Transport of carbonate ions through supported liquid membrane by using Alamine 336 and trioctylphosphine oxide as carriers

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RESEARCH LETTER

Transport of carbonate ions through supported liquid membrane by using Alamine 336 and trioctylphosphine oxide as carriers

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Transport studies were carried out for carbonate ions through supported liquid membrane (SLMs) by using Alamine 336 and trioctylphosphine oxide (TOPO) as carriers. Experimental variables were investigated, such as concentration of carbonate ion (10^{-5} to 4×10^{-2} M), carriers (10^{-5} to 10^{-1} M), and alkali (0.01–0.5); and stirring speed (50–150 rpm) of bulk solutions. The use of combined carriers Alamine 336 and TOPO shows a synergic transport of carbonate ions. The stability of the SLM system in relation to the transport of carbonate ions has been studied. The enrichment of carbonate ions (10^{-6} to 4×10^{-2} M) from the dilute solution was explored. The different combinations of amines with TOPO show synergic permeability of the carbonate ions through SLM system.

Keywords: supported liquid membrane; carbonate ion; Alamine 336; trioctyl phosphine oxide (TOPO); synergic effect

Nomenclature

aq aqueous phase, mL, ml
s   source phase, mL, ml
m   membrane phase, mL, ml
r   receiving phase, mL, ml
t time, sec, min, h
k rate constant, $m^2\ h^{-1}$, $cm^2\ min^{-1}$
R   Alamine 336 (tri-octyl/decyl amine), $mol\ dm^{-3}$, mol L^{-1}, M
S   TOPO (trioctylphosphine oxide), $mol\ dm^{-3}$, mol L^{-1}, M
P permeability coefficient, $m^2\ s^{-1}$
A cross-section area, cm^2, m^2
l thickness of membrane support
V volume, L, mL
C_0 initial concentration at time zero, mol L^{-1}, M
C_t concentration at time t, mol L^{-1}, M

Introduction

The atmosphere of the earth is warming up due to the released heat from heat sources such as refineries, industries, thermal power stations, vehicles, growing population, cooking burners, aircrafts, volcanoes, sun, etc., leading to global warming, which is currently an important issue. The released heat and carbon dioxide (CO_2) from these different sources

should be balanced by increasing the forestry. However, the emission of CO_2 increases and thus it is crossing the threshold limit in the atmosphere. We could reduce the global warming by reducing the use of natural gas, petroleum and coal fuels, and also by developing commercial processes for capturing of CO_2. The atmospheric CO_2 should be transferred to carbonate form, either by chemical or physical capturing processes. Therefore, there is a need to develop mixed metal oxide or amine-based adsorbents, besides the natural process of rain, to capture and transport CO_2 in the form of carbonate. The present research is aimed at achieving the goal of carbonate ion transport using the amine-based and their combination carriers. The solid carrier adsorbents, such as mixed metal oxides, alkali carbonates, zeolites, carbon, and amine-based solid adsorbents need heat to desorb CO_2 from them. However, in the SLM processes, CO_2 desorption from the chemically bonded carrier is carried out with chemical species.

The separations of anions were carried out by solvent extraction, ion exchange, gel permeation chromatography, and electrophoresis. These techniques have disadvantages, such as third-phase formation, large volume, and high-energy input. The reactive and selective separations have been described in details of carbonate ions by using ionic liquids, grafted amines, and supported amines on porous solid

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supports. However, the reactivity and solubility limitations of carbonate ions in the membrane operation make the separations difficult. Therefore, there is a need to develop new methods for the separation and pre-concentration of carbonate, sulfate, and nitrate anions. However, the studies on the separations of carbonate ions have not yet been concerned with the other anions in aqueous solution. Therefore, attempts have been made to explore the transport of carbonate ions through supported liquid anion exchange membranes. High molecular weight amines and phosphates or phosphine oxides form liquid ion exchangers with mineral acids. The formed liquid anion exchangers could be used for the transport of anions.

A brief survey of the literature is presented below. Solvent extractions of anions and cations and their fundamentals have been provided in (*1*). CO_2 separation was explored from flue gas by using gel-supported facilitated transport membrane. The reaction of CO_2 with gel forms carbonates (*2*). Facilitated transports of CO_2 were investigated through the amine carbonate formation separation through SLMs of aqueous amine solutions (*3*). Ionic liquid carbonates formation was used to separate CO_2 from H_2 using facilitated supported ionic liquid membrane (*4*). The reactive separations of CO_2 were carried out using CO_2 selective membranes containing amines in cross-linked poly (vinyl alcohol) (*5*). High molecular ionic solvents are used to separate CO_2 (*6*). The high molecular weight ionic liquids were explored to separate carbonate ions (*7*). High pressure was used to increase the solubility of CO_2 in ionic liquid (*8*). The chemical reactions were carried out using ionic liquid and CO_2 (*9*). Anions were explored to increase the CO_2 solubility into ionic liquids (*10*). The functionalized ionic liquids were used for the absorptive separation of CO_2 (*11*). The binary ionic liquids were used to increase the solubility of CO_2 (*12*). The CO_2 solubility was explored in the ionic liquids at low pressure (*13*). Although ionic liquids are used as non-polluting reagents, they suffer from solubility problems. The solubility of CO_2, C_2H_6, CH_4, O_2, N_2, H_2, Ar, and CO gases was explored in ionic liquids (*14*). The solubility of CO_2 was studied through the supported ionic liquid membranes (*15*). The attempt to separate the acidic gases CO_2, SO_2, and NO_x with supported ionic liquid membranes involved electro-chemical modulated complexation (*16*). The CO_2 by carbonate formation was explored for separation of CO_2 through supported ion liquid membrane (*17*). The global challenges and strategies were explored for the control, conversion, and utilization of CO_2 for sustainable development involving energy, catalysis, adsorption, and chemical processing (*18*). Selective

