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Facilitated Transport of Carbon Dioxide Through an Immobilized Liquid Membrane of Aqueous Carbonate Solution with Additives

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ABSTRACT

An experimental study has been carried out to investigate the characteristics of facilitated transport of CO_2 through hydrophilic polymeric membranes with an immobilized aqueous potassium carbonate solution.

The rate of permeation for CO_2 increased with increasing K_2CO_3 concentration, decreasing membrane thickness, and decreasing CO_2 partial pressure. The permeation rate for CO_2 was predicted by a theoretical model based on mass transfer accompanied by a reversible chemical reaction, such as hydration reaction of CO_2, reaction of CO_2 with OH^-, or dissociation of HCO_3^-. The permeation rate for CO_2 increased by adding K_2SO_3, PEG, or DBC to the aqueous K_2CO_3 solution. By assuming that these additives enhanced the hydration reaction of CO_2, the forward-reaction rate constant was estimated by fitting to the experimental R_A. The values estimated thus were 1.35, 0.98, and 0.56 s^{-1}, for K_2SO_4, polyethyleneglycol, and Dibenzo-18-crown-6, respectively. These values amount to 15–36 times as large as those without additives.

INTRODUCTION

Global warming caused by greenhouse gases has become a matter of great concern, and carbon dioxide, which is produced in massive amounts, has been widely recognized as one of the most significant greenhouse gases. Many fa-

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cilities, such as fossil-fuel-fired power plants, iron and steel works, and cement works discharge a huge amount of CO_2. The fixation and removal of CO_2 from fossil-fuel combustion facilities has been considered as a way to prevent CO_2 buildup. Chemical absorption and membrane-based separation processes, among others, can successfully reduce CO_2 from industrial-waste gases and other gaseous mixtures.

Membranes have been developed that make certain membrane-separation processes economically and technically feasible. Although several polymers, such as silicone rubber and cellulose acetate, are useful membrane materials, in general, polymer materials are not desirable as permselective membranes. Most polymer materials are relatively impermeable to all gases and liquids, and the separation factor of a permeate is low. To overcome the problem of low permeation rate and selectivity, use of facilitated-transport membranes has been proposed (1–4). Facilitated-transport membranes containing carriers, which react reversibly and selectively with permeant species, have been attracting attention, since they have much higher selectivity compared with polymer membranes without carriers (5).

The facilitated-transport process is the transport of a solute through a liquid membrane where an active carrier immobilized in a liquid membrane reacts with the solute of interest, transports it across the membrane, and releases it at the other boundary. Those reversible reactions increase the flux of the solute across the liquid membrane and enhance selectivity.

The facilitated-transport mechanism of CO_2 through a liquid membrane with immobilized aqueous alkaline solutions becomes complicated because of diffusion accompanied by chemical reactions, such as reaction of CO_2 with water and hydroxyl ions, and dissociation of bicarbonate ions. As the governing differential equations for this system are nonlinear because of the reaction terms, a general analytical solution is not derived. Many attempts have been made to obtain an approximate solution of a facilitation factor, which is defined as the ratio of facilitated-transport flux to the flux without carriers. Olander (6) described simultaneous mass transfer combined with an equilibrium chemical reaction. Goddard et al. (7) analyzed the behavior of a facilitated-transport membrane near chemical equilibrium. Friedlander and Keller (8) used a linearized form of the reaction-rate expression to describe the flux of permeate with a reversible chemical reaction in terms of simple diffusional flux. Their assumptions were based on the reaction system being near equilibrium. Ward (9), Smith et al. (10) and Schultz et al. (11) discussed the two limiting cases, i.e., reaction-limited and diffusion-limited. Chee et al. (12) used the concept of a reaction-boundary-layer approximation to explain the physical problems by assuming an instantaneous reaction equilibrium at the membrane boundary. Park et al. (13) presented a model that could handle the governing differential equations easily by means of simplification of the complicated chemical reaction into the overall chemical reaction in the transport of CO_2 through aqueous K_2CO_3–$KHCO_3$ buffer solutions.

It may be worthwhile analyzing the governing differential equations by use of an approximate solution based on the characteristic behavior of each component at the gas–liquid interface. The catalysis of the reaction between CO_2 and water has been utilized in industrial processes. Sharma and Danckwerts (14) studied various aspects of the catalysis of the hydration of CO_2. Crown ether has a characteristic capturing cation in aqueous alkaline solutions that increases the mobility of anions (15). It may be worthwhile investigating the facilitation effect of CO_2 in aqueous alkaline solutions containing K_2SO_3 or crown ether as an additive.

