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Apparatus and Permeability of CO_2 Dissolved in Water through LDPE and Nylon 6 Films

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The apparatus by which the measurement of the permeability coefficient of films of carbon dioxide dissolved in water through films was carried out was constructed. The apparatus consists of a carbon dioxide electrode in a liquid and liquid diffusion cell. Using this, permeability of low density polyethylene (LDPE) film and Nylon 6 film of carbon dioxide dissolved in water through films were measured. Polystyrene (PS) film, which is used as a standard film for oxygen permeability coefficient was also measured. Even for the hydrophobic films, namely LDPE film and PS film, the apparent permeability coefficients were observed to be slightly higher than those in a gas phase due to the effect of absorbed water in the films. The apparent permeability coefficient of Nylon 6 was about two orders of magnitude higher than that in gas phase due to plasticizing effect of water.

Keywords ; Gas permeability, Carbon dioxide, LDPE, Nylon 6

INTRODUCTION

Permeabilities of films of oxygen dissolved in water have been studied to clarify the effect of water on the permeability1)-7). The permeability of dissolved oxygen is mostly determined by applying an oxygen electrode in water and water diffusion cell. One of the authors also reported the effect of water on the oxygen permeability for films having both hydrophilic and hydrophobic monomeric units structures9).

Few researchers9) studied transport of dis solved gas except oxygen in the films using a gas electrode. It seems that no interest have been paid for the transport of carbon dioxide dissolved in water. The concentration of carbon dioxide in packages of foods in sorm cases should be important to keep their quality. Iezdorczyk et. al9). reported diffusion

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coefficients of carbon dioxide dissolved in water through several films by the time lag method, but they did not measure any of permeability. This work dealt with the apparatus for permeability measurement and the permeability coefficients of carbon dioxide dissolved in water through films, which are being used for food packaging, by applying a carbon dioxide electrode in a liquid and liquid permeation cell.

EXPERIMENTAL

Samples used in this study are low density polyethylene (LDPE) film. Nylon 6 film and polystyrene (PS) film (Stylex, Mitsubishi Plastics Ind. Ltd.), which is used as a standard film. Carbon dioxide of more than 99.99% purity was used as received. Ultrapure water by Toraypure LV- 10T reverse osmosis system (Toray Co., Ltd.) was used throughout the experiment.

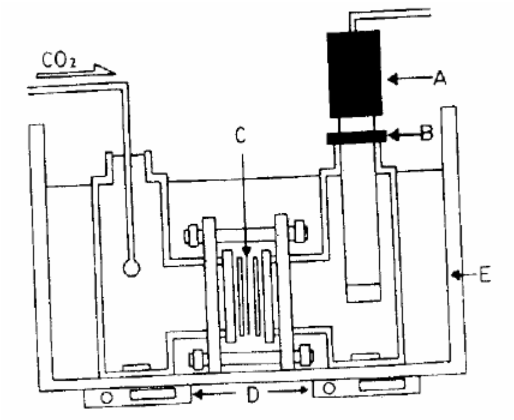


Fig. 1 Diagram of permeation apparatus : (A)CO_2 electrode ; (B)O-ring ; (C) film ; (D) magnetic stirrer ; (E) water bath.

A diagram of the permeation apparatus is shown in Fig. 1. The permeation cell consists of two glass chambers separated by a film.

The cell volume of the upstream or down stream side was 200ml, respectively. The effective film area was $6.84cm^2$. The revolution speed of magnetic spinbars in the cells was controlled (i.e., 430 rpm in this study) by a magnetic stirrer having a revolution meter (HS3D, Iuchi Seiseido Co., Ltd.). The pH-type CO_2 electrode made by TOA Elec tronics Ltd. was used as a sensor to determine the concentration of carbon dioxide. A diagram of the electrode is shown in Fig. 2.

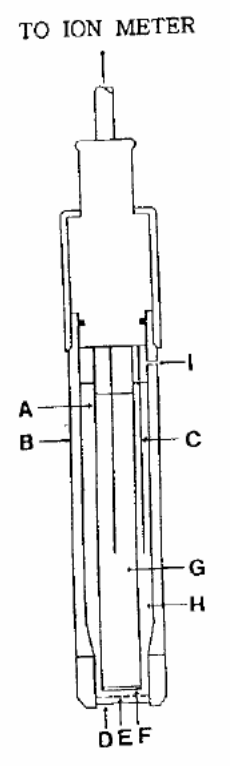


Fig. 2 Structure of CO_2 electrode. A glass electrode ; B sheath; C reference electrode; D Diaphragm ; E spacer ; F high sensitive glass membrane ; H internal filling solution ; I micro hole.