hydrogen polymeric membranes were used from CO_2 (*19*). Hollow fiber membrane solvent extractions were used for the reactive separations of CO_2 (*20*). CO_2 was captured by using ionic liquids (*21*). Phosphate-containing anionic liquids were used to separate gases with supported ionic liquid membranes (*22*). The ionic liquids were used to separate the gases (*23*). The supported amine liquid membranes were used to separate CO_2 by means of reactive separations (*24*). The reaction rate and equilibrium of CO_2 with amine were explored through supported liquid amine membranes (*25*). CO_2 was separated by using CO_2-reactive CO_2-selective polymeric membranes containing amines in cross-linked poly (vinyl alcohol) (*26, 27*). The permeability and selective separations of CO_2 was explored through supported ionic liquid membranes (*28*). The reactive separation of products and reactants were carried out using supported ionic liquid membranes (*29–34*). The synergic ion transport studies were also reported by using PC-88 A and Aliquat 336, liquid cation and anion exchangers, respectively. These liquid anion exchangers could be used for the reactive selective separations of carbon dioxide at 100–150°C by using their reversible chemical reaction with CO_2 (*35*). The synergic ion transports of carbonate ions were also reported by using Primene JMT and tributyl phosphate (TPB) as carriers. These high molecular weight amines and phosphates could be used as liquid anion exchangers in individual or mixtures in presence of moisture for the separation carbon dioxide from flue gas at 100–150°C (*36*). Aliquat 336 and Primene JMT both quaternary and primary high molecular weight amines, respectively, in presence of cation exchanger (PC-88A) and solvating solvent (TBP), chemically bond the CO_2 in presence of moisture. The overall mechanism the liquid anion exchange is supported by cation exchange. In the present investigations the new concept has been explored, apart from the carriers reported earlier (*35, 36*), by selecting both high molecular weight solvating extractants Alamine 336 and TOPO (trioctyl phosphine oxide) for the transports of carbonate ions through the SLM. Aliquat 336 is a quaternary amine with anion exchanging ability of carbonate ions; desorption of carbonate ions from the quaternary amine could be carried out by thermal decomposition of carbonate ions at higher temperature. However, CO_2 is strongly bound to the Primene JMT (primary amine) and hence CO_2 removal from Primene JMT needs higher thermal energy. However, solvating extractants TBP, TOPO, Alamine 336, etc., extract the CO_2 molecules, which are weakly bound, in the presence of moisture. Therefore, the removal of CO_2 and moisture from the solvating extractants needs low thermal energy in

comparison with that of Aliquat 336 and Primene JMT. Therefore, it is an interesting aspect to explore the carbonate ion transport by using the high molecular weight solvating extractants. The high molecular weight solvating extractants, Alamine 336 and TOPO (trioctyl phosphine oxide), with high boiling points after immobilizing over porous solid extractants could be used either individually or in combinations for the reactive selective separations of CO_2 from the flue gas mixture in presence or absence of moisture at post-combustion condition ($<150°C$) by using the temperature as driving force. The temperature is the driving force for the chemical adsorption and desorption of CO_2 over phospahte and amine-based solvating extractants at higher temperatures in the gas, liquid, and solid phases reactions, where solvating extractants were supported over the porous solid support, such as alumina, silica, etc. In the liquid-phase reactions, sodium hydroxide was used as the driving force for the transport of carbonate ions. Therefore, the present investigations express the carbonate ion transports through SLM. The state of the art of research shows that ionic liquids are emerging as CO_2 sequestering reagents at low or high temperature. But it suffers from the CO_2 solubility at high as well as low temperatures. The membrane process for CO_2 sequestrations or separations based on reactions are carried out through carbonate formation either in the liquid or solid form, except, those separations based on the physical gas molecular sizes. Thus, reactive anion transports of carbonate ions are the important aspects to explore either by using ionic liquids or anion exchangers. The present research investigations were proposed for the carbonate ion transports after CO_2 dissolution in distilled water. The solubility of carbonate ions depends on their reaction ability in the liquids or solids at different temperatures.

There is also day-by-day advancement in the separations of anions or cations by the supported solid or liquid membrane. Recently, it has been reported that the transport of Tm (III) and Dy (III) through a dispersion supported liquid membrane (DSLM) consisting of polyvinylidene fluoride membrane (PVDF) as the liquid membrane support and dispersion solution concluding HCl solution as the stripping solution and 2-ethyl hexyl phosphonic acid-mono-2-ethyl hexyl ester (PC-88A) dissolved in kerosene as the membrane solution (37, 38). A new type of particle-loaded membrane adsorber module was prepared by coiling adsorptive fibers. In order to characterize the material and predict the module performance, the protein accessibility and mass flux of single fibers were tested in incubation experiments. The decreasing the distance between two adjacent

fibers during the coiling process affects the flow resistance and the dynamic adsorption capacity of the module (39). The new design of the membrane cell and the new development of the carriers are coming into existence. Two SLMs containing two different carriers but formed by the same polymer support polyvinylidene difluoride (PVDF) and the same organic phase (xylene), were explored to realize the facilitated transport of vanadium ions (VO_2^+) from the concentrated acid solutions. The SLM support was a micro-porous PVDF polymer film of thickness 100 μm with pore size 0.45 μm which had been impregnated with a solution of xylene containing 0.01 M of one of the carriers, the Di-(2-ethylhexyl) phosphoric acid (D_2EHPA) or the Trioctylphosphine oxide (TOPO) (40). The SLM were studied in various fields – analytical, inorganic and organic chemistry, chemical engineering, biotechnology, and biomedical engineering. This technique offers the advantages of active transport, possible usage of expensive carriers, high selectivity, easy scale-up, low energy requirements, low capital and operating costs, etc. A brief overview of mechanisms and kinetic studies of SLM-based separations was reported along with problems concerning the stability and the possible applications of SLM (41). From an environmental view point, the supported liquid or solid membrane is an advantageous technique due to low volume and cost, high efficiency, easy design and operation, no pollution, on line process, easy to carry a unit, etc.

Therefore, it is worthwhile to study the anion transport behavior of carbonate ions with liquid anion exchangers using SLM technique. The proposed liquid membranes have wide applications in separations, purifications, and enrichments of several anions using commercial solvating and amine extractants (carriers). The liquid membrane technique is simple, easy to operate, and economically viable. The transports of carbonate ions through SLM are controlled by their solubility, reactivity, and diffusion through solvent medium. The transports of carbonate anions are explored from source phase to receiving phase through liquid membrane phase in presence of carriers in liquid membrane phase under the steady-state dynamic conditions in which chemical reactions and diffusion processes were in equilibrium. The extracted carbonate ions into liquid membrane phase could be stripped out by alkali metal hydroxide in the receiving phase. Sodium bicarbonate and carbonate are the important products in the commercial markets which are formed during the transport of carbonate ion from source to receiving through membrane phase.