In this study, CO_2 from CO_2–N_2 gas mixtures was separated by a flat-type supported liquid membrane with immobilized aqueous K_2CO_3 solutions adding K_2SO_3, polyethylene glycol(PEG), and dibenzo-18-crown-6(DBC), respectively. The facilitated transport mechanism without additives was established by using the approximate solution to the diffusion equation accompanied by reversible chemical reactions.

THEORY

In the facilitated transport of CO_2 through a supported liquid membrane of an aqueous carbonate solution, the following reactions take place at the membrane side (1);

$$CO_2(A) + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} HCO_3^-(E) + H^+(H) \tag{1}$$

$$CO_2 + OH^-(B) \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} HCO_3^- \tag{2}$$

$$HCO_3^- \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} CO_3^{2-}(F) + H^+ \tag{3}$$

$$H_2O \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} H^1 + OH \tag{4}$$

Chemical equilibrium constants of Eqs. (1)–(4) are defined as follows:

$$K_1 = [HCO_3^-][H^+]/[CO_2]$$

$$K_2 = [HCO_3^-]/[CO_2][OH^-]$$

$$K_3 = [H^+][CO_3^{2-}]/[HCO_3^-]$$

$$K_W = [H^+][OH^+]$$

At a steady state, the diffusion equations for CO_2 and ionic components in the porous membrane and the boundary conditions to be imposed are expressed as follows

$$D_{\mathrm{Ej}} \frac{d^2 C_j}{dx^2} = \varepsilon r_{\mathrm{j}}$$
$$x = 0;\ C_{\mathrm{A}} = C_{\mathrm{Ao}},\ dC_{\mathrm{j}}/dx = 0 \tag{5}$$
$$x = L;\ C_{\mathrm{A}} = C_{\mathrm{AL}},\ dC_{\mathrm{j}}/dx = 0$$

where, j refers to components B, E, F and H. The boundary conditions on component j represent that these species are nonvolatile and constrained within the liquid membrane. D_{Ej} is the effective diffusivity of component j defined as $D_{\mathrm{j}}\varepsilon/\tau$. ε and τ designate porosity and tortuosity of the membrane, respectively.

The reaction rate for each component is expressed as

$$r_{\mathrm{A}} = k_1 C_{\mathrm{A}} - k_{-1} C_{\mathrm{E}} C_{\mathrm{H}} + k_2 C_{\mathrm{A}} C_{\mathrm{B}} - k_{-2} C_{\mathrm{E}} \tag{6}$$

$$r_{\mathrm{B}} = k_2 C_{\mathrm{A}} C_{\mathrm{B}} - k_{-2} C_{\mathrm{E}} + k_4 - k_{-4} C_{\mathrm{H}} C_{\mathrm{B}} \tag{7}$$

$$r_{\mathrm{E}} = -k_1 C_{\mathrm{A}} + k_{-1} C_{\mathrm{E}} C_{\mathrm{H}} - k_2 C_{\mathrm{A}} C_{\mathrm{B}} + k_{-2} C_{\mathrm{E}} + k_3 C_{\mathrm{E}} - k_{-3} C_{\mathrm{F}} C_{\mathrm{H}} \tag{8}$$

$$r_{\mathrm{F}} = -k_3 C_{\mathrm{E}} + k_{-3} C_{\mathrm{F}} C_{\mathrm{H}} \tag{9}$$

$$r_{\mathrm{H}} = -k_1 C_{\mathrm{A}} + k_{-1} C_{\mathrm{E}} C_{\mathrm{H}} - k_3 C_{\mathrm{E}} + k_{-3} C_{\mathrm{F}} C_{\mathrm{H}} - k_4 + k_{-4} C_{\mathrm{H}} C_{\mathrm{B}} \tag{10}$$

The following assumptions are utilized to get an approximate solution to the diffusion equation; (i) the concentration of K^+ is uniform in the membrane, (ii) the concentrations of OH^- and H^+ are negligibly low as compared with those of HCO_3^- and CO_3^{2-} (16), (iii) the total concentration of carbonic acid (C_{c}) is the sum of C_{E} and C_{F}, and the diffusivity of the imaginary species (C) is assumed to be an average value of D_{E} and D_{F}, and (iv) both reactions (3) and (4) attain an equilibrium state.