After water in the cells was equilibrated with CO_2 atomospheri-cally, the upstream water was pumped out and saturated water with CO_2 at 1 atm was immediately injected into the upstream side cell at time=0s. Permeability coefficients were calculated from the concentration change of CO_2 monitored by the CO_2 electrode.

CALCULATION OF THE CO_2 PERMEABILITY COEFFICIENT

The pH changes were monitored by differences of the electromotive forces with the reference electrode. This is expressed as follows :

$$E=E_0 + k\ \text{In}\ a_H^+ \cdots\cdots\cdots\cdots (1)$$

where E is the electromotive force obtained experimentally, Eo is an intrinsic electromotive force in this system, k is RT In 10 / (ZF) (Z=1 in this case), and a_H^+ is an activity of H+.F is the Faraday con－stant. Equation (1) is also expressed as follows :

$$E=E_0 + k\ \text{In}\ (r\,C) \cdots\cdots (2)$$
$$=E_0 + k\ \ln r + k\ \ln C \cdots\cdots (3)$$

where *r* is an activity coefficient.

$$C = 10^{(E - E_0)/k} \cdots\cdots (4)$$

where Eo' =Eo + k In *r*. Fig. 3 shows the relationship between the concentration of CO_2 in the outer solution of the electrode and E. The experiments were performed on the condition of pH= 7.0 at the down stream side ; the self-dissociation of water was neglected.

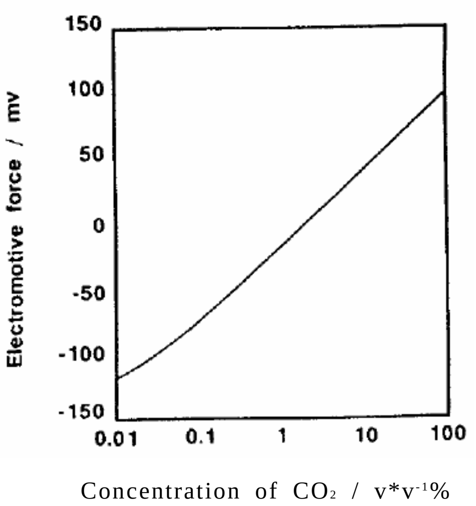


Fig. 3 Plot of electromotive force vs. concentration in gas phase for carbon dioxide electrode at 25°C in this system.

An apparent permeability coefficient for film in such a system is calculated as follows :

The volume permeated is expressed by the following equation :

$$Q = \frac{P\ (P_1 - P_2)\ At}{\ell} \cdots\cdots\cdots (5)$$

where Q is the volume permeated through the film, P is the permeability coefficient, p_1 and p_2 are partial pressure of gas at the upstream side and downstream side of the film, respectively, A is the film area and t is the time. ℓ is the thickness of the film.

$$P = \frac{Q\,\ell}{\Delta PAt} \cdots\cdots\cdots (6)$$

$$\Delta Q = \frac{C_2 - C_1}{t_2 - t_1} \cdots\cdots\cdots (7)$$

Then permeability coefficient is expressed by the following equation :

$$P = \frac{\ell}{\Delta PA} \cdot \frac{C_2 - C_1}{t_2 - t_1} \cdots\cdots\cdots (8)$$

where $\Delta p = p_1 - p_2$ and p_2 is C/α. α is the Bunsen absorption constant of CO_2 (0.759cm Hg^{-1} at 25°C.)[10]. The schematic representation of a transient transport run is shown in Fig. 4. As C in the eq. 4 is the concentration of the CO_2 in the water, it should be transformed into volume of gaseous state, by using eq. 9. The permeability coefficient was determined from the mean values of three to 3 five experiments. All measurements were performed at 25 0.1°C.

$$P = \frac{\ell}{\Delta PA} \cdot \frac{C_2 - C_1}{t_2 - t_1} \cdot \frac{V \cdot 273}{273 + t} \text{ ...... (9)}$$

where V is the cell volume at the downstream side. The permeation experiment was stopped when the concentration of CO_2 of the downstream side reached to 3 % of that of the upstream side. The average partial pressure of CO_2 at the downstream side between t_1 and t_2 was used.