Results and discussions

Evaluation of permeability coefficients (P)

The carbonate ion concentration variation profiles are shown in the Figure 1(a) for the source and receiving phases with respect to time. The permeability coefficients (P) are evaluated by using the cross-section area of membrane (A), volume of source phase (V_s), thickness of membrane (l) and the slope of the plot of log C_t/C_0 vs. t. The plots of log C_t/C_0 vs. t are shown in the Figure 1. The plots C_t/C_o of carbonate ion concentrations variation with respect to time in source phase show the linear plots. The evaluated permeability coefficients (P) were used to asses the experimental data for the transports of carbonate ions through supported liquid Alamine 336 and TOPO membranes at the experimental conditions.
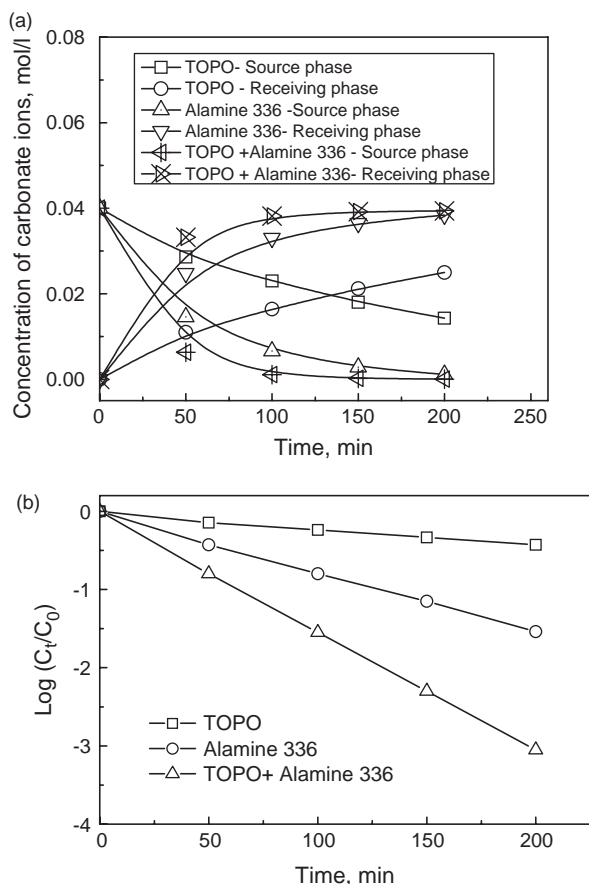

Figure 1. (a) The carbonate ion concentration profile for the source and receiving phases with respect to time, carbonate ion = 0.04 M, Alamine 336 = 0.1 M, TOPO = 0.1 M, NaOH$_r$ = 0.1 M, V_s = 35 ml, V_r = 25 ml, and A = 11.94 cm^2. (b) The plot of log C_t/C_0 vs. time, carbonate ion = 0.04 M, Alamine 336 = 0.1 M, TOPO = 0.1 M, NaOH$_r$ = 0.1 M, V_s = 35 ml, V_r = 25 ml, and A = 11.94 cm^2.

Effect of stirring of bulk phase on permeability coefficients (P)

The stirrings of source and receiving solutions are essentials to achieve the diffusions of carbonate ions in bulk solutions in order to minimize the barriers of diffusion layers in the source, membrane, and receiving phases. The source and receiving bulk phases were independently stirred in the range of 50–150 rpm. The permeability coefficients (P) were evaluated for overall range of rpm 50–150. Log P values were plotted against rpm (Figure 2). The increases in the log P values were observed in the range of 50–120 rpm. The increase in log P shows the minimizations process of the diffusion barriers among source, membrane, and receiving phases. Log P were almost observed constant at 120–150 rpm. The constant log P shows diffusion layers thickness among the source, membrane, and receiving phases. The log P values were explored at 125 rpm for further experiments. In the absence of carriers, the transport of carbonate ions were observed, however, in the presence of carriers, the transports of carbonate ions were observed synergically.

Effect of carbonate ion concentration on permeability coefficients (P)

The carbonate ion transports from the source to receiving through membrane phase has been studied with the variation of carbonate ion concentrations in the source phase. The carbonate ion concentrations in the source phase were varied from 10^{-6} to 0.04 M. The carriers at concentrations of 0.1 M Alamine 336 and 0.1 M TOPO were used in membrane phase 0.1 M NaOH was used in receiving phase for the stripping out the carbonate ions from the membrane phase. The pH of the source phase was the pH of carbonic acid solution. The permeability
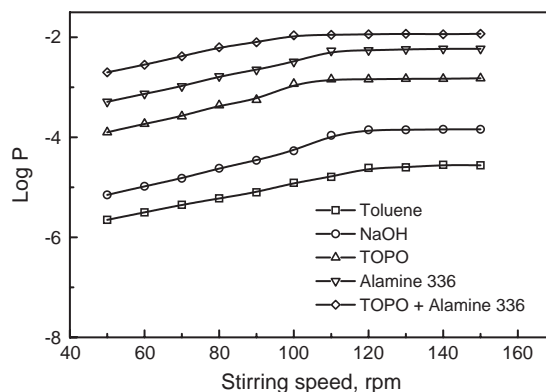

Figure 2. The variation of stirring speed of source and receiving phases on the permeability coefficient (P), carbonate ion = 0.04 M, Alamine 336 = 0.1 M, TOPO = 0.1 M, NaOH$_r$ = 0.1 M, V_s = 35 ml, V_r = 25 ml, and A = 11.94 cm^2.

coefficients (*P*) were calculated and plotted against the initial concentration of carbonate ion (Figure 3(a)). The dependency of the permeability coefficients (*P*) carbonate ions on the carbonate ion concentrations in the source solution have been investigated in the Figure 3(a). The permeability coefficients (*P*) increase along with the increase in the carbonate ion concentrations in the source phase in overall range 0–0. 04 M of carbonate ions. The results indicate that the permeability coefficients (*P*) depend on the initial concentration of carbonate ion in the source solution. The pH of source solution is very important in order to form the liquid ion exchangers of carbonic acid with solvating solvents Alamine 336 and TOPO, therefore, the pH of source solution is the maintained as the pH of presence of carbonic acid in the source phase as it is without the adjustment.

