

Facilitated transport of CO₂ across a liquid membrane: Comparing enzyme, amine, and alkaline

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Abstract

In this work we compare the efficiency of facilitated transport of CO₂ across a liquid membrane by different facilitators as tested in either a supported liquid membrane (SLM) or a hollow fiber contained liquid membrane (HFCLM) configuration. Permeance and selectivity were evaluated by both experimental test and numerical simulation. These comparisons were used to define the best liquid membrane composition to maximize separation performance. We also consider other factors that affect the choice of the facilitator, e.g. operation temperature and cost. Under ambient operating conditions, carbonic anhydrase (CA) combined with an alkaline carbonate gives better performance than does diethanolamine (DEA). © 2006 Published by Elsevier B.V.

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1. Introduction

Carbon dioxide (CO₂) capture is important for both energy production and environmental preservation. Concerns over global warming consequent to the release of CO₂, the most important greenhouse gas, continue to grow [1]. Each year about 28 Gt of CO₂ are released into atmosphere (1 Gt = 1 × 10⁹ metric tonnes) [2]. The exploration of new capture and storage methods for CO₂ is ongoing worldwide. Of the many candidate techniques being studied principal focus is on absorption, adsorption (chemical and physical) and membrane methods.

For low concentration or low pressure CO₂ streams chemical absorption is preferred. The essential choice is between chemistries that yield carbonates or carbamates (produced by means of amines) to realize gas–liquid CO₂ separation [3]. Historically, the preferred operating geometry has been a two-compartment device—absorber and stripper. Absorption occurs rapidly and efficiently but desorption requires substantial additional energy, typically in the form of thermal input, applied at the stripper. Both the thermal requirements and the pumping requirements result in substantial energy consumption. In addition,

these processes present many operational difficulties due to the bulk fluid gas–liquid contacting design. Among the inherent problems are flooding, foaming, channeling and entrainment [4]. Yet another problem is the corrosive character of many of the chemicals used.

Membrane technologies for CO₂ separation are a promising alternative due to their modularity and ease of operation. Membrane is used here to mean a thin film with selective exclusion/inclusion properties. Performance of such a separation medium is based on differences in reactivity, solubility and diffusivity for various gases in the membrane material. For non-reactive materials both permeability and selectivity are typically low [5].

A thin liquid film (liquid membrane (LM)), because of the inherent absence of stable structure, requires a support material for structural integrity. This can be achieved by its deposition into specific pores (immobilized liquid membrane (ILM)), around fibers (supported liquid membrane (SLM)), or between (microporous) surfaces (contained liquid membrane (CLM)). The advantage of these designs is that they operate as contactors avoiding many of the limitations seen in waterfall or bubble mass flow contactors. However, they do have their limitations. SLMs in particular suffer from gravity-based size limitations due to the formation of catenary curve structures. ILM and SLM, insofar as they are not replenished and if the solvent has a high vapor

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pressure can fail due to evaporation (a pore 1 μm in diameter and 25 μm long holds 19.6 fl volume). Evaporation can be minimized by use of a fluid having a lower vapor pressure than the common solvent—water [6]. They will also fail due to excessive transmembrane pressure differences.

The CLM design presents several advantages. One is that the structural geometry is now governed by the support material, largely freeing the design of gravitational limits and thus facilitating scalability. Another is direct access to the fluid to allow replenishment of a high vapor pressure solvent (here water) minimizing if not eliminating failure due to evaporation. A third is that the polymer micropores exhibit high bubble-point pressure. This allows a far higher pressure differential than is possible with an ILM or SLM design. Despite the presence of the polymer separation is based on facilitated transport with the result of higher permeance and selectivity than is easily achieved in a simple polymer film. The CLM design does have its limitations. These include within membrane boundary layers, pore wetting, and surface fouling.

Our prior work has focused on the development of a HFCLM reactor to support absorption and desorption in a single device driven only by partial pressure differences [7]. In one design the permeator is arranged much like a heat exchanger and consists of multiple sets of hollow fiber feed fibers and hollow fiber sweep fibers arranged orthogonally while a carrier fluid, the CLM, fills the space between the feed and sweep fiber bundles. We have also explored spiral wound hollow fiber designs that can operate in either co-current or counter-current mode [8].

