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Facilitated Transport of CO₂ in Liquid Membrane of CsHCO₃ Aqueous Solution

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Abstract: The facilitated transport of CO₂ gas through liquid membranes of aqueous 0 - 6.27 mol/L CsHCO₃ solution was studied. The permeability ratio $P_{\text{CO}_2}/P_{\text{O}_2}$ was found to increase at high CsHCO₃ concentration in the liquid membrane. The pressure dependence of the permeability coefficients was also measured. The concentration profiles of CO₂, HCO₃⁻, CO₃²⁻ and H⁺ were calculated by assuming that the concentration of CO₂ and HCO₃⁻ can be represented as polynomial functions of the position coordinate x in the membrane, and that Fick's second law holds. The experimental results of the permeability coefficients of CO₂ were explained satisfactory by assuming the linear concentration profiles of CO₂ and HCO₃⁻ in the membrane.

1. Introduction

Both high flux and high selectivity are desirable goals in membrane design. Asymmetric membranes and hollow fibers are examples of systems that may be able to satisfy both of these objectives. An alternative approach might be to make use of facilitated transport [1-3], which was first observed by Scholander [4] in 1960. Matson et al. [5] reported in 1977 an interesting study on the selective removal of H₂S from gasified coal, using an immobilized liquid membrane.

In this study we examined the facilitated transport of carbon dioxide through an aqueous solution of a cesium salt (HCO₃⁻ - CO₃²⁻ - Cs⁺), supported by porous polymer membranes. Although many workers [6-17] have already reported on this system, dependence of CO₂ permeability on the concentration of cations (e.g., [Cs⁺]) in the membranes has not yet been clarified in the wide range of the concentration. For example, Suchdeo and Schultz [9] and Ward and Robb [6] investigated in a fixed concentration of

1.0 and 6.4 mol/L, respectively. Otto and Quinn [7] used the potassium solution of up to 2.0 mol/L.

In the present work permeation experiments were performed under various pressures for whole concentration range (0 - 6.27 mol/L) of the aqueous cesium salt solution (HCO₃⁻ - CO₃²⁻ - Cs⁺), (hereafter, we refer to this as the CsHCO₃ solution).

The theoretical equations and calculations for the facilitated transport of carbon dioxide developed by previous investigators [6,7,9,17] and us were critically tested in the interpretation of the experimental results.

2. Theory

The following reactions are taking place in the facilitated transport of carbon dioxide through the liquid membrane having the CsHCO₃ solution [18,19].

The brackets refer to the molar concentration of each species. Eq. 1 is predominant below pH 8 and Eq. 2 above pH 10. These two steps of carbon dioxide hydration have been thought to be rate-limiting, while the steps corresponding to Eqs. 3 and 4 are expected to be so rapid that the equilibrium will be attained. Considering Eqs. 1-4 and electroneutrality in the membrane, we might have a schematic representation of facilitated transport of carbon dioxide as shown in Fig. 1.

The assumption of electroneutrality at any points in the membrane gives the following equation:

$$[\text{H}^+] + [\text{Cs}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (5)$$

Using Eqs. 1-5 and Fick's second law, the following Eq. 6 is obtained [6,7,9]

$$\begin{aligned} \frac{d[\text{CO}_2]}{dx} = & k_1[\text{CO}_2] + \frac{k_2 K_w ([\text{Cs}^+] - [\text{HCO}_3^-]) [\text{CO}_2]}{2K_3(K_w/2K_3 + [\text{HCO}_3^-])} \\ & - \frac{2k_1 K_3 (K_w/2K_3 + [\text{HCO}_3^-]) [\text{HCO}_3^-]}{([\text{Cs}^+] - [\text{HCO}_3^-])} \\ & - k_2 [\text{HCO}_3^-] \end{aligned} \quad (6)$$

The total net flux of carbon, J_{total} , is obtained from the balance equation

$$\begin{aligned} J_{\text{total}} = & J_{\text{CO}_2} + J_{\text{HCO}_3^-} + J_{\text{CO}_3^{2-}} \\ = & D_{\text{CO}_2} \frac{d[\text{CO}_2]}{dx} + D_{\text{HCO}_3^-} \frac{d[\text{HCO}_3^-]}{dx} + D_{\text{CO}_3^{2-}} \frac{d[\text{CO}_3^{2-}]}{dx} \end{aligned}$$

Fig. 1 Scheme of facilitated transport of carbon dioxide at pH > 10.