The charge balance in the membrane and assumptions (ii) and (iii) give the following equations, respectively

$$C_{\mathrm{K}} = C_{\mathrm{E}} + 2C_{\mathrm{F}} \tag{11}$$

$$C_{\mathrm{C}} = C_{\mathrm{E}} + C_{\mathrm{F}} \tag{12}$$

From the above assumptions and Eq. (11), Eq. (5) can be written as

$$D_{\mathrm{EA}} \frac{d^2 C_{\mathrm{A}}}{dx^2} = \varepsilon r_{\mathrm{A}} \tag{13}$$

$$D_{\mathrm{EC}} \frac{d^2 C_{\mathrm{C}}}{dx^2} = -\varepsilon r_{\mathrm{A}} \tag{14}$$

and r_{A} in Eq. (6), C_{B} and C_{H} are rearranged as follows:

$$r_{\mathrm{A}} = (k_1 + k_2\, C_{\mathrm{B}}) C_{\mathrm{A}} - (k_{-1}\, C_{\mathrm{H}} + k_{-2})(2C_{\mathrm{C}} - C_{\mathrm{K}}) \tag{15}$$

$$C_B = (K_W/K_3)(C_K - C_C)/(2C_C - C_K) \tag{16}$$

$$C_H = K_3(2C_C - C_K)/(C_K - C_C) \tag{17}$$

The boundary conditions for Eqs. (13) and (14) are given as

$$x = 0;\ C_A = C_{Ao},\ dC_C/dx = 0 \tag{18}$$

$$x = \mathrm{L};\ C_A = C_{AL},\ dC_C/dx = 0 \tag{19}$$

The dimensionless forms of Eqs. (13), (14), (18), and (19) are written as

$$\frac{d^2a}{dy^2} = \delta^2\left(1 + \alpha\frac{1-c}{2c-1}\right)a - \delta^2 q\left(\beta\frac{2c-1}{1-c} + \eta\right)(2c-1) \tag{20}$$

$$\frac{d^2c}{dy^2} = -\frac{\delta^2}{rq}\left(1 + \alpha\frac{1-c}{2c-1}\right)a + \frac{\delta^2}{r}\left(\beta\frac{2c-1}{1-c} + \eta\right)(2c-1) \tag{21}$$

$$y = 0;\ a = 1,\ dc/dy = 0 \tag{22}$$

$$y = 1;\ a = a_L,\ dc/dy = 0 \tag{23}$$

where $\alpha = k_2K_W/k_1K_3$, $\beta = k_{-1}K_3/k_1$, $\delta = L\sqrt{k_1\tau/D_A}$, $\eta = k_{-2}/k_1$, $q = C_K/C_{Ao}$, $r = D_C/D_A$, $a = C_A/C_{Ao}$, $c = C_C/C_K$ and $y = x/L$.

The facilitation factor, F, is defined as

$$F = -\left(\frac{da}{dy}\right)_{y=0\text{ or }1} \tag{24}$$

It is seen from the above equations that F is a function of seven dimensionless parameters, α, β, δ, η, a_L, q, and r.

It has been widely recognized in an analysis of the rate of gas absorption accompanied by chemical reaction that the absorption rate is mostly determined by the concentrations of reactants at the gas–liquid interface (17). This suggests that for given values of C_{Ao} and C_{AL}, the influx of the permeate at the feed side boundary, N_{Ao}, should be determined by C_{co} and should be influenced little by the concentration at $x = L$. Therefore, it seems reasonable to consider that the carrier influx can be accurately analyzed by assuming that the carrier concentration is uniform approximately at C_{co} throughout the membrane, and C_B and C_H are regarded as constant at C_{Bo} and C_{Ho}, respectively. Then, Eqs. (20) through (23) are written as follows

$$\frac{d^2a}{dy^2} = \delta^2\left(1 + \alpha\frac{1-c_o}{2c_o-1}\right)a - \delta^2 q\left(\beta\frac{2c_o-1}{1-c_o} + \eta\right)(2c-1) \tag{25}$$

$$\frac{d^2c}{dy^2} = -\frac{\delta^2}{rq}\left(1 + \alpha\frac{1-c_o}{2c_o-1}\right)a + \frac{\delta^2}{r}\left(\beta\frac{2c_o-1}{1-c_o} + \eta\right)(2c-1) \tag{26}$$

$$y = 0;\ a = 1,\ c = c_o,\ dc/dy = 0 \tag{27}$$

$$y = 1;\ a = a_L \tag{28}$$

The outflux of the permeate at the stripping side boundary, N_{AL}, can also be analyzed in a manner similar to that mentioned above. Eqs. (20) through (23) are expressed as follows

$$\frac{d^2a}{dy^2} = \delta^2\left(1 + \alpha\frac{1 - c_L}{2c_L - 1}\right)a - \delta^2 q\left(\beta\frac{2c_L - 1}{1 - c_L} + \eta\right)(2c - 1) \tag{29}$$

$$\frac{d^2c}{dy^2} = -\frac{\delta^2}{rq}\left(1 + \alpha\frac{1 - c_L}{2c_L - 1}\right)a + \frac{\delta^2}{r}\left(\beta\frac{2c_L - 1}{1 - c_L} + \eta\right)(2c - 1) \tag{30}$$

$$y = 0;\ a = 1 \tag{31}$$

$$y = 1;\ a = a_L,\ c = c_L,\ dc/dy = 0 \tag{32}$$

At a steady state, the following condition must be satisfied.