Various facilitating chemicals have been used for CO_2 separation in both SLM and HFCLM configurations. Ward and Robb [9] measured the permeance of CO_2 and O_2 in porous cellulose acetate films impregnated with saturated (6.4 M) cesium bicarbonate solutions. For a 5.0% CO_2 feed gas at 1 atm and sweep side of CO_2 partial pressure at 0.005–0.026 atm, the average CO_2 permeance was 3.13×10^{-9} mol/m² s Pa, and CO_2/O_2 selectivity was 1500. With 2.0 M potassium bicarbonate and 2.0 g/l of carbonic anhydrase (CA, E.C.4.2.1.1) in the liquid film, the CO_2 permeance increased by approximately a factor of 6, at about 1.8×10^{-8} mol/m² s Pa. When a saturated cesium bicarbonate solution containing 0.5 M sodium arsenite was used as liquid membrane, the permeance increased about three-fold, to about 1.0×10^{-8} mol/m² s Pa, and selectivity rose to 4100.

Suchdeo and Schultz [10] immobilized 1.0 M sodium bicarbonate containing 0.5 mg/ml CA onto highly porous membrane. The best CO_2 permeance obtained was about 1.8×10^{-8} mol/m² s Pa and CO_2/O_2 separation factor of about 250.

Guha et al. [11] used an SLM of aqueous diethanolamine (DEA) to separate CO_2 from N_2 . Using a 20.0 wt.% DEA solution, a 5.0% CO_2 feed gas at 3.7 atm total pressure, and pure helium as sweep gas, the CO_2 permeance they observed was 1.27×10^{-8} mol/m² s Pa with a CO_2/N_2 selectivity 276.

CA, an enzyme biocatalyst that efficiently converts CO_2 to bicarbonate, has been the principle promoter we have examined [12,13]. We have also studied carbonate with piperazine, cesium carbonate alone and with arsenious acids and the secondary amine diethanolamine (DEA), as it too promotes the

production of bicarbonate [14,15]. While these facilitators have been studied individually it is impossible to compare their efficacy due to differences in test conditions and equipment.

In this short note, we compare these facilitators in our HFCLM permeator to allow head-to-head comparison under identical test conditions. The facilitation mechanisms are presented, and performance, expressed in terms of permeance and selectivity, is compared via experiments and numerical simulations. Other factors affecting liquid membrane selection will also be discussed. As the transport mechanism is the same for both SLM and HFCLM configurations, these comparisons will also be applicable to SLMs.

2. Theory

Chemical facilitation comes from the reversibility of the chemical reaction between CO_2 and chemical facilitator. Each facilitator has its own reaction mechanism. Carbonate is an indirect source of hydroxyl ions while amines react directly with dissolved CO_2 . CA acts as a catalyst for the CO_2 – H_2O reaction thereby yielding enzyme-bound Zn-OH^- to promote bicarbonate formation.

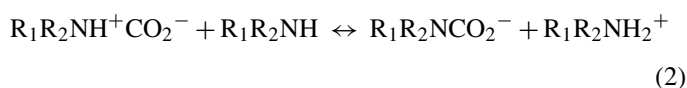
2.1. Amine

The reaction of a secondary amine ($\text{R}_1\text{R}_2\text{NH}$) with dissolved CO_2 is generally described by a zwitterionic mechanism yielding a two-step sequence [16]. The first step is the formation of an intermediate zwitterion:



In the above reaction, the forward reaction rate constant is $k_{1\text{Am}}$, and the reverse reaction rate constant $k_{-1\text{Am}}$.

The zwitterion is deprotonated by the base present in the solution, forming a carbamate ion and a protonated base:



Here the forward reaction rate constant is $k_{2\text{Am}}$ and the reverse reaction rate constant is $k_{-2\text{Am}}$.