Effect of alkali concentration on permeability coefficients (*P*)

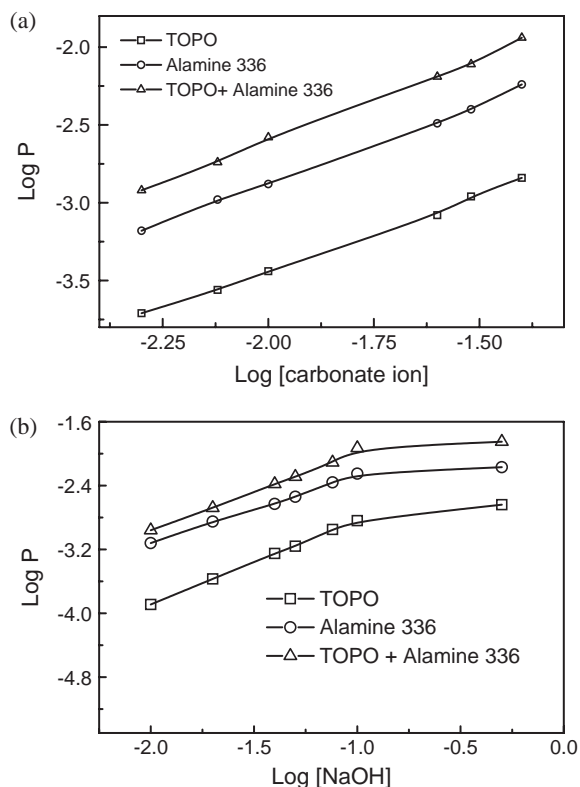The transports of carbonate ions through the source and membrane interface, and of the membrane and

Figure 3. (a) The dependence of *P* with carbonate ion concentration in the source solution, Alamine 336 = 0.1 M, TOPO = 0.1 M, $NaOH_r$ = 0.1 M, V_s = 35 ml, V_r = 25 ml, and *A* = 11.94 cm². (b) The relation between *P* and sodium hydroxide concentration of receiving solution, carbonate ion = 0.04 M, Alamine 336 = 0.1 M, TOPO = 0.1 M, V_s = 35 ml, V_r = 25 ml, and *A* = 11.94 cm².

receiving interface depend on the difference in the gradient concentrations of carbonate ions in source, membrane, and receiving phases. In addition to this, the driving forces for the transport of carbonate ions from the source to receiving through membrane phases are the important parameters. The affinity of carriers toward the carbonate ions at the source and membrane interface is also important factor, and releasing ability of carriers of carbonate ions at the membrane and receiving interface is also essential, therefore, the driving force sodium hydroxide concentration was used for the transports of carbonate ions from the source to receiving through membrane phases. Moreover, the sodium hydroxide concentration was varied in the receiving phase from 0.1 to 0.5 M. The carbonate ion concentration 0.04 M was used in the source phase. The 0.1 M Alamine 336 and 0.1 M TOPO concentrations were used in the membrane phase. The increased alkali concentration in the receiving phase increases the stripping of carbonate ions from the membrane phase. The sodium hydroxide concentration 0–0.5 M was varied in the receiving phase (Figure 3(b)). The sodium hydroxide concentration 0–0.5 M increases log *P* under the same experimental conditions.

Effect of carrier concentration on permeability coefficients (*P*)

In the absence of the carriers, the carbonate ion transports through the supported liquid membrane have been studied. It was observed that in the presence of the carriers in the membrane phase enhances the transport of carbonate ions through the supported liquid membrane. Therefore, the concentrations of carriers of Alamine 336 and TOPO were varied in the membrane phase in order to asses the role of carriers as individual or in mixed. The carrier concentrations were varied in the range from 10^{-4} to 0.5 M at the concentrations of 0.04 M carbonic acid and 0.1 M NaOH in the source and receiving phases, respectively. The permeability coefficients (*P*) were calculated for the different concentrations of Alamine 336 and TOPO. The measured permeability coefficients values were used for the interpretation of results of carbonate ions. The permeability coefficients (*P*) of carbonate ions show the higher value with the increased concentrations of the Alamine 336 over the studied range (Figure 4(a)). However, carbonate ion transports were less in the individual carriers Alamine 336 or TOPO supported liquid membrane systems in the comparison with that of Alamine 336 and TOPO mixed carriers supported liquid membrane systems. The concentrations 10^{-4} to 0.5 M of TOPO were explored for the permeation studies of carbonate
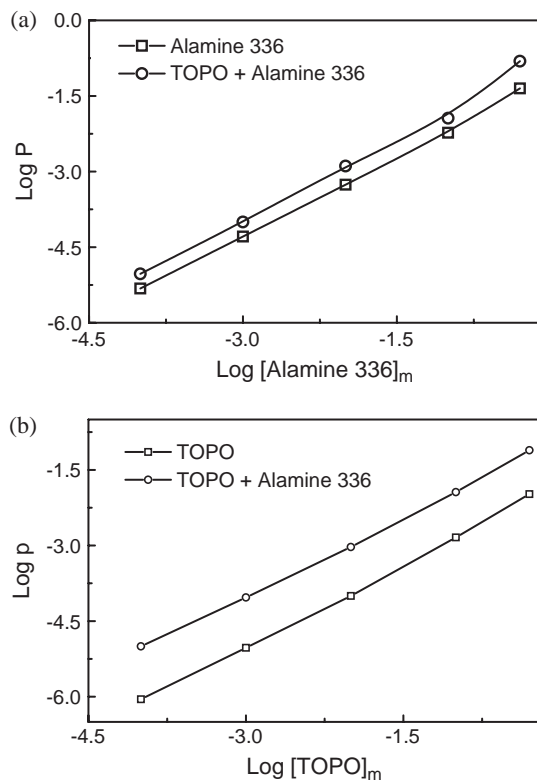
Figure 4. The effect of carrier concentration on permeability coefficient (P). (a) Carbonate ion $=0.04$ M, TOPO $=0.1$ M, NaOH$_r$ $=0.1$ M, V_s $=35$ ml, V_r $=25$ ml, A $=11.94$ cm^2, and Alamine 336 variation. (b) carbonate ion $=0.04$ M, TOPO $=0.1$ M, NaOH$_r$ $=0.1$ M, V_s $=35$ ml, V_r $=25$ ml, A $=11.94$ cm^2, and TOPO variation.

