

Sorption and Permeation Behavior of Water Vapor and Carbon Dioxide Gas through Ethylene Ionomer Membranes

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Synopsis

Sorption and permeation of water vapor and carbon dioxide gas through ethylene ionomer membranes were studied as a function of pressure. Water sorption increased with an increase of the acid content and especially degree of neutralization of ethylene ionomers. The sodium salt ionomer enhanced water sorption compared to the zinc salt ionomer. However, there was no remarkable difference of permeability coefficient of water vapor through the sodium and zinc ionomer membranes. Diffusion coefficient of the sodium salt ionomer is one order smaller than that of zinc salt ionomer, corresponding to an immobilized water structure in the sodium salt ionomer. Differential scanning calorimetry studies on water sorbed to membrane manifested that water sorbed was almost nonfreezable. Sorption of carbon dioxide gas in ethylene ionomers was a dual-mode type. The pressure dependence of permeability coefficient of carbon dioxide gas was interpreted in terms of a partial immobilization model, independent of the kind of the metal salt in ethylene ionomer.

INTRODUCTION

It is well known that salt groups in ethylene ionomers form ionic aggregates separated from hydrocarbon phases.¹⁻⁴ The ionic aggregates are composed of multiplets of a few ion pairs in the case of less than a few mole percents of salt groups and of clusters in the case of more than a few mole percents.³ Although many models⁵⁻⁸ of the cluster are proposed, the model of MacKnight-Taggart-Stein,⁹ which consists of a core structure of densely packed ions and a surrounding matrix ion separated by a shell of hydrocarbon chains, is reasonable to accept. The characteristic mechanical properties of ethylene ionomer were interpreted in terms of apparent physical crosslinking existing in the core ion domain. Such domains, in addition, might manifest other specific properties than mechanical properties. In fact, Nafion membrane, a polymer based on a perfluoroethylene backbone with a side chain of sulfonic acid, was used as separator in electrochemical applications. This membrane has the diffusion coefficient of water close to the self-diffusion coefficient of water.⁹ This is suggestive of a very loose structure of Nafion membrane. Ethylene ionomers exhibited a disappearance of the small angle X-ray scattering cluster ring with increasing water content.¹⁰ Bonotto and Bonner¹⁰ suggested that small quantities of water

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are absorbed into the ionic domain, while larger quantities of water could solvate the ions and destroy the cluster. Thus, knowledge of water behavior in ionomers is very important to understand the characteristics of ionomers.

In this study, the sorption and permeation behaviors of water vapor were examined in the light of the interaction between water vapor and the ionic domain in ethylene ionomer. Thermal analysis of water sorbed was carried out to aid an understanding of the sorption and permeation behavior of water vapor. Furthermore, we studied the sorption and permeation of carbon dioxide gas which has less interaction with the ionic domain than does water vapor.

EXPERIMENTAL

Several kinds of ethylene ionomers supplied by Mitsui Polychemical Co. Ltd. were used. As usual, the sample abbreviation of ethylene ionomers was as follows; E-aMAA-bM means that major component is ethylene (E), minor component methacrylic acid (MAA), a is mole fraction of MAA, M counterion, and b fractional degree of neutralization. The sample designation, mole fraction of MAA and degree of neutralization of ethylene ionomers used here are tabulated in Table I. The sample isothermally crystallized at 50°C for one day was used for sorption and permeation experiments.

Water vapor sorption experiment was made at 25°C by a standard gravimetric sorption apparatus using a quartz spring.¹¹ The sample was dried under 10^{-5} mmHg until a variation of its elongation was not observed at all. Sorption amount of water vapor to the dry sample thus obtained was evaluated by an elongation of the quartz spring.

Carbon dioxide gas sorption experiment was carried out with a recording electrobalance (Model RG, Cahn Division, Ventron Instrument Corp, Paramount CA). The sample was completely dried similarly to the water vapor sorption experiment and then sorption amount of carbon dioxide gas was determined at a pressure range of 0–40 cmHg. A detailed procedure of sorption experiment was described elsewhere.¹²

The permeation of water vapor and carbon dioxide gas through ethylene ionomer membrane of 30 μm thick was measured at 25°C and at a certain pressure with a Rouse-type apparatus in which the pressure on the delivery side was maintained to be essentially zero. From the steady-state straight line of permeation curve, the permeability coefficient was evaluated.