The reason for selecting a secondary amine as a facilitator is the ease of reversibility of the chemical reaction between secondary amine and CO_2 . Primary amines react with CO_2 much faster, but the binding constant is high and desorption is difficult and energy consuming, whereas the tertiary amine and CO_2 reaction is slow.

The CO_2 diffusion–reaction transport equation is expressed as:

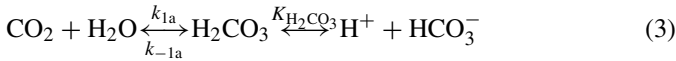
$$D_{\text{CO}_2} \frac{d^2[\text{CO}_2]}{dx^2} = \frac{k_{1\text{Am}}}{(1 + (k_{-1\text{Am}}/k_{2\text{Am}}[\text{R}_1\text{R}_2\text{NH}]))} \times \left([\text{CO}_2][\text{R}_1\text{R}_2\text{NH}] - \frac{[\text{R}_1\text{R}_2\text{NCO}_2^-][\text{R}_1\text{R}_2\text{NH}_2^+]}{K_{\text{EqAm}}[\text{R}_1\text{R}_2\text{NH}]} \right)$$

where the total reaction equilibrium constant, K_{EqAm} , is defined as

$$K_{\text{EqAm}} = \frac{[\text{R}_1\text{R}_2\text{NCO}_2^-][\text{R}_1\text{R}_2\text{NH}_2^+]}{[\text{R}_1\text{R}_2\text{NH}]^2[\text{CO}_2]} = \frac{k_{1\text{Am}}k_{2\text{Am}}}{k_{-1\text{Am}}k_{-2\text{Am}}}$$

2.2. Alkaline

The chemical reactions taking place in the alkaline CLM are:



where k_{1a} and k_{-1a} are the forward and reverse reaction rate constant of (3), respectively. k_{2a} and k_{-2a} are the forward and reverse reaction rate constant of (4). K_{1a} and K_{2a} are the chemical equilibrium constants for (3) and (4), respectively, and

$$K_{\text{H}_2\text{CO}_3} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{H}_2\text{CO}_3]}$$

The following two reactions (Reactions (5) and (6)) are also involved in the CLM, but comparing to slow Reactions (3) and (4), Reactions (5) and (6) are sufficiently rapid and chemical equilibrium may be assumed.



The chemical equilibrium constants are defined as

$$K_{\text{HCO}_3^-} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$K_{\text{H}_2\text{O}} = [\text{H}^+][\text{OH}^-]$$

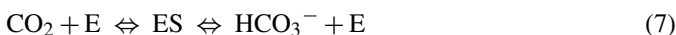
Reaction (4) is very fast, compared to Reaction (3). For any solution at pH >10, Reaction (3) will be more than 30 times faster than Reaction (4) [17].

The CO_2 diffusion–reaction transport equation is expressed as:

$$D_{\text{CO}_2} \frac{d^2[\text{CO}_2]}{dx^2} = k_{1a}[\text{CO}_2] + \frac{k_{2a}K_{\text{H}_2\text{O}}}{K_{\text{HCO}_3^-}} \frac{[\text{CO}_3^{2-}][\text{CO}_2]}{[\text{HCO}_3^-]} - k_{-2a}[\text{HCO}_3^-] - \frac{k_{-1a}K_{\text{HCO}_3^-}}{K_{\text{H}_2\text{CO}_3}} \frac{[\text{HCO}_3^-]^2}{[\text{CO}_3^{2-}]}$$

2.3. Carbonic anhydrase (CA)

The overall mechanism of CA-catalyzed CO_2 hydration and dehydration can be simply expressed as reversible enzymatic reaction:



where E is the free enzyme (CA), ES is intermediate enzyme–substrate complex. Internally the forward reaction involves two

steps (a ping-pong process) where the first step deprotonates water to produce hydroxyl ions and the second step combines CO_2 and hydroxyl ions to produce bicarbonate.

