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Dynamic Sorption and Anomalous Diffusion of Small Molecules in Dense Polyimide Membranes

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Series of polyimide membranes with different thicknesses have been prepared using pyromellitic dianhydride and 4,4′-diaminodiphenylether monomers, and the properties of polyimide membranes have been measured by experimental techniques. The dynamic sorption and steady permeation behaviors of water, methanol, ethanol, and dichloromethane as well as the steady permeation of the methanol/dichloromethane binary system in polyimide membranes were investigated. The experimental results show that the diffusion of water in polyimide membranes is more rapid than those of other penetrants in this study, and the diffusion behavior of water exhibits the typical characteristics of Fickian diffusion. However, the sorption curves of methanol, ethanol, and dichloromethane are typical of a sigmoid shape, and there are no evident linear relationships between the flux and the reciprocal of membrane thickness. This is in conflict with the Fickian law, and it can be concluded that the diffusion behaviors of methanol, ethanol, and dichloromethane in polyimide membranes under the experimental conditions belong to the anomalous diffusion.

Introduction

The preferential sorption and diffusion of small molecule penetrants in dense polymer membranes is the prerequisite for membrane separation processes such as pervaporation, vapor permeation, and gas separation.[1,2] Several models of transmembrane mass transfer have been established to describe these processes such as the solution−diffusion model,[3] the pore-flow model,[4] and the irreversible-thermodynamics model.[5] Among them, the solution−diffusion model seems to be accepted by the majority of membrane researchers. In this model, the mass transport process consists of three consecutive steps: (i) sorption of the penetrant from the feed to the membrane, (ii) diffusion of the penetrant in the membrane, and (iii) desorption of the penetrant from the membrane on the downstream side of the membrane.

The diffusion of small molecules into amorphous polymers has been divided into three basic modes of transport, depending on the relative rates of penetrant diffusion and polymer chain relaxation:[6] (1) Case I or Fickian diffusion—occurs when the diffusion rate of penetrant molecules is much slower than the polymer chain relaxation rate and the sorption equilibrium is established rapidly; (2) Case II diffusion—occurs when the penetrant diffusion rate is much faster than the polymer chain relaxation; (3) Case III or anomalous diffusion—occurs when the penetrant mobility and polymer chain relaxation rates are comparable. Among these three kinds of diffusion behaviors, anomalous diffusion, which commonly occurs in the case of liquid penetrants diffusing into glassy polymer membranes, is the most complicated. A number of researchers have studied the diffusion of penetrants in different membranes such as poly(ethylene−co-vinyl acetate), polyurethane, and acid-form Nafion membranes.[1,7−10]

Polyimides are a class of thermally stable polymers with excellent mechanical, electrical, and solvent-resistance properties and have been widely used in applications such as aircraft parts, electronic packaging, adhesives, and membranes especially the vapor separation membranes.[11,12] Because of the introduction of phenyl rings in the main chains, polyimide chains often exhibit high rigidity, and the diffusion of small molecule penetrants in polyimide membranes often do not obey the Fickian diffusion law.

In the present work, series of polyimide membranes with different thicknesses have been prepared using pyromellitic dianhydride (PMDA) and 4,4′-diaminodiphenylether (ODA) monomers, and the properties of polyimide membranes have been measured by experimental techniques.[1] We also investigated the dynamic sorption and steady permeation behaviors of water, methanol, ethanol, and dichloromethane as well as the steady permeation of the methanol/dichloromethane binary system in the PMDA−ODA polyimide membranes. Some features of anomalous diffusion were found.

Experimental Section

Materials. The PMDA and ODA monomers were purchased from Fluka Chemical Corp., and they were purified by recrystalization in acetic acid and ethanol before polymerization, respectively. *N*,*N*-Dimethylformamide (DMF) was obtained from Beijing Yili Chemicals Co. Ltd. and purified on distillation under reduced pressure over calcium hydride and stored over molecular sieves (4 Å).