$$= \text{constant} \quad (7)$$

where x denotes the position coordinate in the membrane, in the direction of transport. D_{CO_2} , $D_{\text{HCO}_3^-}$ and $D_{\text{CO}_3^{2-}}$ are the diffusion coefficients of CO_2 , HCO_3^- and CO_3^{2-} in the membrane, respectively. The boundary at the high pressure side is at $x = 0$, and that of the low pressure side is at $x = 1$. The boundary conditions on CO_2 are

$$[\text{CO}_2]_{x=0} = p_1(\text{CO}_2) S_{\text{CO}_2}$$

$$[\text{CO}_2]_{x=1} = p_2(\text{CO}_2) S_{\text{CO}_2} \quad (8)$$

where $p_1(\text{CO}_2)$ is the partial pressure of CO_2 at the high pressure side, and $p_2(\text{CO}_2)$ is that at the low pressure side. S_{CO_2} is the solubility of carbon dioxide. With Eqs. 5-8, it should be possible to estimate the permeability coefficient of CO_2 , P_{CO_2} , but the nonlinear terms in Eq. 6 make an analytical solution of the equations difficult. Three approximate methods for calculating the solution have already been proposed. In the first method (case A) [6,7,9], for the simplicity of the mathematical treatment, an equilibrium represented by Eq. 1 is assumed, even though this is not attained in the transport process, since the hydration of CO_2 is very slow [7,9]. The following equation is obtained from Eqs. 3-5.

$$[\text{HCO}_3^-] = (K_1/4K_3)[\text{CO}_2](-1 + \sqrt{1 + 8K_3[\text{Cs}^+]/(K_1[\text{CO}_2])}) \quad (9)$$

P_{CO_2} is calculated numerically with Eqs. 7-9.

In the second method (case B), for certain special condition, e.g., in the concentration range of 0.25 mol/L to 2.0 mol/L for $[HCO_3^-]$, which was used in the experiments performed by Otto and Quinn [7], it may be possible to assume that $[HCO_3^-]$ is constant throughout the membrane. Eq. 6 can then be linearized by assuming that $[HCO_3^-]$ is constant in the membrane. This approximation was first proposed by Ward and Robb [6] and was studied by Otto and Quinn [7].

In the third method (case C), the numerical method of quasilinearization [17] is used for solving Eq. 6. This method was proposed by Suchdeo and Schultz [9,17]. For solving Eq. 6 [9,17] the following boundary condition was also used.

$$\frac{d[HCO_3^-]}{dx} = \frac{d[CO_3^{2-}]}{dx} = 0 \quad \text{at } x = 0, 1 \quad (10)$$

3. Experimental

3.1 Materials

99.99% purity of O_2 and CO_2 was purchased from Kayama Sanso Co. Ltd. Acetone, methanol, cyclohexanol, Cl_2 and $CsHCO_3$ were special reagents (Wako Ltd.). Distilled water was used in this study.

3.2 Liquid membrane

Porous membranes were prepared from cellulose acetate (Eastman, acetyl 39.4%, ASTM visc. 45 sec), acetone, methanol, cyclohexanol and $CaCl_2$ using microphase separation [20]. We adopted the impregnation method [6], in which the liquid, $CsHCO_3$ aqueous solution, is immobilized by

means of its surface tension in the polymer matrix of the membrane. The surface tension, γ is given as [21]

$$\gamma = r\rho g l/2 \quad (11)$$

where g is the gravitation constant, l is the capillary rise. ρ is the density of the solution, and r is the capillary radius. By using this equation, the condition of liquid retention can be estimated. For example, assuming the pressure difference between the two sides of the membrane to be 1 atm, and the pore radius of the membrane r to be less than 1.48×10^{-4} cm, the liquid is certainly retained in the membrane matrix. As shown in Table 1, the pore radii of the membranes used here were far smaller than 1.48×10^{-4} cm. Thus the impregnation method can be safely employed for the immobilization of the liquid in this study. The liquid membrane was prepared by soaking the membrane assembly in $CsHCO_3$ solution for at least one day.

3.3 Gas permeation measurements

The apparatus used for gas permeation experiments was exactly the same device used in our previous studies [22-23]. Before starting the experiments, all gases except saturated water vapor were completely evacuated from the device of gas permeation measurements. At the beginning of the experiments, the gas (CO_2 and O_2) was introduced in the upstream side, and the apparent permeability of the gas was determined by measuring the pressure change of the downstream side with a manometer. During the experiments the pressure of the upstream side was assumed to be constant,

Table 1 Characteristics of porous cellulose acetate membranes^{a)}

ϵ	H^b	r (μm)	Pore density ^{c)} (million number/cm ²)	$\pi(CO_2)$	$\pi(O_2)$
0.61 ± 0.03	0.64 ± 0.03	0.247 ± 0.05	164 ± 18	3.6 ± 0.2	3.6 ± 0.2

^{a)} Data are expressed as the means $\pm$ S.D. of four independent measurements.