The maximal turn-over of CA is in excess of $1 \times 10^6 \text{ s}^{-1}$ [18] making it the fastest catalyst for CO_2 hydration reaction. The actual reaction rate is proportional to the CA concentration in the liquid membrane, which is usually quite small (<1 mM). Thus, the overall reaction rate (CO_2 hydration rate) is comparable to that of other facilitators. (Note however that the energy requirement is small –163 kJ/mol). The CO_2 hydration and dehydration reactions are pH dependent as may be inferred from first step. As CO_2 reacts with H_2O , the liquid membrane is acidified and chemical equilibrium is easily reached. This limits the CO_2 uptake capacity of the liquid membrane. One way to overcome this problem is to use CA with buffer and/or an alkaline (bicarbonate/carbonate) solution. A liquid membrane containing CA and an alkaline carbonate has been shown to be an effective way of using CA for purposes of CO_2 separation [19].

Thus, for facilitated CO_2 transfer across a liquid membrane, during absorption at the feed side, the chemical reaction will rapidly convert CO_2 into other species (HCO_3^- or carbamate) in the liquid membrane. The HCO_3^- or carbamate diffuses across the liquid film under its concentration gradient. During desorption at the sweep side, HCO_3^- or carbamate is converted back to CO_2 , which is carried away by the sweep (gas, liquid or vacuum). Thus, in addition to transport being limited to the dissolved CO_2 moving through the liquid membrane, there is an extra mechanism of HCO_3^- or carbamate transport that greatly improves the total CO_2 mass transfer.

The CO_2 diffusion–reaction transport equation is expressed as:

$$D_{\text{CO}_2} \frac{d^2[\text{CO}_2]}{dx^2} = R_{\text{CO}_2}$$

$$R_{\text{CO}_2} = \left(\frac{[E_0]k_{\text{cat}}}{([\text{CO}_2] + [\text{HCO}_3^-]K_{\text{m}}^{\text{CO}_2}/K_{\text{m}}^{\text{HCO}_3^-} + K_{\text{m}}^{\text{CO}_2}) + k_{\text{CO}_2} + [\text{OH}^-]k_{\text{OH}^-}} \right) ([\text{CO}_2] - [\text{HCO}_3^-]/K_{\text{Eq}})$$

where k_{cat} is the turn-over number for CA, k_{CO_2} the rate constant for un-catalyzed CO_2 and H_2O reaction (same as k_{1a}), k_{OH^-} is rate constant for CO_2 and OH^- reaction (same as k_{2a}) and K_{Eq} is the chemical equilibrium constant for (7). Note that $[\text{OH}^-]$ is a very small number.

We have measured and modeled the CO_2 mass transport across a liquid film facilitated by CA in bicarbonate/carbonate solution or by a secondary amine (DEA) [15,20]. The 1D-simplified model includes the known chemical reaction mechanisms, as well as various factors (temperature, ionic strength, etc.) that affect such transport properties including diffusivity and solubility. Details are given in Refs. [15,20].

3. Experimental

We constructed a heat exchanger type design (mutually orthogonal fiber orientation) from microporous polypropylene hollow fiber membrane mat, Celgard® X40-200 (Membrana-Charlotte, Charlotte, NC). The outer diameter of the fiber is 300 μm , the inner diameter 200 μm , nominal porosity is 40% and effective pore size is 0.04 μm . The total feed membrane area is about 0.1885 m^2 . The liquid membrane is on the shell side and can flow in the direction perpendicular to both of the fiber mats. The minimum achievable thickness of the liquid membrane is controlled by the yarn diameter used to weave the hollow fiber mat. A thicker liquid membrane can be achieved by use of spacers sandwiched between the hollow fiber mats.

Air containing a specific percentage of CO_2 (1–20%) was fed to the feed fibers via a computerized mass flow controller (EnviroNics, Series 2020); ultrahigh purity argon was used as the sweep. Under real-world conditions a sweep gas will not be used. Rather, the sweep side permeation is driven either by a vacuum or vacuum combined with a water vapor stream.

Both the feed and sweep gas streams were humidified through Nafion humidifiers. The HFCLM reactor was placed in a liquid bath controlled to constant operating temperatures. The composition of each gas stream was analyzed by a residual gas analyzing mass spectrometer (Extrel).