Four penetrants (i.e., water, methanol, ethanol, and dichloromethane) were obtained from the Institute of Microelectronics of Tsinghua University, the Beijing Chemicals Factory, and the Beijing Yili Chemicals Co. Ltd., respectively. They were of reagent grade, and their physical properties are shown in Table 1. (The values of van der Waals volume were obtained from elsewhere.[13])

Preparation of Polyimide Membrane. The polyimide membrane was prepared by the so-called two-step method (Figure

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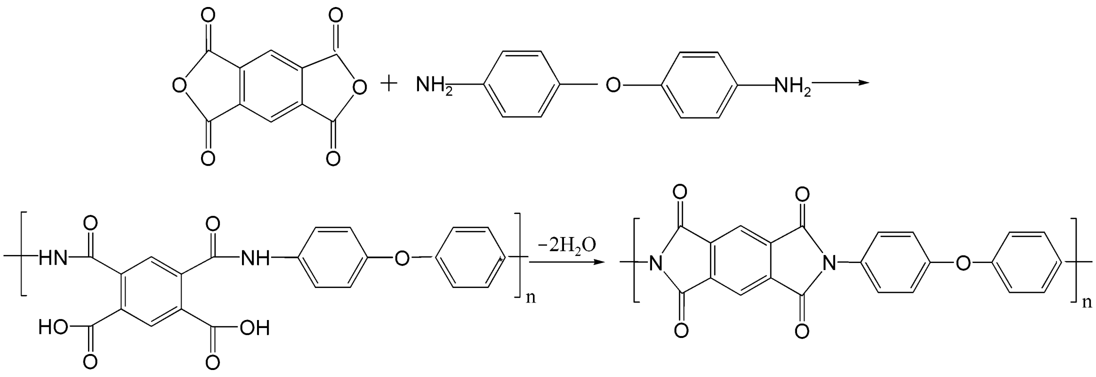

Figure 1. Chemical structure of PMDA−ODA polyimide.

Table 1. Physical Properties of Penetrants

penetrant	M/g·mol^{-1}	ρ^a/g·m^{-3}	$V_w{}^b$/Å^3
H_2O	18.01	0.999	29.9
CH_3OH	32.04	0.791	67.2
CH_3CH_2OH	46.07	0.789	96.9
CH_2Cl_2	48.47	1.335	106.3

[a] ρ is the density of penetrants at 293 K. [b] V_w is the van der Waals volume.[14]

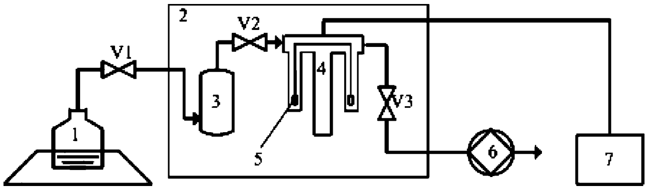

Figure 2. Schematic diagram of the apparatus used for measurement of the dynamic sorption behavior. 1, vapor generator; 2, thermostat; 3, cushion jar; 4, electrical balance; 5, membrane; 6, vacuum pump; 7, data recorder (V1−3, valves).

1). The polyamic acid (PAA) precursors of polyimides were prepared by solution condensation polymerization at ambient temperature and at a concentration of 12 % solids by weight in DMF. The aromatic dianhydride monomer was added to an equimolar amount of aromatic diamine dissolved in the solvent.

The obtained PAA solution was cast onto a soda-lime glass plate to form a casting membrane. Then the casting film was placed into a vacuum dryer for 24 h to remove some residual solvent. Thermal conversion of the PAA membranes to the corresponding polyimides was performed by heating in a vacuum oven for 2 h each at (453, 523, and 573) K. Upon cooling, the membranes were removed from the glass plates. Finally, the homogeneous polyimide membranes with uniform thickness were obtained.

In this study, four different thickness polyimide membranes were prepared. Their thicknesses were (25.4, 50.8, 76.2, and 127) μm, and they were designated as PI1, PI2, PI3, and PI4, respectively.

Characterization. The physical property parameters of polyimide membranes are presented in Table 2. The density of polyimide membrane at 298 K was measured by flotation in a mixed solution. The solution was prepared by ethanol ($\rho = 1.599$ g·cm^{-3}) and carbon tetrachloride ($\rho = 0.79$ g·cm^{-3}). The glass transition temperature (T_g) of polyimide was determined by differential scanning calorimetry (DSC) with a Seiko EXSTAR6000 instrument at a heating rate of 10 K·min^{-1}, from (298 to 673) K. Wide-angle X-ray diffraction (WAXD) patterns were measured by a Bruker D8 wide-angle X-ray diffractometer using Cu Kα radiation wavelength. The top of broad peaks on each X-ray pattern for noncrystalline polymers is attributed to intersegmental interference and is thus a representative of average intersegmental distance called the mean interchain distance (d-spacing). The d-spacing can be calculated from Bragg's equation.[14] Free volumes are calculated by Bondi's model of group contribution, and the parameters and details have been described elsewhere.[15] The elemental composition of polyimide membranes tested by EA 1112 elemental analyzer (Carlo Erba Instruments, Italy) are in good agreement with their theoretical values for the proposed chemical structure.