$$N_{Ao} = N_{AL} \tag{33}$$

EXPERIMENT

Chemicals used in this study were reagent grade and used without further purification. The supporting membrane was hydrophilic microporous cellulose acetate–nitrate membrane (AA-WP Type from Millipor Co.; thickness of 150 μm, tortuosity of 3.05, and 47 mM in diameter, having an average pore size of 0.8 μm and porosity of 0.82).

The permeation cell with a flat-type membrane and the experimental procedure used to measure permeation rate of CO_2 were the same as those reported in an earlier study (13). The experiment was carried out under atmospheric circumstances at a constant temperature of 25°C.

The permeation rate of CO_2 was obtained from the concentration difference of CO_2 and the flow-rate difference of gas mixtures between the inlet and outlet of the feed side at steady state. The concentration of K_2CO_3 ranges from 0.5 to 2.0 kmol/m^3, and the partial pressure of CO_2 at the feed side ranges form 10.1 to 101 kPa. The pressure at the stripping side was regulated at 664 Pa by a vacuum pump. The concentrations of K_2SO_3 and PEG were fixed at 0.1 and 0.01 kmol/m^3, respectively, and an aqueous solution of DBC was saturated with toluene containing 0.01 kmol/m^3 DBC, because of the low solubility of DBC in water. Single-sheet and double-sheet membranes were used.

RESULTS AND DISCUSSION

Physicochemical Properties

It is necessary to determine the physicochemical properties such as diffusivity, solubility of CO_2 in aqueous K_2CO_3 solutions, and reaction rate constants to calculate the theoretical values of the permeation rate of CO_2.

Because the diffusivity and solubility of an acidic gas in an aqueous solution were dependent on the ionic strength of aqueous electrolyte solution, these values were obtained from the empirical equation, which took the ionic strength into consideration (13), and were listed in Table 1.

The reaction rate constants, k_1, k_{-1}, k_2, and k_{-2}, and equilibrium constants, K_3, and K_W, were obtained from previous studies (18, 19), and their values were 0.0375 s^{-1}, 5.5×10^4 m^3/kmol·s, 8500 m^3/kmol·s, 2×10^{-4} s^{-1}, 4.4×10^{-11} kmol/m^3, and 1×10^{-14} $kmol^2/m^6$, respectively.

Simulation for the Facilitated Transport of CO_2

For a given set of parameters such as α, β, δ, η, a_L, q and r, five unknown values, b_o, b_L, c_o, c_L and F can be determined by using Eqs. (25), (26), (29), (30), and (33), from which the concentration profiles of a and c can be obtained. The concentrations of HCO_3^- and CO_3^{2-} can be calculated from Eqs. (15) and (16). Typical examples of the dimensionless concentration profiles of CO_2, HCO_3^-, and CO_3^{2-} were plotted in Fig. 1, where α, β, δ, η, a_L, q and r were fixed at 51.52, 6.45×10^{-6}, 3.49, 5.33×10^{-3}, 0, 286, and 0.8528, respectively. These values were typical values obtained in experimental conditions.

As shown in Fig. 1, the concentrations of CO_2, and HCO_3^- are higher at the feed side of the film exposed to a high partial pressure of CO_2, (side 1), while the concentration of CO_3^{2-} is higher at the stripping side of the film (side 2). Near side 1, bicarbonate produced by the forward reactions of reactions (1) and (2) diffuses across the film, and near side 2 decomposes into carbon diox-

TABLE 1
Solubility and Diffusivity in Aqueous Carbonate Solution at 25°C and 101 kPa

K_2CO_3 (mol/L)	$C_{Ai} \times 10^5$ (mol/cm^3)	$D_A \times 10^5$ (cm^2/s)	$D_E \times 10^5$ (cm^2/s)	$D_F \times 10^5$ (cm^2/s)
0	3.5	1.97	1.6870	1.6731
0.5	2.6920	1.7128	1.4667	1.4546
1.0	2.0705	1.4556	1.2465	1.2362
1.5	1.5925	1.1985	1.0263	1.0179
2.0	1.2248	0.9413	0.8001	0.7995