TABLE I
The Sample Designation, Mole Fraction of MAA (a), and Degree of Neutralization (b) of Metal (M) Ionomers and the Degree of Hydration at 25°C

Sample	a	b M	Degree of hydration (g/g)
II-1	0.035	0	0.0019
II-2	0.035	0.4 Na	0.030
II-3	0.035	0.5 Na	0.061
III-1	0.054	0	0.0019
III-3	0.054	0.6 Zn	0.0035
III-5	0.054	0.6 Na	0.102

The differential scanning calorimetry (DSC) of water sorbed to ethylene ionomers was analyzed with a highly sensitive differential scanning calorimeter (SSC 560U) manufactured by Seiko Denshi Kogyo Ltd. After the sorption of water to about 30 mg of the ethylene ionomer under different water vapor pressures, the specimen was sealed up tightly and water content remained constant even after DSC measurement. The DSC measurement was carried out at the heating rate of 0.5°/min.

RESULTS AND DISCUSSION

Water Vapor Sorption and Permeation

Different ethylene ionomer membranes of about 2 g and 150 μm thick were immersed into water for 10 days at 25°C. The degree of hydration evaluated (weight of water content sorbed/weight of dry ethylene ionomer) is also shown in Table I. It was found that the ethylene ionomer with an increasing neutralization could sorb water considerably and the sodium salt of ethylene ionomers could hydrate about 30 times more water than the zinc salt. Thus acid content, degree of neutralization, and kinds of the metal salt influence remarkably the degree of hydration. Sorption isotherms of water vapor to the different ethylene ionomers are shown in Figure 1. One can see the sigmoidal sorption isotherm for II-2, II-3, and III-5. It is reasonable to consider the sorption to the polar sites in ethylene ionomers at a low relative vapor pressure, which are mainly composed of ionic pairs, multiplet, and/or cluster. Solution-type sorption is likely to begin to occur at about 0.3 relative vapor pressure for II-2, II-3, and III-5, indicating a swelling of ionic domains. A smaller amount of water sorbed to the zinc

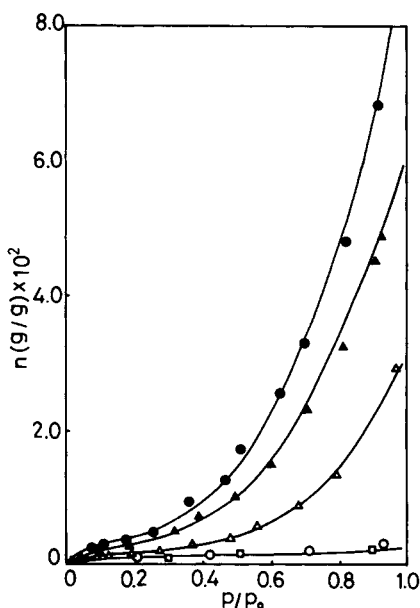


Fig. 1. Sorption isotherms of water vapor to the different ethylene ionomers at 25°C; II-1 (\square), II-2, (\triangle), II-3, (\blacktriangle), III-3 (\circ), III-5 (\bullet).

salt of ethylene ionomer is considered to be due to a difficult swelling because of an ionic bonding by the divalent zinc salt and also due to less dissociation of the zinc salt.

Sorption isotherm only in a low relative vapor pressure appears to exhibit a dual-mode sorption mechanism¹³⁻¹⁶ which is usually applied to glassy polymers containing microvoids. Dual-mode sorption parameters were estimated using the low pressure isotherm and following equation describing dual-mode sorption mechanism;

$$\begin{aligned} C &= C_D + C_H \\ &= k_D p + \frac{C'_H b p}{1 + b p} \end{aligned} \quad (1)$$

where C is the amount of water sorbed, C_D is the amount of water sorbed by Henry's law-type sorption, C_H is the amount of water sorbed by Langmuir-type sorption, k_D is Henry's law solubility coefficient, p is pressure, C'_H is maximum capacity of sorbable sites by Langmuir-type sorption, b is affinity constant to Langmuir sorption site. Dual-mode sorption parameters of III-5 and II-2 for water vapor are shown in Table II. C'_H of III-5 was larger than that of II-2, indicative of many Langmuir sites in the III-5 ionomer which contained more cluster or ionic domain.