4. Results and discussion

Simulations were performed under experimental conditions for CLMs made of CA+alkaline, amine and pure alkaline, respectively. As shown in the transport equations, the O_2 and N_2 in the feed gas has no effect on facilitated CO_2 transport, and their permeances were determined simply by diffusion-solution mechanism. In our models we did not include calculations for the transport of argon gas across the CLM to the feed/retentate. Argon was measured at 1.07% in the feed and 99% in the sweep. In recent experiments in a smaller permeator, with flow rates of 1:1, the measured retentate argon concentration increased to only 1.26% or 17.8%. In the experiments reported here the respective flow rates were in a ratio of 2.5:1, thus the expected argon flux would be even lower, $\sim 7\%$.

Fig. 1 shows the simulated CO_2 permeances for four different CLMs considered. At maximum CA turn-over, the liquid membrane made of 3.0 mg/ml CA and 1.0 M bicarbonate solution yields higher permeance than is the case with DEA. At 15.0% CO_2 feed concentration, the permeance with the CA + bicarbonate system is about 109% greater than with 20.0% DEA, and 52% greater than with 30% DEA. Fig. 1 also includes the carbonate facilitator without any catalyst. It clearly demonstrates that liquid membrane made of bicarbonate/carbonate solution without CA gives poor CO_2 permeance.

Our experimental results are shown in Fig. 2 along with literature data obtained using the SLM configuration. The source of literature data is shown in the legend. The measured CO_2 permeances, using the above mentioned facilitators, are plotted against the feed CO_2 concentrations. While a direct comparison between the literature data and our experimental data is difficult,

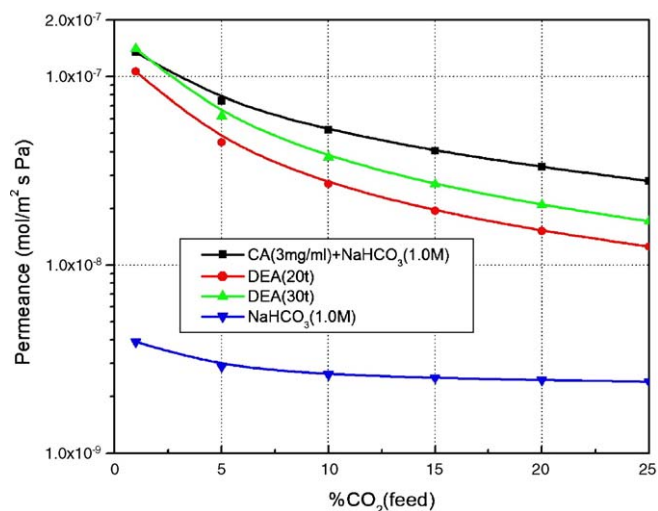


Fig. 1. Simulated permeance for each facilitator as a function of feed CO_2 concentration.

as the literature data were obtained using different configurations and experimental conditions (e.g. CO_2 partial pressure difference, liquid membrane thickness and composition), the data do provide some understanding of the effectiveness of each facilitator in promoting CO_2 permeance. The data show that the CA–bicarbonate liquid membrane always performs better than does DEA. At 10.0% CO_2 feed, the measured CO_2 permeance facilitated by 20.0 wt.% DEA is only 33.5% of that by 1.0 M NaHCO_3 + 3 mg/ml CA. Only at much higher CO_2 concentration (20%), is there a convergence between CA + NaHCO_3 and DEA. Given the diminished role of the facilitator as $p\text{CO}_2$ increases this result is not unexpected.