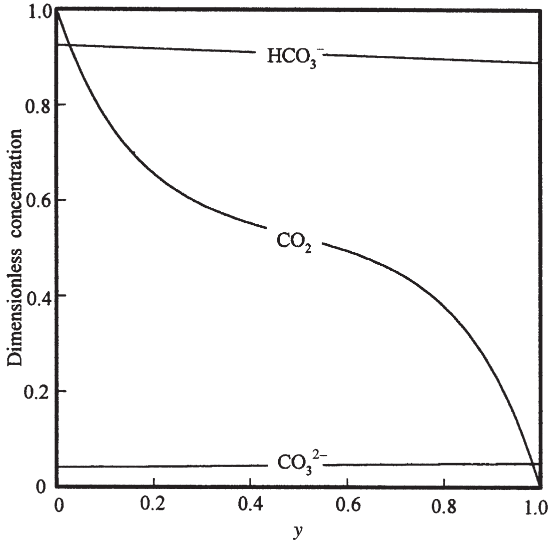

FIG. 1 Dimensionless concentration profiles of CO_2, HCO_3^-, and CO_3^{2-} at $\alpha = 51.52$, $\beta = 6.45 \times 10^{-5}$, $\delta = 3.49$, $\eta = 5.33 \times 10^{-3}$, $a_L = 0$, $q = 286$, $r = 0.853$.

ide. Near side 2, carbonate produced by the forward reaction of reaction (3) diffuses across the film, and near side 1 is consumed. Thus carbon dioxide transport across the film is facilitated by the diffusion of bicarbonate.

The facilitation factor (F) was calculated for various values of α or β. Figure 2 shows a plot of F against α and β with the same values of parameters listed in Fig. 1 except α or β.

As shown in Fig. 2, F increased with increasing α. It may be said that the forward rate constant of reaction (2) can be more effective on the increase of the facilitation factor than that of reaction (1), because α is equivalent to the ratio of k_2 to k_1 from its definition.

As shown in Fig. 2, F was almost constant at low values of β up to 1×10^{-5}, but rapidly increased at β exceeding 1×10^{-4}. When a chemical equilibrium among CO_2, HCO_3^- and CO_3^{2-} exists in an aqueous alkaline solution contacted with CO_2 (1), its reaction and equilibrium constant are written as

$$CO_2 + H_2O + CO_3^{2-} \underset{k'}{\overset{k}{\rightleftarrows}} 2HCO_3^- \tag{34}$$

$$K = \frac{k}{k'} = \frac{[HCO_3^-]^2}{[CO_2][CO_3^{2-}]} \tag{35}$$

where reaction (34) is obtained from reactions (1) and (3).

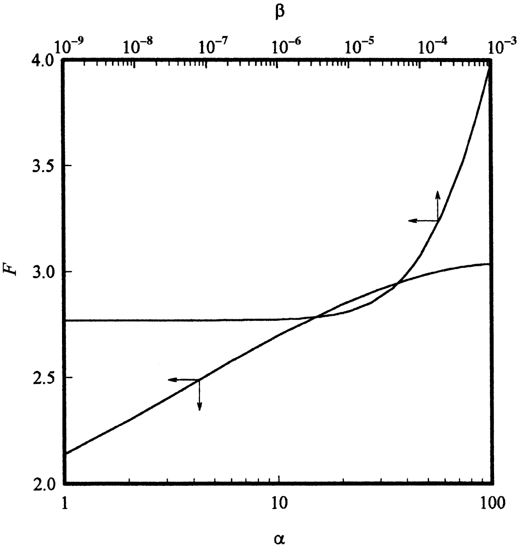

FIG. 2 Effect of α and β on facilitation factor with the same values of parameters as listed in Fig. 1.

β becomes inversely equal to equilibrium constant K from its definition. Therefore, it can be said that for large values of β or small values of K, the reversibility of the overall reaction increases, which results in a high releasing rate of CO_2 at the interface of the stripping side.

Figure 3 shows a typical plot of F against η and q with the same values of parameters as in Fig. 1 except η or q. As shown in Fig. 3, F was almost constant at low values of η below 1×10^{-4}, but rapidly increased at η above 1×10^{-3}. It may be said that the backward rate constant of reaction (2) can be more effective on the increase of the facilitation factor than the forward rate constant of reaction (1); that is, the facilitation of CO_2 is influenced by the release of CO_2 on the stripping side rather than the hydration of CO_2 on the feed side.

As shown in Fig. 3, F increased with increasing q. It may be said from this result that the concentration of the carrier or the solubility of gas promotes CO_2 transport.

Effect of Experimental Variables on Permeation Rate of CO_2

The permeation rate is generally used rather than the facilitation factor in the study of permeation of a solute across the membrane.