Dynamic Sorption Experiments. Figure 2 shows the dynamic sorption apparatus. It contains the vapor generator, the data recorder, the vacuum system, and the thermostat. The electrical balance (model TG-200, sensitivity 5 μg, made by Tianjin University, People's Republic of China) is located in the thermostat. Prior to each sorption test, the membrane sample is put in the basket of the balance, and then the vacuum system is opened (pressure < 0.1 Pa) to desorb gas from the membrane over 8 h. Simultaneously, the temperature of the thermostat was regulated to a given value. Then the vapor is introduced into the balance compartment, and the sorption test begins. The mass of the membrane is recorded by the data recorder in time until the sorption equilibrium, which is determined when no measurable change is observed within 1 h, is obtained. All sorption tests are carried out at 303.2 K.

Permeation Experiments. The permeation apparatus of liquid feeds through flat-sheet membranes is shown schematically in Figure 3. In the membrane cell, the membrane sample is supported on a porous sintered stainless plate, and its active surface area is 47.76 cm^2. Vacuum is produced by a vacuum pump (model 2X-15 from Beijing Equipment Factory) in the permeation compartment of the membrane cell. In each permeation test, the feed solution is circulated between the membrane cell and a large feed vessel of about 1.5 L, which keeps the feed at a constant temperature. The permeate sample

Table 2. Physical Properties of PMDA−ODA Polyimide Membrane

					elemental analysis^b/%				
polyimide	ρ/g·cm^{-3}	T_g/K	M^a/g·mol^{-1}	d-spacing/Å	C	H	N	$V_m{}^c$/cm^3·mol^{-1}	FFV^d
PMDA-ODA	1.413	572	382.31	4.6	67.30 (69.12)	2.50 (2.64)	7.32 (7.33)	186.60	0.1034

[a] M is the molar weight of the repeat unit. [b] The data in parentheses are theoretical values calculated from chemical structure. [c] V_m is the molar van der Waals volume of the repeat unit calculated from group contribution method.[16] [d] FFV is the fractional free volume of the repeat unit.[16]

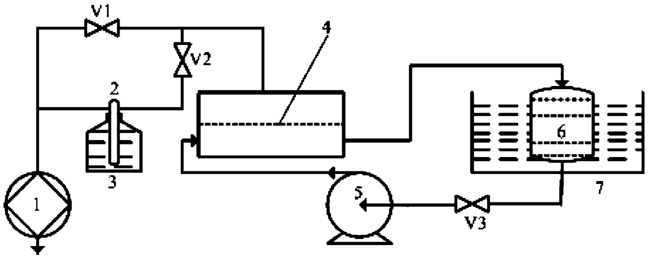

Figure 3. Flowsheet of steady permeation experiments. 1, vacuum pump; 2, permeate collector; 3, cold trap; 4, polyimide membrane; 5, feed pump; 6, feed; 7, thermostat (V1−3, valves).

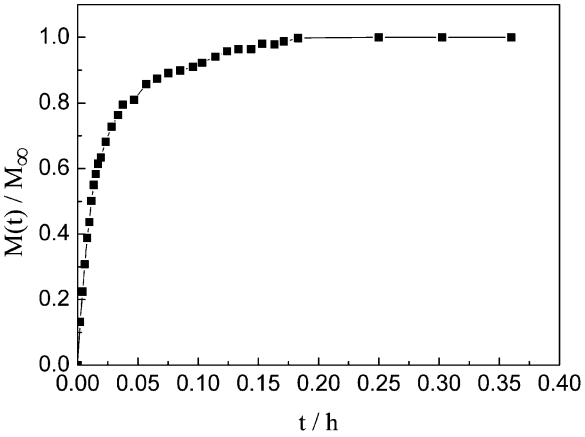

Figure 4. Dynamic sorption curve of water in PI4 membrane.

is drawn out by the vacuum pump and collected by a cold trap cooled with liquid nitrogen. All tests are done at 303.2 K, and pressure in the permeation compartment is 650 Pa.

Theory

Fickian Diffusion Law. Diffusion is the process responsible for the movement of matter from one part of a system to another.[16] The first mathematical treatment of diffusion was established by Fick, who developed a law for diffusion in one dimension:

$$J = -D\frac{\partial c}{\partial z} \tag{1}$$

where J is the flux per unit area, D is the diffusion coefficient, c is the concentration, z is the distance, and $\partial c/\partial z$ is the gradient of the concentration along the z-axis. This equation is also known as Fick's first law.