ions through the supported liquid membranes. Increased permeability coefficients were observed for the TOPO concentrations from 10^{-4} to 0.5 M (Figure 4(b)). Moreover, carbonate ion transports were less in the individual carrier TOPO-supported liquid membrane systems in comparison with that of Alamine 336 and TOPO mixed carriers supported liquid membrane systems. However, in the comparison of supported liquid membrane systems with the solvent extraction systems, the results indicate that the carbonate ion transports can be carried out from the source to the receiving phase through membrane phases with the use of 30–40 times less volume of membrane phase (extractants) in the supported liquid membrane system in comparison with those of organic phase in the solvent extraction systems. Thus, the supported liquid membrane systems become economically viable by use of low volume of membrane phases, and extractions and stripping can be carried out efficient way simultaneously and continuously. The carbonate ion transport results show that the individual carrier supported liquid membrane systems show low transports of

carbonate ions from source to receiving through membrane phases in comparison with those of mixed carriers supported liquid membrane systems. The synergic effects by using mixed carriers in the supported liquid membrane systems have been observed for the transports of the carbonate ions.

Permeability coefficient for different anions

Ion exchange and solvent extraction techniques were used for the separation and enrichment of anions and cations. The attempts have been made to study the selective transports of anions by using the different anions, such as sulfate, nitrate, and carbonate. Transport studies of different anions sulfate, nitrate, and carbonate were carried out from source to receiving through membrane phase. The transports of anions from the mixture of different anions from the source phase are important in order to study the competitive transports of carbonate or bicarbonate anions from the mixture of these anions. Each of the sulfate, carbonate or bicarbonate, and nitrate anion in acidic form was used in a separate experiment in the source phase at the same concentration of 0.04 M, while 0.1 M Alamine 336 and 0.1 M TOPO were used in the membrane phase, and 0.1 M NaOH were used in the receiving phase. The observed permeability coefficients for these anions are illustrated in the Figure 5. The carbonate anions were transported more selectively in comparison with those of nitrate and sulfate anions. However, nitrate anions were transported more selectively in comparison with those of sulfate anions. Similar trends were observed in the individual or mixed carriers supported liquid membrane systems.
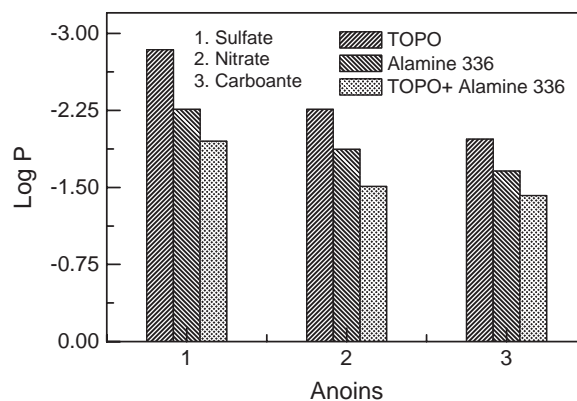

Figure 5. The permeability coefficients for different anions, carbonate or sulphate or nitrate ion $=0.04$ M, Alamine 336 $=0.1$ M, TOPO $=0.1$ M, NaOH$_r$ $=0.1$ M, V_s $=35$ ml, V_r $=25$ ml, and A $=11.94$ cm^2.

Enrichment of carbonate ions

The enrichment of carbonate ions were carried at the membrane phase concentrations of the carriers 0.1 M Alamine 336 and 0.1 M TOPO. The initial concentrations of carbonate ions in the source solution were varied in the range of 10^{-6} to 10^{-2} M. The low concentrations of carbonate ions were prepared from the higher standardized concentrations of carbonate ion solutions. The observed enrichment factors (EF is a ratio of carbonate ion concentrations at time in the receiving to source phase) with respect to initial carbonate ion concentration in source solution have been given in the Figure 6(a). The EF decrease with the increase in the initial carbonate ion concentrations in the source phase. Thus, the enrichment of carbonate ions can be carried out from dilute solutions. The sodium hydroxide 0.1 M concentration is the driving force for the uplift of carbonate ion concentrations from the source to receiving though membrane phases. The volume of receiving phase can be reduced with the maintaining same of sodium hydroxide concentration in the receiving phase. The
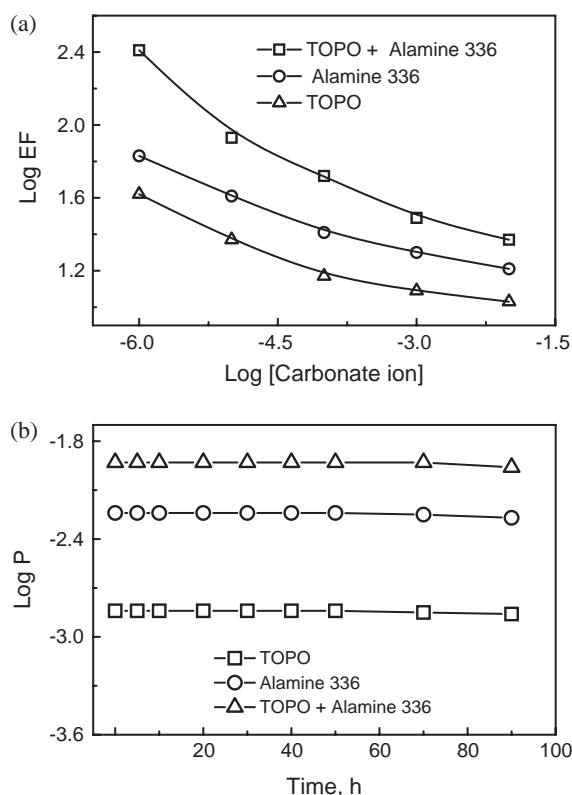
maximum concentration of carbonate concentrations (10^{-6} M) from the dilute carbonate ion concentrations from source solution were lifted up to receiving phase. However, the uplifting of carbonate ion concentrations from higher carbonate ion concentrations (0.01 M) were the equilibrium constraints prohibit the uplifting of maximum carbonate ions from the higher concentrations of carbonate ions from the source solution.