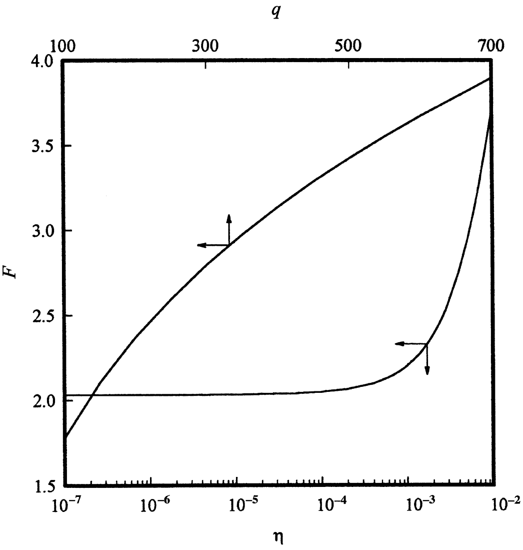

FIG. 3 Effect of η and q on facilitation factor with the same values of parameters as listed in Fig. 1.

The permeation rate of CO_2 is defined as

$$R_A = \frac{22400FD_{EA}\,(C_{Ao} - C_{AL})}{L(p_{Ao} - p_{AL})} \tag{36}$$

Figure 4 shows a typical plot of the measured value of R_A against the partial pressure of CO_2 at K_2CO_3 concentration of 1 kmol/m^3 and membrane thickness of 457.5 μm. The full curve in this figure represents the calculated values of R_A from Eq. (36). As shown in Fig. 4, the calculated R_A closely approaches the experimental values, which decrease with increasing CO_2 partial pressure at the feed side. R_A is influenced by F, C_{Ao} and p_{Ao} at fixed values of C_{AL} and p_{AL} as suggested in Eq. (36), but R_A is mainly influenced by F, because C_{Ao} is equal to C_{Ai}, and F decreases with increasing C_{Ao} as shown in Fig. 3.

Figure 5 shows a typical plot of the permeation rate of CO_2 against the concentration of K_2CO_3 at p_{Ao} of 20.2 kPa and membrane thickness of 457.5 μm. It is apparent in this figure that the permeation rate of CO_2 increases with an increase in K_2CO_3 concentration. This tendency can be explained by the behavior depicted in Fig. 3.

To observe the effect of membrane thickness on the permeation rate of CO_2, the permeation rates of CO_2 measured with one-sheet and two-sheet mem-

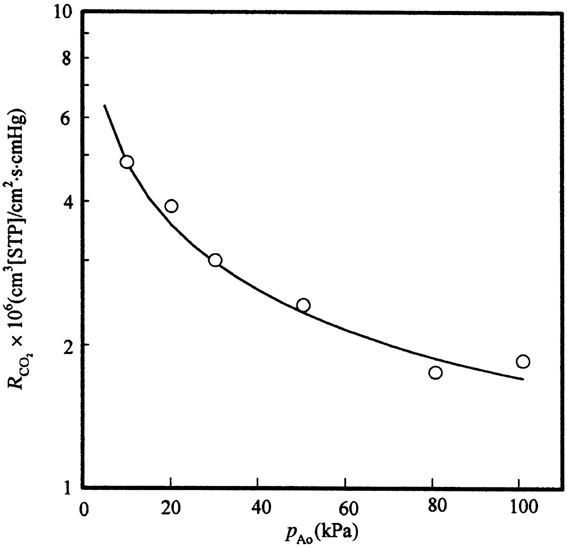

FIG. 4 Effect of partial pressure of CO_2 on the rate of permeation of CO_2 at K_2CO_3 concentration of 1 kmol/m^3 and membrane thickness of 457.5 μm.

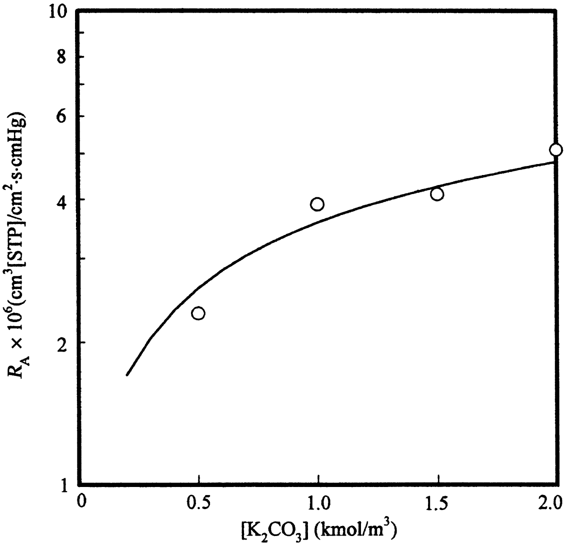

FIG. 5 Effect of concentration of K_2CO_3 on the rate of permeation of CO_2 at CO_2 partial pressure of 20.2 kPa and membrane thickness of 457.5 μm.

branes were plotted in Fig. 6 at K_2CO_3 concentration of 1 kmol/m^3 and p_{Ao} of 20.2 kPa. As shown in this figure, the permeation rate decreases with increasing membrane thickness. R_A also decreased linearly with the slope of -1 up to 100 μm of L. This means that the permeation of CO_2 is governed by physical diffusion in a small range of x (i.e., near upstream surface), and facilitated by chemical reaction in a large range of x.