^{b)} H is water retention defined by $H_2O(g)/(H_2O + \text{polymer}(g))$

^{c)} Pore density is estimated by scanning electron microscope.

since the volume of the upstream side was more than 500 times larger than that of the downstream side. Permeation experiments for CO_2 and O_2 were performed at different concentrations (0.00, 0.97, 1.89, 2.75, 3.57, 4.35, 5.09, 5.77 and 6.27 mol/L) of the CsHCO_3 solution. The apparent permeability was calculated according to the following equation [24].

$$P' = (273/T)(1/76)V_2(\delta p_2(i)/\delta t)(1/A \cdot L)(1/(p_1(i) - p_2(i))) \quad (12)$$

where

V_2 : the volume of the downstream side (cm^3)

L : membrane thickness (cm)

$p_1(i)$: partial pressure of species i in upstream side (cmHg) at time t

$p_2(i)$: partial pressure of species i in downstream side (cmHg) at time t

T : temperature (K)

A : membrane area (cm^2)

All measurements were performed at $20 \pm 0.1^\circ\text{C}$.

4. Results and Discussion

4.1 Estimation of real permeability

Since the permeation of gases in a polymer is much slower than that in a liquid, we assume that a penetrant permeates only through the liquid phase (the permeability coefficients of O_2 in a homogeneous cellulose acetate membrane and in H_2O are 0.48×10^{-10} [25] and $0.95 \times 10^{-8} \text{ cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ [26,27], respectively). We therefore use Eq. 13 to calculate the real permeability coefficient, P (hereafter it is called permeability coefficient) from the apparent permeability coefficient, P' obtained experimentally.

$$P' = P\varepsilon/\tau \quad (13)$$

where ε is porosity of the membrane and τ is the tortuosity. In order to establish estimates of ε and τ , the apparent permeabilities P'_{CO_2} and P'_{O_2} were measured for a liquid membrane of distilled water. Using published measurements of P_{CO_2} and P_{O_2} in H_2O [26,27], both the tortuosity τ and the

characteristic ratio, τ/ε were calculated from Eq. 13 and summarized in Table 1. Table 1 shows that $\tau(\text{CO}_2) = \tau(\text{O}_2)$. This suggests that there is little or no interaction between these two penetrants and the polymer matrices.

4.2 Facilitated transport of CO_2

The relationship between the ratio ($P_{\text{CO}_2}/P_{\text{O}_2}$), which gives a measure of selective separation, and the concentration of the CsHCO_3 solution is given in Fig. 2. The higher the concentration of the CsHCO_3 solution, the larger the ratio $P_{\text{CO}_2}/P_{\text{O}_2}$ becomes (120 in 6.27 mol/L CsHCO_3 solution). Ward and Robb [6] reported the ratio to be 1500 in 6.4 mol/L CsHCO_3 solution. This discrepancy can be attributed to the differences in the experimental conditions. In both cases, the ratio $P_{\text{CO}_2}/P_{\text{O}_2}$ is much higher than the value in H_2O (25.2 [26,27]). The steep rise of $P_{\text{CO}_2}/P_{\text{O}_2}$ in the high concentration range is attributed to the increase of the HCO_3^- concentration (cf. Eq. 2 at $\text{pH} > 10$).

It is well known that NaAsO_3 acts as a catalyst [6,14,18,19] in the hydration reaction of CO_2 . As shown in Fig. 2, NaAsO_3 is effective for facilitated transport of CO_2 , as reported [6].

Fig. 2 Dependence of permeability ratio, $P_{\text{CO}_2}/P_{\text{O}_2}$, on CsHCO_3 concentration in liquid membrane of aqueous CsHCO_3 solution (●) and aqueous $\text{CsHCO}_3 + 0.5 \text{ mol/L NaAsO}_3$ (○) at $p_1(\text{CO}_2) = 60 \text{ cmHg}$, $p_2(\text{CO}_2) = 0 \text{ cmHg}$ and 293 K . Data are expressed as the means $\pm$ S.D. of four independent measurements.