Stability of supported liquid membrane

In this paper, the polymeric porous solid membrane support polypropylene with an average pore size 0.04 μm was used. The supported liquid membranes were prepared by soaking the porous solid support in the toluene solutions containing the Alamine 336 and TOPO carriers in the desired concentrations. The supported liquid membrane systems have been continuously used for the stability by using same source and receiving phases for the 90 h. The intact of the carriers in the membrane phase was checked in the immobilized form in the porous solid membrane support during the operations (Figure 6(b)) by analyzing the permeability coefficient (P) of carbonate ions. After 60 h, the permeability coefficients of carbonate anions decrease with the increase in the operation time. During this operation, the immobilized carriers slowly get leaked from the membrane phase to aqueous phase by losing their immobilization intact in the pores of porous solid membrane support. The micro-porous polypropylene supports were stable during the whole operation process of the supported liquid membrane systems (first case).

The stability of the supported liquid membrane was also tested by carrying out the transport studies repeatedly using the same supported liquid membrane for many consecutive runs using fresh solutions of source and receiving phases for each of run in both the compartments (second case). In the first case, the stability of supported liquid membrane was more competitive than in comparison with that of second case. The losses of the carriers were observed from the membrane to the aqueous phases in the second case.

Effect of different amines on permeability coefficient of carbonate ions

The different amine solvating carriers were used in the membrane phase to study the effect of amine carriers on the transports of carbonate ions through the supported liquid membrane systems. Figure 7 shows the effect of primary (Primene JMT), secondary (Amberlite LA1), and quaternary (Aliquat 336) amine in presence of TOPO on the transport of

Figure 6. (a) The pre-concentration of carbonate ion, Alamine 336 = 0.1 M, TOPO = 0.1 M, $NaOH_r$ = 0.1 M, V_s = 35 ml, V_r = 25 ml, and A = 11.94 cm². (b) The stability of supported liquid membrane, carbonate ion = 0.04 M, Alamine 336 = 0.1 M, TOPO = 0.1 M, $NaOH_r$ = 0.1 M, V_s = 35 ml, V_r = 25 ml, and A = 11.94 cm².
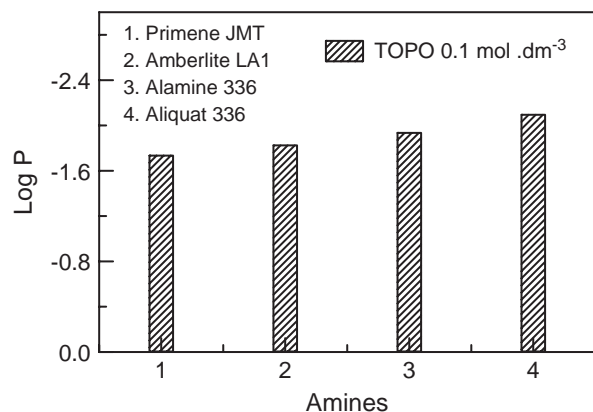
Figure 7. The permeability coefficient for different amines, carbonate ion = 0.04 M, Amine (Primene JMT, Amberlite LA1, Alamine 336 and Aliquat 336) = 0.1 M, TOPO = 0.1 M, $NaOH_r$ = 0.1 M, V_s = 35 ml, V_r = 25 ml, and A = 11.94 cm^2.

carbonate ions from source to receiving through membrane phase. The results indicate that primary amine (Primene JMT) in the presence of TOPO effectively transports carbonate ions from source to receiving through membrane phase in comparison with that of other amines under the same experimental conditions.

Experimental

Reagents and apparatus

The reagents used during the experimental studies were TOPO (TOPO, Mol. wt 386.63) (Aldrich Chemicals CO, USA), Alamine 336 (tri-octyl/decyl amine), Amberlite LA 1 (N-dodecenyl (trialkyl-methy1) amine), Primene JMT (Roam and Haas Co), and NaOH (Aldrich Chemicals CO, USA) (99.99% with purity). Toluene and other reagents were used from Merck India Ltd. Carriers solutions in toluene in the concentration range of 10^{-5} to 10^{-1} M were prepared by mechanically shaking for an hour at with an equal volume of aqueous solution containing same concentration range of 10^{-5} to 1.4×10^{-2} M of carbonic or sulfuric or nitric acid. After equilibration, the aqueous and organic phases were separated by centrifugation. The different concentrations in the range 10^{-5} to 10^{-1} M of the carriers were used to impregnate by repeated treatment of soaking in the micro-porous polypropylene membrane support. The lower concentrations of carriers' solutions were prepared by diluting a certain volume of higher concentrated carrier solution with toluene. Carbonate ion solutions were prepared by passing 20–30 ml/min of flow rate of CO_2 in the distilled water for 3–4 h. The dilute solutions of

carbonate, sulfate, and nitrate ions were prepared from the standardized higher concentrated (0.03–0.05 M) solutions. The low concentrations of carbonate, sulfate, and nitrate ions were determined by ion-selective electrodes. The higher concentrations of carbonate, sulfate, and nitrate ions in the solutions were estimated by acid–base titrations.