To observe the effect of additives such as K_2SO_3, PEG, and DBC on the permeation rate of CO_2, R_A was measured for the liquid membrane of an aqueous K_2CO_3 solution containing these additives by changing p_{Ao}, and plotted against p_{Ao} in Fig. 7. This figure definitely shows the promoted permeation rates of CO_2 by additives.

K_2SO_3 exhibits similar behavior in the aqueous solution to K_2CO_3, which facilitates the transfer rate of an acidic gas such as CO_2. The crown ether, in this case DBC, has a property that can capture cations such as K^+ in aqueous K_2CO_3 solutions, and the movement of dissociated anions such as CO_3^{2-} is more active than that of CO_3^{2-} under the condition where K^+ is not combined with DBC (15). The increase in R_A by the addition of DBC can be explained by the capture ability of K^+. The increase of R_A by the addition of PEG can also be explained by the capture ability of PEG, because PEG, whose molecular weight is lower than 400, behaves in a similar manner to crown ether (15).

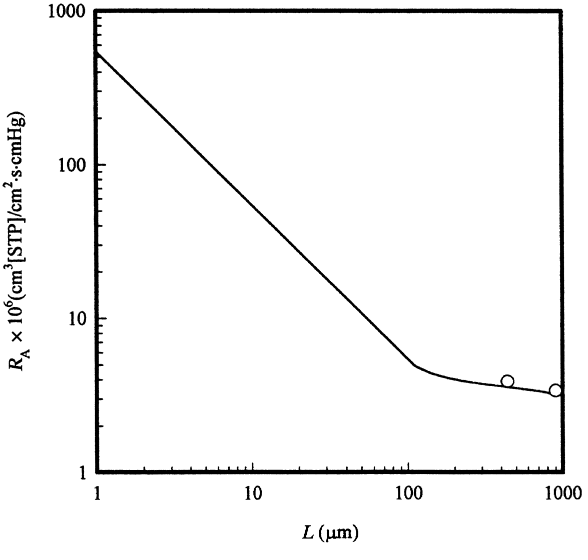

FIG. 6 Effect of membrane thickness on the rate of permeation of CO_2 at K_2CO_3 concentration of 1 kmol/m^3 CO_2 partial pressure of 20.2 kPa.

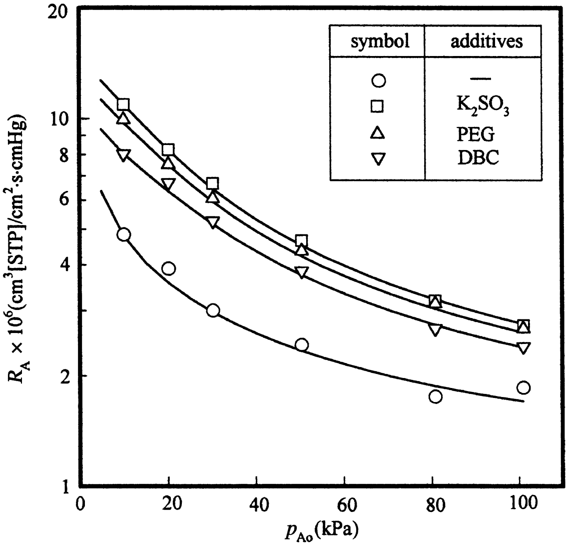

FIG. 7 Effect of additive on permeation rate of CO_2 at K_2CO_3 concentration of 1 kmol/m^3 and membrane thickness of 457.5 μm.

It is not simple to get the kinetic expression of CO_2 in aqueous K_2CO_3 solutions containing these additives. The additives, such as DBC, PEG, and K_2SO_3, are assumed to take part in the hydration reaction of CO_2, such as reaction (1) rather than reactions (2) and (3), because the concentrations of OH^-, HCO_3^-, and CO_3^{2-} depend on the concentration of K_2CO_3 through reactions (2) and (3). Assuming that the increase of R_A by these additives was brought about by an increase in the forward rate constant of reaction (1), k_1 was estimated by conforming to the experimental values of R_A depicted in Fig. 7. The values of k_1 were 1.35, 0.98, and 0.56 s^{-1} for K_2SO_3, PEG, and DBC, respectively. These values were 15–36 times as large as those for K_2CO_3.