Steady-state permeability coefficient (\bar{P}) of water vapor through III-3 and III-5 membranes is shown in Figure 2. \bar{P} of III-5 increased with relative vapor pressure, reflecting remarkable sorption amount at higher relative vapor pressure, whereas \bar{P} of III-3 remained almost constant, and is close to \bar{P} of low-density polyethylene, 9.0×10^{-9} (cc(STP)cm / cm² · s · cmHg).¹⁷ Although the amount of water sorbed to III-3 is one-tenth smaller than that to III-5, \bar{P} of III-3 at low relative vapor pressure is larger than that of III-5, suggestive of very high diffusion coefficient of III-3.

Steady-state diffusion coefficient (\bar{D}) of water vapor was calculated by \bar{P}/S , where S is solubility coefficient obtained by sorption isotherm. \bar{D} of III-3 and III-5 is shown in Figure 3. \bar{D} of III-3 is approximately one decade larger than that of III-5 as expected above. \bar{D} of III-5 increases gradually with relative vapor pressure up to relative vapor pressure of 0.3 and then it decreases and levels off. On the other hand, \bar{D} of III-3 is slightly increased at low relative vapor pressure. This suggests that water molecule in III-3 membrane may be more diffusible than that in III-5 and that the interaction between water molecule and ionic domain of the zinc salt be weaker than that of the sodium salts in which water molecule is almost nonfreezable as described later.

TABLE II
Dual-Mode Sorption Parameters of III-5 and II-2 for Water Vapor

Sample	k_D (cm ³ stp/cm ³ atm)	C'_H (cm ³ stp/cm ³)	b (atm ⁻¹)
III-5	214	4.38	485
II-2	149	1.04	1230

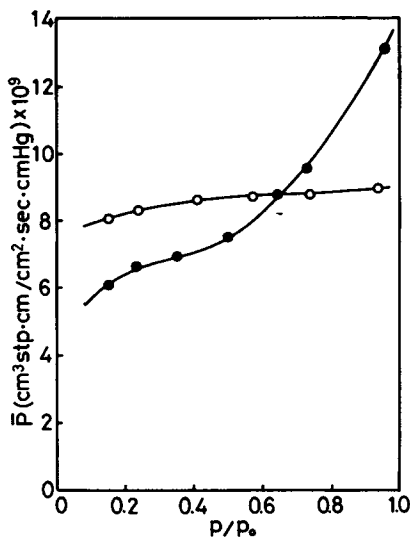


Fig. 2. Steady-state permeability coefficient (\bar{P}) of water vapor through III-3 and III-5 membranes at 25°C against relative vapor pressure: III-3 (\circ) and III-5 (\bullet).

Carbon Dioxide Gas Sorption and Permeation

Sorption isotherms of carbon dioxide gas in the different ethylene ionomers at 25°C are shown in Figure 4. Sorption isotherms of carbon dioxide gas depend upon only acid content, not upon the degree of neutralization. Sorption isotherms exhibited a typical dual-mode sorption mechanism as well as sorption isotherms of water vapor in the low relative vapor pressure as described before. Dual-mode sorption parameters for carbon dioxide gas are tabulated in Table III. There was no difference of b parameter compared to two kinds of ethylene ionomers with different acid contents, II and III series, whereas one could see the difference of K_D and C'_H . K_D and C'_H of III series are larger than those of II series, corresponding to larger sorption sites for III series.

Steady-state permeability coefficients of carbon dioxide gas through III-3 and III-5 membranes at 25°C are shown in Figure 5. The pressure depen-

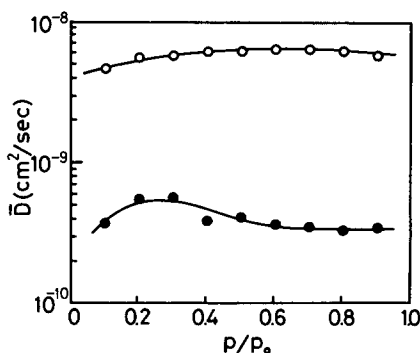


Fig. 3. Steady-state diffusion coefficient (\bar{D}) of water vapor through III-3 and III-5 membranes at 25°C against relative vapor pressure; III-3 (\circ) and III-5 (\bullet).