The facilitators in CLMs not only determine the CO_2 permeance, but also affect the selectivity of CO_2 to non-reactive gas. Facilitators that improve CO_2 permeance will also improve selectivity. However, the primary effect on selectivity is controlled by the chemistry of the CLM that affects the solubility and diffusivity of non-reactive gases. For instance, at

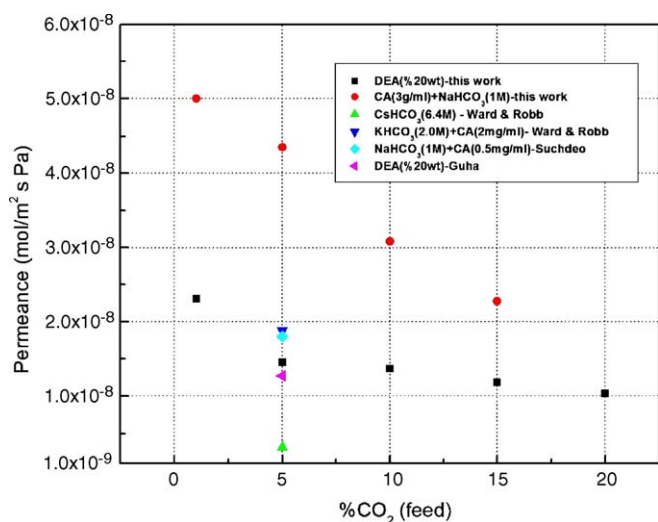


Fig. 2. Experimental data illustrating CO_2 permeance as a function of feed CO_2 concentration. The comparative data derive from Refs. [9,10].

10.0% CO₂ feed, the measured CO₂/O₂ selectivity facilitated by 20.0 wt.% DEA is 152, only 65% of that achieved by 1.0 M NaHCO₃ + 3 mg/ml CA.

The comparison made so far is only based upon CO₂ permeance and CO₂/O₂ selectivity, with CA being a better facilitator. Many other factors come into play for a comprehensive comparison. CA is a family of enzymes each with a preferred temperature range. The upper temperature bound, using a thermophilic enzyme is about 85 °C [21]. The reaction rate is only modestly temperature sensitive. In contrast, the reaction rate between CO₂ and amine (or alkaline alone) increases with temperature. Higher temperature will likely benefit amine or alkaline more than CA. Each of these facilitators has limitations. Amines, for example, are recognized as being corrosive and corrosion inhibitors are needed to allow long-term operation. These inhibitors extract a performance cost. Also, amines are oxygen sensitive and require routine replenishment. For CA, very long-term stability may be a concern, even though good short-term stability has been demonstrated, i.e. up to 40 days or discontinuous use and more than 50 days of continuous use [19,20]. Literature studies indicate lifetimes of 3–6 months or longer [22].

5. Conclusions

Comparisons were made for facilitated CO₂ transport across a liquid membrane containing three different facilitators: the biocatalyst CA, the secondary amine DEA and various alkaline carbonates. The facilitated mechanisms were presented, and the performance of each facilitator was illustrated in terms of the CO₂ permeance and the CO₂/O₂ selectivity. We report that CLMs made of CA and alkaline solutions give higher permeance and selectivity than those made of DEA or alkaline alone. We conclude that CA is a preferred catalyst that when combined with an alkaline buffer and in a CLM configuration can provide a highly efficient method for CO₂ capture.