CONCLUSION

The permeation rate of CO_2 was measured through a hydrophilic polymeric membrane with immobilized aqueous potassium carbonate solutions under conditions where the partial pressure of CO_2 at the feed side ranges from 10.1 to 101 kPa, the concentration of K_2CO_3 ranges from 0.5 to 2.0 kmol/m^3 and the membrane thickness is fixed at 457.5 or 915 μm at 25°C and an atmospheric pressure.

The permeation rate of CO_2 increased with increasing K_2CO_3 concentration, decreasing CO_2 partial pressure, and decreasing membrane thickness. An approximate solution of the facilitation factor in the facilitated transport has been derived for the case where reversible reactions such as hydration of CO_2, reaction of CO_2 with OH^-, and dissociation of HCO_3^- occur inside the liquid membrane. The permeation rate of CO_2 increased by addition of K_2SO_3, PEG, or DBC to aqueous K_2CO_3 solutions. By assuming that an additive such as K_2SO_3, PEG, or DBC enhances the hydration reaction of CO_2, the forward-reaction rate constant was estimated by fitting to the experimental values of R_A. The values estimated for additives of K_2SO_3, PEG, and DBC were 1.35, 0.98, and 0.56 s^{-1}, respectively. These values amount to 15–36 times as large as those without additives.

NOMENCLATURE

a	dimensionless concentration of component A defined as C_A/C_{Ao}
A	CO_2
B	OH^-
c	dimensionless concentration of carbonic acid (c) defined as C_c/C_K
C_{Ai}	solubility of CO_2 in the aqueous carbonate solution (kmol/m^3)
C_j	concentration of species j (kmol/m^3)
D_{Ej}	effective diffusion coefficient of species j (m^2/s)
D_j	diffusion coefficient of species j (m^2/s)
E	HCO_3^-
F	CO_3^{2-} or facilitation factor defined as Eq. (24)
H	H^+
k_1, k_{-1}	forward- and backward-reaction rate constants, respectively, appearing in reaction (1) (sec^{-1}), (m^3/kmol·sec)
k_2, k_{-2}	forward- and backward-reaction rate constants, respectively, appearing in reaction (2) (m^3/kmol·sec), (sec^{-1})
k_3, k_{-3}	forward- and backward-reaction rate constants, respectively, appearing in reaction (3) (sec^{-1}), (m^3/kmol·sec)
k_4, k_{-4}	forward- and backward-reaction rate constants, respectively, appearing in reaction (4) (sec^{-1}), (m^3/kmol·sec)
k, k'	forward- and backward-reaction rate constants, respectively, appearing in reaction (34) (m^3/kmol·sec)
K	chemical equilibrium constant defined as $[HCO_3^-]^2/[CO_2][CO_3^{2-}]$
K_1	chemical equilibrium constant defined as $[HCO_3^-][H^+]/[CO_2]$ (kmol/m^3)
K_2	chemical equilibrium constant defined as $[HCO_3^-]/[CO_2][OH^-]$ (m^3/kmol)
K_3	chemical equilibrium constant defined as $[H^+][CO_3^{2-}]/[HCO_3^-]$ (kmol/m^3)
K_W	ionic product of water defined as $[H^+][OH^-]$ ($kmol^2/m^6$)

L	membrane thickness (m)
N_{Ao}	mass transfer rate of component A at feed side (kmol/m^2·s)
N_{AL}	mass-transfer rate of component A at stripping side (kmol/m^2·s)
p_A	partial pressure of component A (kPa)
q	dimensionless concentration defined as C_K/C_{Ao}
r	ratio of diffusivity of carbonic acid to that of component A
R_A	permeation rate of component A at standard condition (cm^3[STP]/cm^2·s·cmHg)
r_j	reaction rate of species j (kmol/m^3·s)
x	distance coordinate from upstream surface of liquid membrane
y	dimensionless distance coordinate defined as x/L

Greek Symbols

α	dimensionless quantity defined as $k_2 K_W/k_1 K_3$
β	dimensionless quantity defined as $k_{-1} K_3/k_1$
δ	dimensionless quantity defined as $L\sqrt{k_1\tau}/D_A$
ε	porosity of membrane
η	dimensionless quantity defined as k_{-2}/k_1
τ	tortuosity of membrane

Subscripts

A	CO_2
B	OH^-
c	carbonic acid
E	HCO_3^-
F	CO_3^{2-}
H	H^+
j	species
K	potassium ion
L	stripping side boundary
o	feed-side boundary

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