Preparation of supported liquid membrane (SLM)

A membrane 2500 (Celenease Co., USA) is a micro-porous polypropylene membrane of thickness 2.5×10^{-3} cm, average pore size 0.04 μm, porosity 45% was used as the membrane support for the immobilization of individual carrier or mixed carriers through toluene solvent medium (Table 1). The carriers were used in the immobilized form in the porous solid support. The amounts of carriers used in the supported liquid membrane were 30–40 time less to solvent extraction process. Sodium hydroxide was used as stripping agent. The carriers were immobilized in the pores of the porous solid membrane supports by soaking in the desired concentration, either of individual carrier or mixed carriers in the range of 10^{-5} to 5×10^{-1} M at the ambient conditions for 2 h. The amounts were determined of immobilized carriers in the porous solid supports by weighing the porous solid membrane support before and after the immobilization of carriers at the ambient conditions. The experimental apparatus used in this investigation to measure the permeability coefficient (P) is described in Figure 8. The used supported liquid membrane was with an interfacial area 11.94 cm^2. The ion transport studies have been carried out at ambient conditions.

Experimental procedure

The design of the membrane cell is shown in the Figure 8. The cell has two round bottom flak compartments which are connected by round contact surface area. A source solution in the concentration range of 10^{-5} to 5×10^{-2} M of carbonate or sulfate or nitrate ion in 35 ml volume in the one compartment of the cell, and the 25 ml receiving solution containing the sodium hydroxide concentration in the

Table 1. Characteristics of porous solid membrane support.

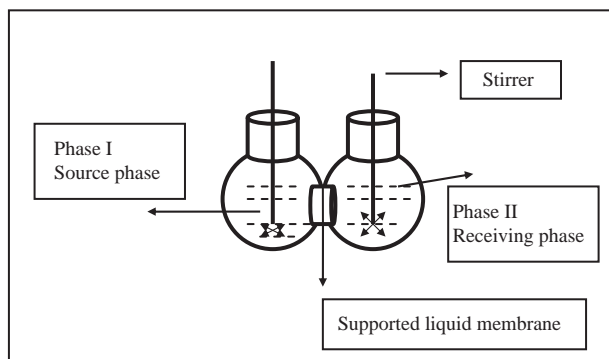| Sr. no.	Characteristics	Value
1	Material	Polypropylene
2	Porosity	45%
3	Thickness	2.5×10^{-3} cm
4	Pore size	0.04 μm
5	Cross-section area	11.94 cm^2

Figure 8. The schematic presentation of the membrane cell.

range of 0.01–0.5 M in the other compartment of the cell were taken (Table 2). The source and receiving solutions separated by the supported liquid membrane were in the contact without leakage into each other. The low concentrations of carbonate, sulfate, and nitrate ions were determined by ion-selective electrodes. The higher concentrations of carbonate, sulfate, and nitrate ions in the solutions were estimated by acid–base titrations. The samples of the source and receiving solutions were withdrawn and analyzed for carbonate ions or other anions. The ion transport experiments have been carried out at ambient conditions.

Table 2. Some quantities and properties of supported liquid membrane system.

Sr. no	Property of membrane cell	Quantity
1	Volume, ml	35
	Source phase	1.26×10^{-3}
	Membrane phase	25
	Receiving phase	
2	Concentration, mol/l (M)	10^{-5} to 0.05
	Carbonic acid	10^{-5} to 0.5
	Carriers	0.01 to 0.5
	Sodium hydroxide	
3	Boiling point, °C	
	Alamine 336	200 and 300
	TOPO	213
	Melting point °C, TOPO	50
4	Solubility in aqueous	
	Alamine 336	Negligible (<0.1%)
	TOPO	Insoluble in cold and hot water
	Solubility in toluene	
	Alamine 336	Soluble
	TOPO	Soluble
5	Specific gravity, g/cm^3	
	Alamine 336	0.825
	TOPO (water = 1)	0.88
6	Viscosity value, cP (25°C)	1.59
	Alamine 336	

Ion transport mechanism

The solvent extraction is carried out in two steps: extraction and stripping for separation or enrichment of carbonates ions. In the conventional solvent extraction, the extraction and stripping processes are carried out one after the other. However, during these processes, different modes of occurrences 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. The membrane technique eliminates all such shortcomings. Figure 9 illustrates the transport of carbonate ions from source to receiving through liquid membrane phase. The continuous ion transport of carbonate ions in supported liquid membrane can be simultaneously carried out as extraction and stripping processes.

In the supported liquid membrane cell, the rate of change of concentration of carbonate or bicarbonate ion (C^s) in the source phase with respect to time (t) through a cross-section area (A), volume of source phase (V_s), and membrane thickness (l) can be given by Equation (1), where k is a rate constant.

$$-dC^s/dt = k.A/(V_s \cdot l) \cdot C_0^s. \qquad (1)$$

After integrating Equation (1), the permeability coefficient (P) of transport of carbonate ions is obtained by Equation (2).

$$\mathrm{Ln}\,(C_t^s/C_0^s) = -(A/V_s) \cdot (P/l) \cdot t, \qquad (2)$$

where C_0 is the value of C_t at time zero and P is permeability coefficient.

The distribution ratios of carbonic acid and sodium hydroxide for aqueous and toluene determined were 10.75 and 2.10, respectively. The distribution ratios of carbonate ions indicate that the there is transports of ions through supported liquid membrane containing toluene phase in absence of carriers. The use of carriers show the synergic transport of carbonate ions through supported liquid
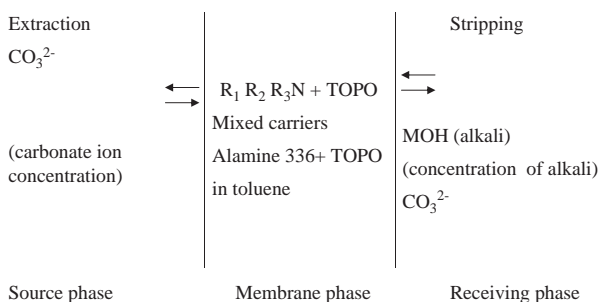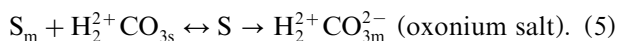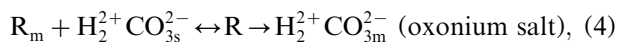