Table 2.1 Equilibrium constants and reaction constants. [7,18]

Equilibrium constants				Reaction constants			
K_1	K_2	K_3	K_w	k_1	k_{-1}	k_2	k_{-2}
$4.17 \times 10^{-7} \text{ M}$	$4.25 \times 10^7 \text{ M}^{-1}$	$4.69 \times 10^{-11} \text{ M}$	10^{-14} M^2	0.03 sec^{-1}	$7.2 \times 10^4 \text{ sec}^{-1} \text{ M}^{-1}$	$8500 \text{ sec}^{-1} \text{ M}^{-1}$	$2 \times 10^{-4} \text{ sec}^{-1}$

Table 2.2 Diffusion coefficients and solubility in H_2O . [26,27]

Gas	$D \text{ (cm}^2\text{/sec)}$	$S \text{ (cmHg}^{-1}\text{)}$
CO_2	1.77×10^{-5}	1.66×10^{-2}
O_2	1.98×10^{-5}	4.08×10^{-4}

4.3 Concentration profiles in liquid membrane

Concentration profiles of CO_2 , HCO_3^- , CO_3^{2-} and H^+ in the liquid membrane were estimated by means of the following procedure, using the experimental measurements of the CO_2 flux. This procedure is the same as Suchdeo and Schultz's method [9,17]. But the boundary conditions of HCO_3^- and CO_3^{2-} (Eq. 10) have not been used in this study.

(1) The local concentrations of CO_2 and HCO_3^- are assumed to be approximated by polynomial functions of the distance x . That is

$$[\text{CO}_2] = \sum_{n=0}^m A_n x^n \quad (14)$$

$$[\text{HCO}_3^-] = \sum_{n=0}^m B_n x^n$$

where A_n and B_n are parameters.

(2) Eq. 6 holds.

(3) Eq. 8 holds.

$$(4) J_{\text{total}} = D_{\text{CO}_2}([\text{CO}_2]_{x=0} - [\text{CO}_2]_{x=1}) + D_{\text{HCO}_3^-}([\text{HCO}_3^-]_{x=0} - [\text{HCO}_3^-]_{x=1})$$

$$+ D_{\text{CO}_3^{2-}} \left(\frac{[\text{HCO}_3^-]_{x=0}(1 - [\text{HCO}_3^-]_{x=0})}{K_w/K_3 + 2[\text{HCO}_3^-]_{x=0}} - \frac{[\text{HCO}_3^-]_{x=1}(1 - [\text{HCO}_3^-]_{x=1})}{K_w/K_3 + 2[\text{HCO}_3^-]_{x=1}} \right) \quad (15)$$

Where J_{total} is the total flux of CO_2 including the facilitated transport of CO_2 in the membrane. Eq. 15 was obtained from Eqs. 3-5 and 7 by assuming that $[\text{H}^+]$ is negligible compared to the other ion concentrations. Eq. 6 applies at any point in the membrane. When the numerical values of $p_1(\text{CO}_2)$, $p_2(\text{CO}_2)$ and $[\text{Cs}^+]$ are determined, estimates of the series of parameters $A_0 - A_m$ and $B_0 - B_m$ can be obtained from Eqs. 6, 8, 14 and 15 by using a nonlinear least squares method. There is, however, great difficulty in determining the parameters, A_n and B_n , where m is chosen to be more than 4. And we found that there is no essential difference between the results for the cases $m = 2$ and $m = 3$. The difference between the concentrations calculated for each of these cases was, in fact, not greater than 0.5%.

To estimate the concentration profiles of CO_2 , HCO_3^- , CO_3^{2-} and H^+ , physico-chemical data such as the diffusion coefficients of CO_2 , HCO_3^- and CO_3^{2-} , the reaction rate constants, the equilibrium constants and the solubilities of CO_2 in various concentrations of CsHCO_3 solution have to be determined. These values were obtained from the literature [7,18,26,27] and from the experiments in this study. The values used for the calculation are summarized in Table 2. The concentration profiles thus estimated for the conditions $p_1(\text{CO}_2) = 60 \text{ cmHg}$, $p_2(\text{CO}_2) = 0 \text{ cmHg}$, $[\text{Cs}^+] = 6.27 \text{ mol/L}$ and $m = 3$ are shown in Fig. 3. It was found that the concentration profiles for CO_2 , HCO_3^- , CO_3^{2-} and H^+

Fig. 3 Concentration profiles of chemical species in facilitated transport of CO_2 through liquid membrane at $p_1(\text{CO}_2)=60$ cmHg, $p_2(\text{CO}_2)=0$ cmHg, $[\text{Cs}^+]=6.27$ mol/L and $m=3$.