Acknowledgements

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References

- [1] P.A. Stott, D.A. Stone, M.R. Allen, Human contribution to the European heat wave of 2003, *Nature* 2 (2003) 432.
- [2] World Energy Outlook. International Energy Agency, 2002.
- [3] G. Astarita, Savage, A. Bisio, Gas Treating with Chemical Solvents, John Wiley and Sons, New York, 1984.
- [4] A. Gabelman, S.T. Huang, Hollow fiber membrane contactors, *J. Membr. Sci.* 159 (1996) 61–106.
- [5] D. Yang, S. Majumdar, S. Kovenklioglu, K.K. Sirkar, Hollow fiber contained liquid membrane pervaporation system for the removal of toxic volatile organics from wastewater, *J. Membr. Sci.* 103 (1995) 195–210.
- [6] A.S. Kovvali, K.K. Sirkar, Stable liquid membranes recent developments and future directions, *Ann. N. Y. Acad. Sci.* 984 (2003) 279–288.
- [7] M.C. Trachtenberg, R.M. Cowan, S.L. Goldman, J.J. Ge, Y.J. Qin, M.L. McGregor, Enzyme based membrane reactor for CO₂ capture, in: Proceedings of the 33rd International Conference on Environmental Systems, SAE 2003-01-2499, 2003.
- [8] R.M. Cowan, J.J. Ge, Y.J. Qin, M.L. McGregor, M.C. Trachtenberg, CO₂ capture by means of an enzyme-based reactor, *Ann. N. Y. Acad. Sci.* 984 (2003) 453–470.
- [9] W.J. Ward, W.L. Robb, Carbon dioxide–oxygen separation: facilitated transport of carbon dioxide across a liquid film, *Science* 156 (1976) 1481–1484.
- [10] S.R. Suchdeo, J.S. Schultz, Mass transfer of CO₂ across membranes: facilitation in the presence of bicarbonate ion and the enzyme carbonic anhydrase, *Biochim. Biophys. Acta.* 352 (1974) 412–440.
- [11] A.K. Guha, S. Majumdar, K.K. Sirkar, Facilitated transport of CO₂ through an immobilized liquid membrane of aqueous diethanolamine, *Ind. Eng. Chem. Res.* 29 (1990) 2093–2100.
- [12] M.C. Trachtenberg, M.L. McGregor, C.K. Tu, P.J. Laipis, R.C. Willson, J.F. Kennedy, M. Paterson, F.B. Rudolph, Enzyme-enhanced membranes for gas separation, in: Proceedings of the 29th International Conference on Environmental Systems, SAE 1999-01-1961, 1999.
- [13] M.C. Trachtenberg, C.K. Tu, R.A. Landers, R.C. Willson, M.L. McGregor, P.J. Laipis, J.F. Kennedy, M. Paterson, D.N. Silverman, D. Thomas, R.L. Smith, F.B. Rudolph, Carbon dioxide transport by proteic and facilitated transport membranes, *Life Support Biosphere Sci.* 6 (1999) 293–302.
- [14] J.J. Ge, M.C. Trachtenberg, M.C. Cowan, M.L. McGregor, Enzyme-based facilitated transport: use of vacuum induced sweep for enhanced CO₂ capture, in: Proceedings of the 31st International Conference on Environmental Systems, Orlando, FL, 2001.
- [15] L.H. Bao, M.C. Trachtenberg, Modeling CO₂ facilitated transport across a diethanolamine liquid membrane, *Chem. Eng. Sci.* 60 (2005) 6868–6875.
- [16] G.F. Versteeg, L.A.J. Dijk, P.M. Swaaij, On the kinetics between CO₂ and alkanolamines both in aqueous and non-aqueous solutions. An overview, *Chem. Eng. Commun.* 144 (1996) 113–158.
- [17] P.V. Danckwerts, *Gas–Liquid Reactions*, McGraw-Hill, New York, 1970.
- [18] R.G. Khalifah, The carbon dioxide hydration activity of carbonic anhydrase. I. Stop-flow kinetic studies on the native human isozymes B and C, *J. Biol. Chem.* 246 (1971) 2561–2573.
- [19] L.H. Bao, S.L. Goldman, M.C. Trachtenberg, CO₂ transfer across a liquid membrane facilitated by carbonic anhydrase. Paper presented to AIChE Annual Meeting, Austin, TX, 2004.
- [20] L.H. Bao, S.L. Goldman, M.C. Trachtenberg, Facilitated CO₂ transport modeling of an enzyme-based, hollow fiber contained liquid membrane module, *AIChE J.*, submitted for publication.
- [21] B.C. Tripp, K. Smith, J.G. Ferry, Carbonic anhydrase: new insights for an ancient enzyme, *J. Biol. Chem.* 276 (2001) 48615–48618.
- [22] A.L. Crumblis, K.L. McLachlan, J.P. O'Daly, R.W. Henkens, Preparation and activity of carbonic anhydrase immobilized on porous silica beads and graphite rods, *Biotech. Bioeng.* 31 (1988) 796–801.