

Gas permeability of hydrogen-bonding interpolymer complex and their metal-ion complex membranes

Zhong Yun, Mei-Yu Huang, and Ying-Yan Jiang*

Institute of Chemistry, Academia Sinica, Beijing 100080, Peoples Republic of China

Summary

Several hydrogen-bonding interpolymer complex membranes were prepared by casting of the corresponding complex solutions composed of proton-donors and proton-acceptors. Their permeability to CO₂, O₂ and N₂ was investigated. Some effects of metal-ions such as Fe²⁺, Cu²⁺ and Mn²⁺ on the permeability were also discussed. It was found in the experiments that the permselectivities to CO₂ over O₂, α_{CO_2/O_2} , of these hydrogen-bonding interpolymer complex membranes were smaller than one, which was contrary to those of all the reported polymer membranes.

Introduction

Interpolymer complexes are those formed when two different polymer chains interact with each other through the secondary forces, such as hydrogen-bonding, coulombic forces, electron donor-acceptor interactions, van der Waals forces and hydrophobic interactions. Their distinctive structures have endowed with them many characteristics different from those possessed by other ordinary polymers. A lot of achievements have been made in many aspects since they were put into investigation (1-2). However, most work has been, so far, mainly focused on the interpolymer complexes formed through coulombic forces (i.e. Polyelectrolyte complexes). The properties and applications of the hydrogen-bonding interpolymer complexes, unfortu-

* To whom offprint requests should be sent

nately, have received little attention. Their permeability to liquids and gases haven't been reported yet.

The present work deals with the permeability of the hydrogen-bonding interpolymer complex membranes to carbon dioxide, oxygen and nitrogen. It has been found that these complex membranes possess some special permeability which is different from that of the ordinary polymer membranes. The effects of metal-ions on the permeability is also discussed.

Experimental

Preparation of polyvinyl alcohol (PVA)-polyacrylamide (PAAm) and polyvinyl alcohol (PVA)-polyvinyl pyrrolidone (PVP) complex membranes

At room temperature, 2% aqueous PVA ($\bar{P} = 1700$, OH content: 88%) was mixed with 2% aqueous PAAm ($\bar{M}_n = 5.0 \times 10^5$) or PVP (K value: 27-33) equivalently under stirring for about 15 min. Then, the two complex solutions were cast onto a glass plate, respectively, to form the complex membranes by natural evaporation of the solvent at room temperature.

Preparation of polyvinyl alcohol (PVA)-polyacrylic acid (PAA) and polyvinyl alcohol (PVA)-polymethacrylic acid (PMAA) complex membranes

1% aqueous PVA was mixed at room temperature with 1% aqueous PAA ($[\eta]^{25^\circ} = 8.917$) or PMAA ($\bar{M}_n = 10.8 \times 10^4$) at certain molar ratios, respectively. Ethanol was necessarily added into the reaction system if complex precipitate appeared during mixing. After reaction for about 20 min, the two complex solutions were cast, respectively, onto a glass plate to form the complex membranes.

Preparation of PVA-PAA-metal-ion complex membranes

The molar ratio of PVA to PAA in all PAA-PVA-metal-ion

complexes was kept at 1:1. In order that complexation wouldn't be affected by the salt formation between PAA and metal-ions, it was necessary that aqueous PVA (0.8-1%), salt solution (0.07-0.1M), such as FeSO_4 , CuCl_2 or MnCl_2 , and ethanol (the ratio of water to ethanol was about 1:1) were first mixed for 15 min under stirring; then aqueous PAA (0.8-1%) was added at a speed of 2 ml/min. More ethanol was needed if the complex precipitated during the addition of PAA. The mixture was stirred for another 30 min after PAA was added. The whole reaction was carried out at room temperature. The complex membranes were formed by casting the complex solutions onto a glass plate.

Measurement of gas permeabilities

The procedure was similar to what was described in the book "Technology in Polymer Experiments" published by the Fudan University Press in 1983.