RESULTS AND DISCUSSION

Fig. 5 shows the dependence of apparent permeability coefficients on C for LDPE and PS films. The term "apparent permeability

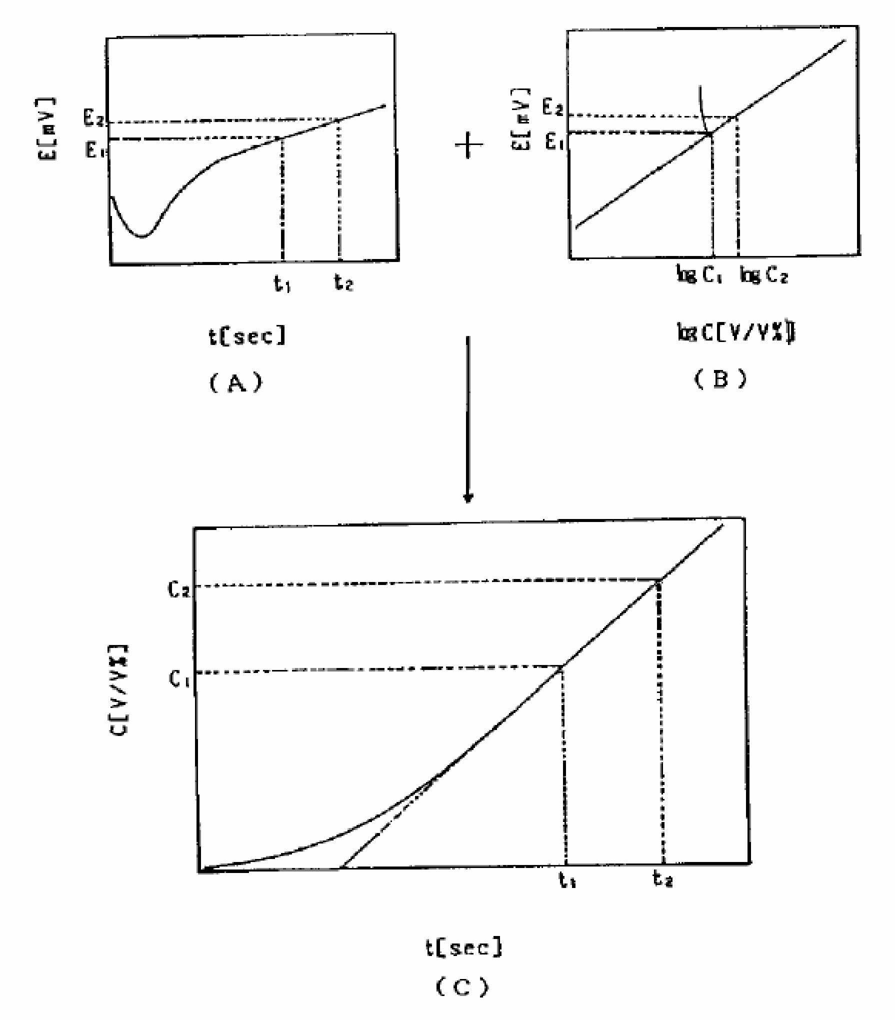


Fig. 4 Schematic representation of a transient transport run.