Figure 9. The presentation of carbonate ion transport through supported liquid membrane.
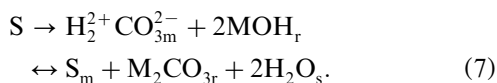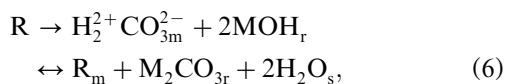
membrane. The driving forces for the transport of carbonate ions from source to receiving solution through membrane phase are the solubility of carbonate ions in water and toluene, and difference in concentration gradients in the source solution, membrane and receiving phases. The extraction and stripping processes from the source to membrane phases, and membrane to receiving phases can be given reversibly, respectively. The overall carbonate ion formation was given under the chemical species concentrations through supported liquid membrane by the following equation:

$$2MOH + H_2CO_3 \leftrightarrow M_2CO_3 + 2H_2O, \quad (3)$$
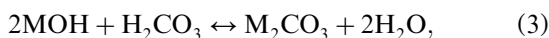
where M is the monovalent metal ion. The solvating solvents, TOPO and Alamine 336, form the oxonium salts with carbonic acid, H_2CO_3. These oxonium salts act as liquid anion exchangers for reversibly extraction and stripping of carbonate ions from the source to membrane phases, and also membrane to receiving phases, respectively. The use of Alamine 336 and TOPO carriers in the membrane phase synergically enhances the carbonate ion transports. The Alamine 336 (tertiary amine) and TOPO for simplicity are represented by R and S, respectively. The formations of liquid anion exchangers of TOPO and Alamine 336 with carbonic acid were given by the following equations:

$$R_m + H_2^{2+}CO_{3s}^{2-} \leftrightarrow R \rightarrow H_2^{2+}CO_{3m}^{2-} \text{ (oxonium salt), (4)}$$

$$S_m + H_2^{2+}CO_{3s} \leftrightarrow S \rightarrow H_2^{2+}CO_{3m}^{2-} \text{ (oxonium salt). (5)}$$
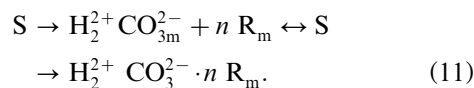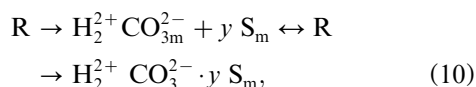
The formed liquid anion exchangers transport bicarbonate anions from the source and membrane interface to the membrane to receiving interface as presented by the following equations:

$$R \rightarrow H_2^{2+}CO_{3m}^{2-} + 2MOH_r$$
$$\leftrightarrow R_m + M_2CO_{3r} + 2H_2O_s, \quad (6)$$

$$S \rightarrow H_2^{2+}CO_{3m}^{2-} + 2MOH_r$$
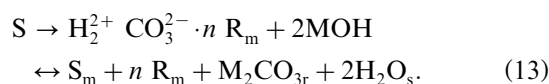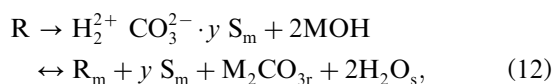$$\leftrightarrow S_m + M_2CO_{3r} + 2H_2O_s. \quad (7)$$

The solvating solvents also form the solvating complexes with carbonate ions at source and membrane interface. The formations of solvating complexes are given by Equations (8) and (9).

$$Y S_m + H_2CO_{3s} \leftrightarrow y S_m \cdot H_2CO_3, \quad (8)$$

$$n R + H_2CO_{3s} \leftrightarrow n R_m \cdot H_2CO_3. \quad (9)$$

The synergic complex formations also took place at the source and membrane interface. Those complex formations are given by the following equations

$$R \rightarrow H_2^{2+}CO_{3m}^{2-} + y S_m \leftrightarrow R$$
$$\rightarrow H_2^{2+} CO_3^{2-} \cdot y S_m, \quad (10)$$

$$S \rightarrow H_2^{2+}CO_{3m}^{2-} + n R_m \leftrightarrow S$$
$$\rightarrow H_2^{2+} CO_3^{2-} \cdot n R_m. \quad (11)$$

Here y and n stand for the number of molecules were used of TOPO and Alamine 336 for the solvation of carbonate ions. The formed complexes diffuse from the source and membrane interface to the membrane and receiving interface. Then, these complexes are dissociated at the membrane and receiving interface. The carbonate ions CO_3^{2-} were released to receiving phase. The liquid anion exchangers and solvating extractants were diffused back to the source and membrane interface for repeatedly utilization for the transport of carbonate ions.

$$R \rightarrow H_2^{2+} CO_3^{2-} \cdot y S_m + 2MOH$$
$$\leftrightarrow R_m + y S_m + M_2CO_{3r} + 2H_2O_s, \quad (12)$$

$$S \rightarrow H_2^{2+} CO_3^{2-} \cdot n R_m + 2MOH$$
$$\leftrightarrow S_m + n R_m + M_2CO_{3r} + 2H_2O_s. \quad (13)$$

At higher temperature, the temperature is the driving force for the CO_2 reaction over and removal from the solvating extractants. The selective separations could be carried out of CO_2 in the presence of moisture from the flue gas mixture at 100–150°C; the temperature is the driving force for the reactive removal of CO_2. This mechanism could be explained as follows:

$$R \text{ or } S + H_2O + CO_2 \leftrightarrow R \text{ or } S$$
$$\rightarrow H_2^{2+} CO_3^{2-}. \quad (14)$$
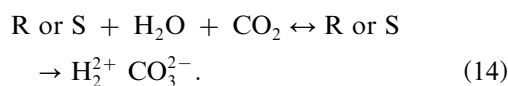
Therefore, present research investigations focus on the transport of carbonate ions through supported liquid (TOPO) and Alamine 336 membranes by using sodium hydroxide as the driving force.

Conclusions

The transport of carbonate ions from source to receiving through supported liquid membrane phase show the synergistic effect in the presence of mixed carriers Alamine 336 and TOPO in the toluene membrane phase. The carbonate ion concentration (0.04 M) in source phase, carrier concentration (0.1 M) membrane phase and alkali concentration (0.1 M) in receiving phase have been optimized. The mixed carriers Alamine 336 and TOPO have been found efficient for the pre-concentration of the carbonate ions from dilute solutions. The primary amine (Primene JMT) in presence of TOPO effectively transports carbonate ions from source to receiving through membrane phase in comparison with that of other amines, such as secondary, tertiary, and quaternary under the same experimental conditions.

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