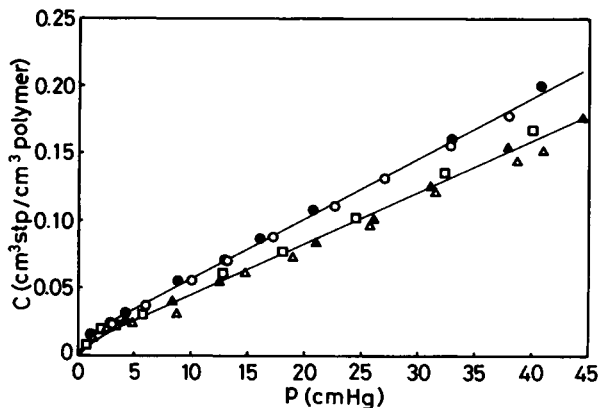


Fig. 4. Sorption isotherms of carbon dioxide gas to the different ethylene ionomers at 25°C; III series III-3 (○) and III-5 (●) and II series II-1 (□), II-2 (△), and II-3 (▲).

dence of \bar{P} was observed in a low pressure range and there was no difference of \bar{P} between two membranes. The pressure dependence suggests the partial immobilization model proposed by Paul et al.^{18,19} as follows;

$$\bar{P} = k_D D_D + \frac{D_B C'_H b}{1 + b p} \quad (2)$$

where D_D is diffusion coefficient for Henry's law-type diffusion, and D_H diffusion coefficient for Langmuir-type diffusion. The plot of \bar{P} of III-3 and III-5 membranes against $(1 + b p)^{-1}$ shown in Figure 6 gave a straight line. The permeation mechanism of carbon dioxide gas through ethylene ionomer membranes could be interpreted by the partial immobilization model. The existence of ionic domains or cluster is likely to support this model, indicating it to be a sorption site. We could obtain the value of $k_D D_D$ and $D_H C'_H b$ from an intercept and a slope of Figure 6. D_D and D_H of III series are shown in Table IV. D_H is approximately half of D_D , suggestive of the interaction between carbon dioxide gas and ionic domain or cluster. D_D is considerably smaller than the diffusion coefficient of polyethylene.²⁰ This indicates that the molecular motion in the amorphous region of ethylene ionomers is remarkably restricted also by ion pairs and multiplet, compared to the polyethylene amorphous region.

Differential Scanning Calorimetric Analysis of Water Sorbed

DSC thermograms of water sorbed to III-5 membranes are drawn in Figure 7. The increase of water content raised the endothermic peak temperature toward 0°C where pure water melted and also increased the transition

TABLE III
Dual-Mode Sorption Parameters for Carbon Dioxide Gas

Sample	k_D (cm ³ stp/cm ³ atm)	C'_H (cm ³ stp/cm ³)	b (atm ⁻¹)
III	0.34	0.013	96
II	0.29	0.007	95

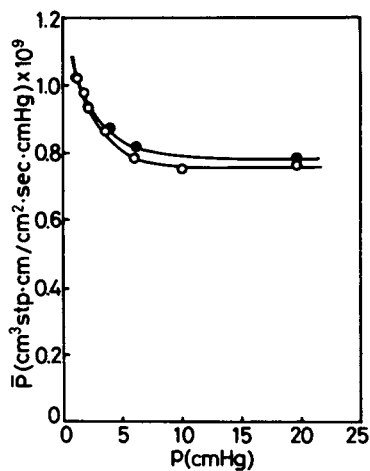


Fig. 5. Steady-state permeability coefficient of carbon dioxide gas through III-3 and III-5 membranes at 25°C against pressure; III-3 (○) and III-5 (●).

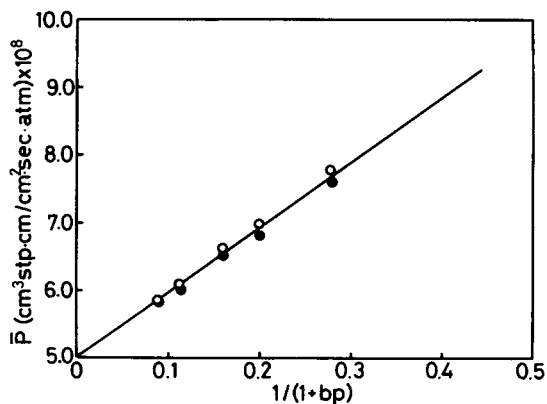


Fig. 6. Plot of steady-state permeability coefficient of carbon dioxide gas through III-3 (○) and III-5 (●) membranes at 25°C against $(1 + bp)^{-1}$.