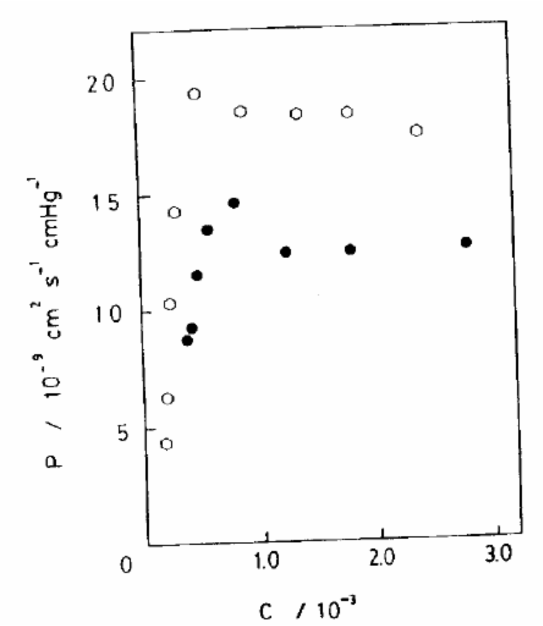


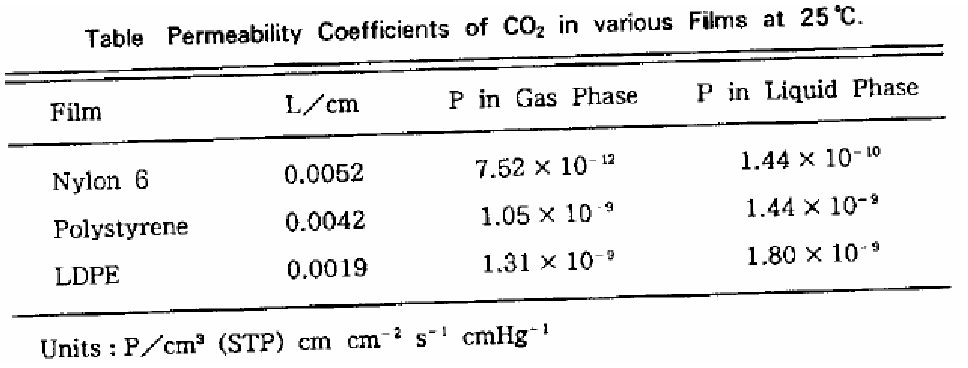
Fig. 5 Dependence of permeability coefficients of CO_2 on C, for LDPE(O)and PS (●) films at 25℃ and po=1atm.

coefficient" means the permeability coefficient which composed of the intrinsic permeability of polymer film and the permeability of water layer on the film. Both films show the permeability coefficient increase with the increasing C at C < 0.001 (cm^3 (STP) /cm^3) and give a maximum near C=0.001. This behavior probably arises from the slow response time of the electrode at the low concentration of CO_2. It was shown that it took 12 min.from atmospherical concentration of CO_2 (0.0003cm^3 (STP) /cm^3) to C = 0.001 and 4 min. from the atmospherical concentration to C =0.01 to show the actual potential by the electrode11). The apparent permeability coefficient shows lower values due to the limit of response time at the beginning (C< 0.001). When C increases at the concentration C = 0.001, response rate becomes faster to catch up with the increasing rate of CO_2 at the downstream side, and this contributes to the increase of the apparent permeability coefficient. When C comes near 0.001, the response rate can follow the increasing of CO_2 concentration at the down-stream side. This contributes to the higher apparent permeability coefficient than the permeability coefficient, P, which is calculated by eq. 9 indicates the response rate rather than the permeating rate of CO_2. Therefore, each curve in Fig. 5 has the permeability coefficient.

At C > 0.001, the permeability coefficient is independent of C at because the measured potential coincides with the actual potential without delay due to the fast response time of the electrode. The permeability coefficients which were obtained at C > 0.001 are considered to be independent on concentration of carbon dioxide. Such permeability coefficients are expressed as P in liquid phase. The permeability coefficients of CO_2 through the films measured in gas phase (high vacuum method) are summarized in Table 1 and are compared with those in the gas phase.

In the liquid phase a boundary layer resistance was supposed to exist on the film interface and this made to detect lower permeability values than those in the gas phase1)4)6) and this resistance may contribute to the lower permeability than value measured in the gas phase. Table 1 shows, however, that the apparent permeability coefficients in the liquid phase are higher than those in the gas phase, for not only on the hydrophilic

Table Permeability Coefficients of CO_2 in various Films at 25°C.



Film	L/cm	P in Gas Phase	P in Liquid Phase
Nylon 6	0.0052	7.52×10^{-12}	1.44×10^{-10}
Polystyrene	0.0042	1.05×10^{-9}	1.44×10^{-9}
LDPE	0.0019	1.31×10^{-9}	1.80×10^{-9}

Units : P/cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$

film, nylon 6, but on hydrophobic films such as PS and LDPE.

Since the measurable lower limit of permeability coefficient capable of being measured in the liquid phase is estimated to be 1 x 10"" cm3 CSTP) cm/ cnV'S'cm Hg from the blank lest* the higher permeability coef-ficient observed in the liquid phase is not due to the leak of COa at the downstream side. The permeability coefficient of the nylon 6 film in the liquid phase especially observed to be twoorders of magnitude higher than the permeability coefficient in the gas phase. This can be explained by the plasticizing effect 12 of the water molecule in the film. The plasticizing effect is predominant over the reduction of the permeability due to the boundary layer's resistance and this results in the higher permeability in the liquid phase.

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