Results and Discussion

Distinctive permeability of hydrogen-bonding interpolymer complex membranes to CO_2 over O_2

As known to us all, almost all the common polymer membranes have greater permeability to CO_2 than to O_2 . Their permselectivities to CO_2 over O_2 , $\alpha_{\text{CO}_2/\text{O}_2}$, vary between 6 and 4. However, the $\alpha_{\text{CO}_2/\text{O}_2}$ value for the polyelectrolyte complex membrane, sodium poly(styrenesulfonate)-poly(vinylbenzylmethylammonium) chloride (water content: 80%), is as great as 20, which is 4 or 5 times greater than those of the common polymer membranes (3). It is apparent that this is the result of the special chemical structures and aggregation structures of the polyelectrolyte complex membranes.

The permselectivity of hydrogen-bonding interpolymer complex membranes to CO_2 over O_2 is also rather distinctive. As shown in Table 1, the $\alpha_{\text{CO}_2/\text{O}_2}$ values for these complex mem-

Table 1
Permselectivities of Various Polymer Membranes to CO₂ over O₂

Membranes	$P_{CO_2} \times 10^{10}$	$P_{O_2} \times 10^{10}$	α_{CO_2/O_2}
Polydimethylsiloxane	3240	605	5.4
Polyethylene (h.d.)	1.80	0.4	4.5
Polystyrene	10.5	2.63	4.0
Nylon-6	0.16	0.038	4.2
PSSNa-PVBMA ^a (80% H ₂ O)	680	34	20
PVA-PAA ^b	0.143	0.90	0.16
PVA-PAA-FeSO ₄ (0.5%) ^c	0.223	1.17	0.19
PVA-PAA-MnCl ₂ (2%) ^c	0.91	1.29	0.71

P: cm³ (STP) cm cm⁻²sec⁻¹cmHg⁻¹; measured at 25°C and permeation pressure of 0.8 kg/cm².

a: sodium poly(styrenesulfonate)-poly(vinylbenzylmethylammonium) chloride

b: molar ratio: 1:1

c: figures in parentheses are molar content of metal-ions, molar ratio of PAA to PVA is 1:1.

Table 2
Effect of the Strength of Interpolymeric Hydrogen-Bonding on CO₂ Permeability

Membranes	$P_{CO_2} \times 10^{11}$
PVA-PAA ^a	1.08
PVA-PMMA ^b	1.35
PVA-PAA ^b	1.43
PVA-PVP ^b	1.69
PVA-PAAM ^b	5.73

Decrease in strength

Increase in permeability

P: cm³ (STP) cm cm⁻²sec⁻¹cmHg⁻¹, measured at 25°C and permeation pressure of 0.8 kg/cm².

a: OH group content of PVA: 99%

b: OH group content of PVA: 88%

Table 3

Effect of Metal-Ions on Permselectivity α_{O_2/N_2}

Membranes	$P_{O_2} \times 10^{10}$	$P_{N_2} \times 10^{10}$	α_{O_2/N_2}
PVA-PAA ^a	0.90	0.36	2.5
PVA-PAA-MnCl ₂ ^b	1.3	0.52	2.5
PVA-PAA-CuCl ₂ ^c	1.6	0.62	2.6
PVA-PAA-FeSO ₄ ^c	1.1	0.39	2.8

P: cm^3 (STP) $\text{cm}^{-2} \text{sec}^{-1} \text{cmHg}^{-1}$, measured at 25°C and permeation pressure of 0.8 kg/cm².

a: the molar ratio of PVA to PAA in all the membranes was 1:1.

b: molar content of the ion: 2%.

c: molar content of the ions: 0.5%.

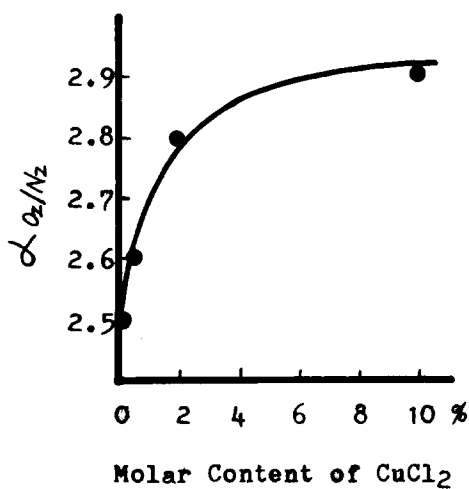


Fig.1 Effect of Cu^{2+} content on the permselectivity of PVA-PAA-CuCl₂ membrane

Molar ratio of PVA to PAA: 1:1.