TABLE IV
 D_D and D_H of III Series

Sample	D_D (cm ² /s)	D_H (cm ² /s)
III	1.4×10^{-7}	0.8×10^{-7}

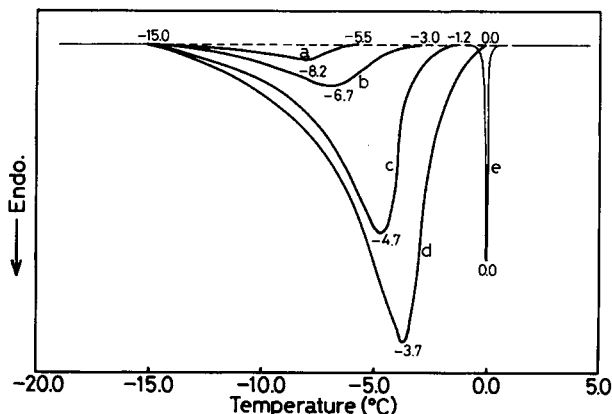


Fig. 7. Differential scanning calorimetry thermogram of ethylene ionomer (III-5) with different water contents; a: 6.2%, b: 7.0%, c: 9.4%, d: 10.0%, and e: water.

enthalpy. Such DSC peak was attributed to melting of freezable water. One could evaluate freezable water content under the assumption that the heat of fusion of 79.7 cal/g for pure water was able to apply to the freezable water appeared in DSC thermograms. Freezable water content ratio to total water content, W_f is plotted against water content sorbed in Figure 8. Below 6% water content sorbed (g water/g polymer) the endothermic peak of the freezable water disappeared, therefore, all the waters below 6% water content sorbed were classified into nonfreezable water, whereas only a small amount of water, say, several percent*, was freezable above 6% water content sorbed and the rest was nonfreezable water. It is reasonable to consider that water sorbed might interact with the strong polar sites such as ionic domain or cluster and behave like bound water. Therefore, it can be said that such nonfreezable water is not available to diffusion of water through the membrane.

In conclusion, water sorption to ethylene ionomers was controlled by the

* e.g., 7% of water at 10% water content.

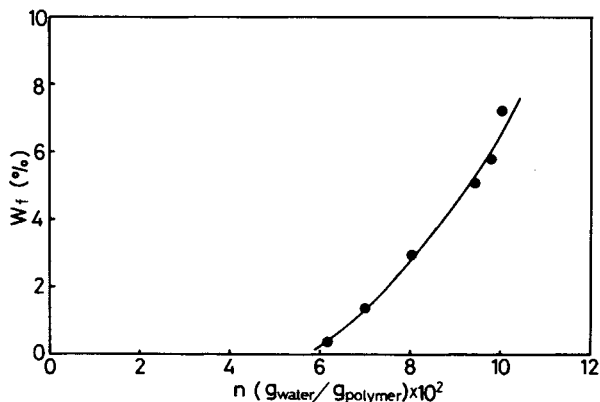


Fig. 8. Plot of freezable water content evaluated by DSC method against water content sorbed to III-5 membrane (g water/g polymer).

factor of acid content, degree of neutralization, and the kind of metal salts. The more acid content and degree of neutralization, the more water sorption. The sodium salt ionomer sorbed a great amount of water compared to the zinc salt ionomer. There was no remarkable difference of \bar{P} of sodium and zinc salt ionomers. On the other hand, \bar{D} of the sodium salt ionomer is one order smaller than that of the zinc salt ionomer, reflecting that water sorbed to the sodium ionomer was nearly nonfreezable water. Sorption of carbon dioxide gas to ethylene ionomers was of the dual-mode type. Permeation behavior of carbon dioxide gas was interpreted by the partial immobilization model, resulting in no effect on the kind of salt in contrast to the water vapor permeation.

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