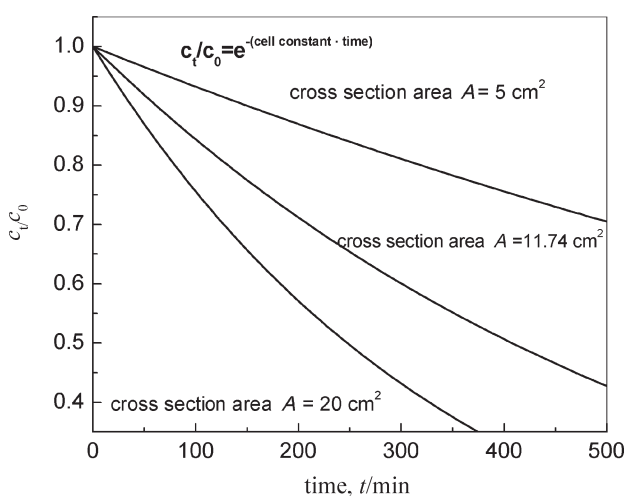
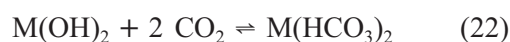


Fig. 11 – Model for the concentration variation of carbonate ion in the source phase with respect to the time at the different cross section area of the membrane

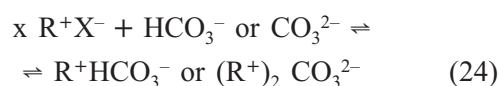
Conclusions

The facilitated transport of carbonate or bicarbonate ion through supported liquid membrane system consisting of source, liquid membrane (Aliquat-336 and PC-88A in toluene), and receiving phase were investigated. The results show that there is transport of carbonate or bicarbonate ion in supported liquid membrane system in absence and presence of carriers. The carriers show enhanced transport of carbonate or bicarbonate ions. The toluene and carriers are required in small amounts. The permeability coefficient increases for the stir-

ring speed of source and receiving phase in the range $n = 40$ to 110 min^{-1} . The increase in P value along with an increase in the carbonate ion concentration was observed for the $c = 0$ to 0.04 mol dm^{-3} range. The P value increases with the increase in sodium hydroxide concentration range from $c = 0$ to 1 mol dm^{-3} . The permeability coefficients were determined for the different anions. The durability of microporous polypropylene support was satisfactory. The liquid membrane system is easy to operate and simple. The carbonate ions can be continuously pre-concentrated from the dilute solutions. Hydrogen peroxide shows the enhanced permeability coefficient of carbonate or bicarbonate ions. Carbon dioxide sequestration can be carried out in a simple way with less effort and without creating polluting chemicals. The illustrated model shows the effect of cross-section area of membrane on the transport of carbonate ions through supported liquid membrane. It was concluded that the reactive molecular separation of carbon dioxide was observed with metal oxide or metal hydroxide or metal carbonate. Where M is divalent or monovalent ion



The reactive separation of CO_3^{2-} and HCO_3^- ions were observed by ion exchange mechanism where x is one or two.



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List of symbols

- A – cross-section area, cm^2 , m^2
- c – concentration, mol dm^{-3}
- d – average pore diameter, μm
- J – permeability of ions, $\text{mol m}^{-2} \text{ s}^{-1}$
- K – equilibrium constant
- l – membrane thickness, cm
- n – stirring speed, min^{-1}
- P – permeability coefficient, $\text{m}^2 \text{ s}^{-1}$
- t – time, min , h
- V – volume, L , mL
- R^+ – liquid anion exchanger
- L^- – liquid cation exchanger

Subscripts

- aq* – aqueous phase
s – source phase
m – membrane phase
r – receiving phase

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