Temperature: 22°C

Permeation pressure: 0.8 kg/cm².

branes are all smaller than one, which is contrary to those for the common polymer membranes and the electrolyte complex membranes whose $\alpha_{\text{CO}_2/\text{O}_2}$ values are always greater than one. Further investigation has shown that the permeability of CO_2 through the interpolymer complex membranes increases with the decrease in the strength of the interpolymeric hydrogen-bonding, as shown in Table 2. From these results, it may be postulated that the hydrogen-bonding nature of these hydrogen-bonding interpolymer complex membranes would be responsible for their distinctive behaviour in permeation of CO_2 and O_2 .

Effect of metal-ions on the permeability of the interpolymer complex membranes

As we have known, there exist strong interactions between some metal-ions and certain gas molecules. So, it is certain that the permeability will be changed if some metal-ions are introduced into the PVA-PAA complex membrane. Table 3 has shown the effect of different metal-ions on the permselectivity of the PVA-PAA complex membrane to O_2 over N_2 . It can be seen that Mn^{2+} gives the smallest effect while Fe^{2+} , the greatest. Furthermore, the effect degree increases with the increase of ion contents in the PVA-PAA complex membrane. As shown in Fig.1 the permselectivity, $\alpha_{\text{O}_2/\text{N}_2}$, of the PVA-PAA complex membrane containing Cu^{2+} increases with the increase of Cu^{2+} content.

Dependence of permeability on permeation pressure

We have known from the DSC data (not shown) that all the studied hydrogen-bonding interpolymer complex membranes including those containing metal-ions exist in the glassy state under the experimental conditions. According to the Dual Sorption Theory for glassy polymers (4), two concurrent modes of sorption are operative in a microheterogeneous medium. One is the normal dissolution (Henry's Law), and the other belongs to the non-linear Langmuir-type sorption that accounts for immobilization of penetrant molecules at fixed sites within the medium. Therefore, the expression of concentration c in the First

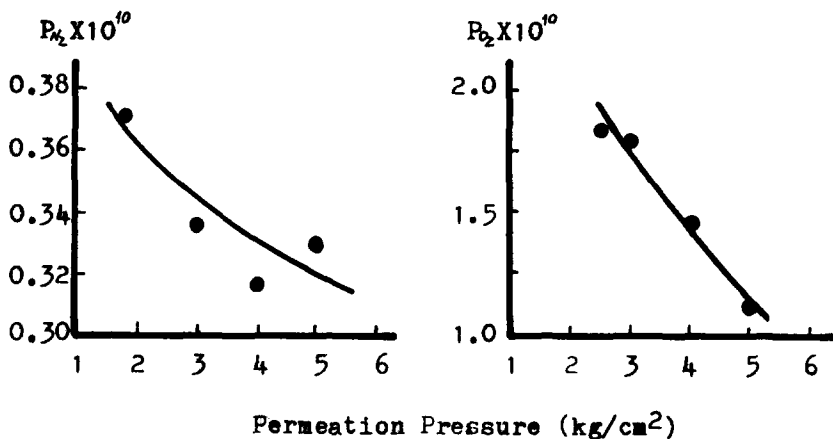


Fig. 2 Dependence of O₂ and N₂ permeabilities on the permeation pressure

a: P, cm³ (STP) cm cm⁻² sec⁻¹ cmHg⁻¹, was measured at 23°C and

b: The membrane was PVA-PAA containing 2% (molar) FeSO₄.

Fickian Law $J = -D dc/dx$ (at constant T and P) has become:

$$c = c_H + c_L = k_H p + \frac{c'_L b p}{1 + bp}$$

where c_H and c_L represent the concentrations by normal dissolution and by Langmuir sorption, respectively; c'_L , k_H and b are constants. By mathematical deduction we have:

$$P = k_H D (1 + K/1+bp)$$

where P is the gas permeability and $K = c'_L b / k_H$.

As predicted by this formula, the gas permeability of the hydrogen-bonding interpolymer complex membranes decreases with the increase of permeation pressure. The agreement between the experimental results and the above theoretical prediction has

been proved by Fig. 2 in which the oxygen and nitrogen permeabilities of the PVA-PAA-FeSO₄ complex membrane decrease as the driving pressure across the membrane increases. It can be further predicted that this property is commonly shared by other hydrogen-bonding complex membranes mentioned above because all of them exist in the glassy state under the same experimental conditions. This latter prediction has been proved again to be correct by our further studies.

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