Fig. 4 Dependence of permeability coefficients of CO_2 (●) and O_2 (○) on CsHCO_3 concentration in liquid membrane at $p_1(\text{CO}_2)=60$ cmHg, $p_2(\text{CO}_2)=0$ cmHg and 293 K. The calculated lines from case A, B, C and D are also shown.

are almost linear as a function of x . Boundary conditions of HCO_3^- and CO_3^{2-} are usually written as Eq. 10 by several investigators [7,9,17]. However the concentration profiles for HCO_3^- and CO_3^{2-} are almost linear in Fig. 3. We are suspicious about the validity of Eq. 10 because HCO_3^- is generated from CO_3^{2-} at $x=0$ and CO_3^{2-} is also generated from

Fig. 5 Pressure dependence of permeability coefficients of CO_2 at $[\text{Cs}^+]=6.27$ mol/L, $p_2(\text{CO}_2)=0$ cmHg and 293 K. The calculated lines from case A, B, C, and D are also shown.

HCO_3^- at $x=1$. The boundary condition of HCO_3^- and CO_3^{2-} should be given as Eq. 16.

$$D_{\text{HCO}_3^-} \frac{d[\text{HCO}_3^-]}{dx} + D_{\text{CO}_3^{2-}} \frac{d[\text{CO}_3^{2-}]}{dx} = 0 \quad (16)$$

Eq. 16 indicates that the flux of CO_3^{2-} changes to the flux of HCO_3^- by the addition of H^+ to CO_3^{2-} at $x=0$, and the flux of HCO_3^- changes to the flux of CO_3^{2-} by the subtraction of H^+ from HCO_3^- at $x=1$ from Fick's second law.

4.4 Estimation of P_{CO_2} from calculation

By assuming that the concentration profiles of CO_2 and HCO_3^- are linear ($m=1$ in Eq. 14) as a function of x in the liquid membrane without using Eq. 10, we can estimate P_{CO_2} (case D).

Experimental results and P_{CO_2} calculated by the case D, together with the values calculated by the methods of case A, case B and case C as described in the theory of this paper, are shown in Figs. 4 and 5 and Table 3. The CsHCO_3 concentration dependence of P_{CO_2} and P_{O_2} for the boundary conditions $p_1(\text{CO}_2)=60$ cmHg, $p_2(\text{CO}_2)=0$ cmHg, $p_1(\text{O}_2)=60$ cmHg and $p_2(\text{O}_2)=0$ cmHg is shown in Fig. 4. As for the experimental results, P_{O_2} decreases linearly to a great extent with increase of the CsHCO_3 concentration. This is caused by the decrease of both the diffusion coefficient and the

Table 3 Comparison of permeability coefficients of CO₂ and facilitated ratio calculated by Case A, Case B, Case C and Case D and experimental result at [Cs⁺]=6.27 mol/L, $p_1(\text{CO}_2)=60$ cmHg, $p_2(\text{CO}_2) = 0$ cmHg and 293 K.

	$P_{\text{CO}_2} \times 10^8$ (cm ³ (STP)·cm/cm ² ·sec·cmHg)	$J_{\text{total}} / J_{\text{CO}_2}$
Experimental result	9.9 ± 0.8^a	4.9 ± 0.4^a
Case A	29.2	14.3
Case B	2.09	1.03
Case C	2.08	1.02
Case D	5.15	2.53

^a)Data are expressed as the means $\pm$ S.D. of four independent measurements.

solubility of the O₂. In the case of CO₂, the decreasing tendency of P_{CO_2} is almost the same as that for O₂ up to a 4 mol/L CsHCO₃ solution concentration. In the concentration range above 4 mol/L, the permeability begins to increase. This indicates that the facilitated transport of CO₂ is more effective in the higher concentration range, and is consistent with the tendency found in Fig. 2.

The curve calculated for case A deviates considerably from the experimental results. In case B, the calculated curve also deviates far from the experimental results in the region from 5 mol/L to 6.27 mol/L, where facilitated transport is effective. Furthermore the results of case C are observed to be practically the same as those of case B. The curve calculated for case D is found to explain the experimental results better than the curves calculated for case A, case B and case C in Fig. 4, although the slight increase of experimental P_{CO_2} in the high concentration range of [Cs⁺] could not be reproduced.

P_{CO_2} as a function of $p_1(\text{CO}_2)$ is shown in Fig. 5, for the conditions of $p_2(\text{CO}_2) = 0$ cmHg and 6.27 mol/L CsHCO₃ solution. The values calculated for case A, case B and case C again fail to explain the experimental results. From Figs. 4 and 5, case D seems to be reasonable, in that it explains the

experimental results more satisfactory than other methods, case A, case B and case C. The failure of case C to explain our experimental results probably comes from the boundary conditions of HCO₃⁻ and CO₃²⁻.

The values obtained by case D are, however, always lower than the experimental results. The reasons for this are probably due to the fact that the reaction rate constants and equilibrium constants, which were obtained from the literature, may not be correct in the liquid membrane with high concentration (6.27 mol/L) of CsHCO₃ solution.

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