Fickian Diffusion. As mentioned in the introduction, Fickian diffusion (Case I) is often observed in polymer networks when the temperature is well above the T_g of the polymer. According to the Fickian diffusion law, the permeation flux J is proportional to the reciprocal of membrane thickness L^{-1}, and the percentage mass gain $M(t)/M_\infty$ in the early stage of sorption ($M(t)/M_\infty < 1/2$) is proportional to the square root of time:[16]

$$\frac{M(t)}{M_\infty} = \left(\frac{16Dt}{\pi L^2}\right)^{1/2} \tag{2}$$

where $M(t)$ is the amount of solvent absorbed per unit area of polymer at time t, M_∞ is the saturate sorption amount, L is the membrane thickness.

Anomalous Diffusion. Anomalous diffusion is mainly observed in glassy polymers (i.e., when the temperature of study is below the T_g of the polymer). At a specific temperature below T_g, the polymer chains are not sufficiently mobile to permit immediate penetration of the solvent in the polymer core.[17] For the anomalous diffusion, the percentage mass gain $M(t)/M_\infty$ does not obey eq 2 (i.e., the percentage mass gain $M(t)/M_\infty$ in the early stage of sorption is not proportional to the square root of time).

Results and Discussion

The sorption experiments of nine groups (i.e., water/PI4, ethanol/PI3, ethanol/PI4, methanol/PI2, methanol/PI3, methanol/PI4, dichloromethane/PI1, dichloromethane/PI2, and dichloromethane/PI3) were carried out. The dynamic sorption curves are given in Figures 4 and 5. In addition, the relationships between the percentage mass gain $M(t)/M_\infty$ and the square root of time $t^{1/2}$ of these penetrants in polyimide membranes are presented in Figures 6 to 8. Tables 3 and 4 show the steady permeation flux of methanol, ethanol, and dichloromethane and the binary system of methanol/dichloromethane in PI1, PI2, PI3, and PI4 membranes.

As shown in Figure 4, in the region of (0 to 80) %, the percentage mass gain $M(t)/M_\infty$ of water in PI4 membrane increases rapidly with time t. In contrast, it increases more and more slowly with time t above 80 %, and reaches 100 % after a relatively long period of time. Differently, the sorption behaviors of dichloromethane, methanol, and ethanol show some other features (Figure 5a−c). The most important feature is that there is a plateau region at about 50 %. In this plateau region, the percentage mass gain $M(t)/M_\infty$ increases very slightly with the time t. For example, the time t increases from (5.15 to 8.44) h, while the percentage mass gain $M(t)/M_\infty$ of ethanol in PI4 membrane only increases from (50 to 56) % in the period of time.

In summary, it can be found from Figures 4 and 5 and Table 1 that the time of different penetrants reaching the saturated sorption in the same polyimide membrane increases as the Van der Waals volume of penetrants increases. For example, the percentage mass gain $M(t)/M_\infty$ of water reaches 100 % in approximate 0.17 h, while that of ethanol reaches 100 % in approximate 17.5 h. It can be concluded that the diffusion of penetrants in polyimide membranes becomes slower with an increase of the penetrants' van der Waals volume. The diffusion of penetrants in dense polymer membrane is influenced by many factors, and one of the most important factors is the size of penetrants. In general, the bigger the size of penetrants is, the more difficult the diffusion of penetrants is. In addition, typical polyimide membranes are water selective. All these factors will make the diffusion of water in polyimide membranes become much easier than that of methanol, ethanol, and dichloromethane.

As mentioned in the theory, the percentage mass gain $M(t)/M_\infty$ of Fickian diffusion is proportional to the square root of time $t^{1/2}$ in the early stage of sorption according to the Fickian diffusion law. In Figures 6 to 8, it can be seen that the linear plot of $M(t)/M_\infty$ with $t^{1/2}$ shows the typical characteristics of Fickian diffusion in the early stage of sorption curves for the diffusion of water in polyimide membranes. However, for other penetrants such as dichloromethane, methanol, and ethanol, their sorption curves are typical of a sigmoid shape. Consequently, it is evident that the diffusion behaviors of dichloromethane, methanol, and ethanol in polyimide membranes under the experimental conditions do not obey the Fickian law.

The data of steady permeation flux are listed in Table 3 for dichloromethane, methanol, and ethanol in polyimide membranes. There are no evident relationships between the flux J and the van der Waals volume of penetrants. It is possibly

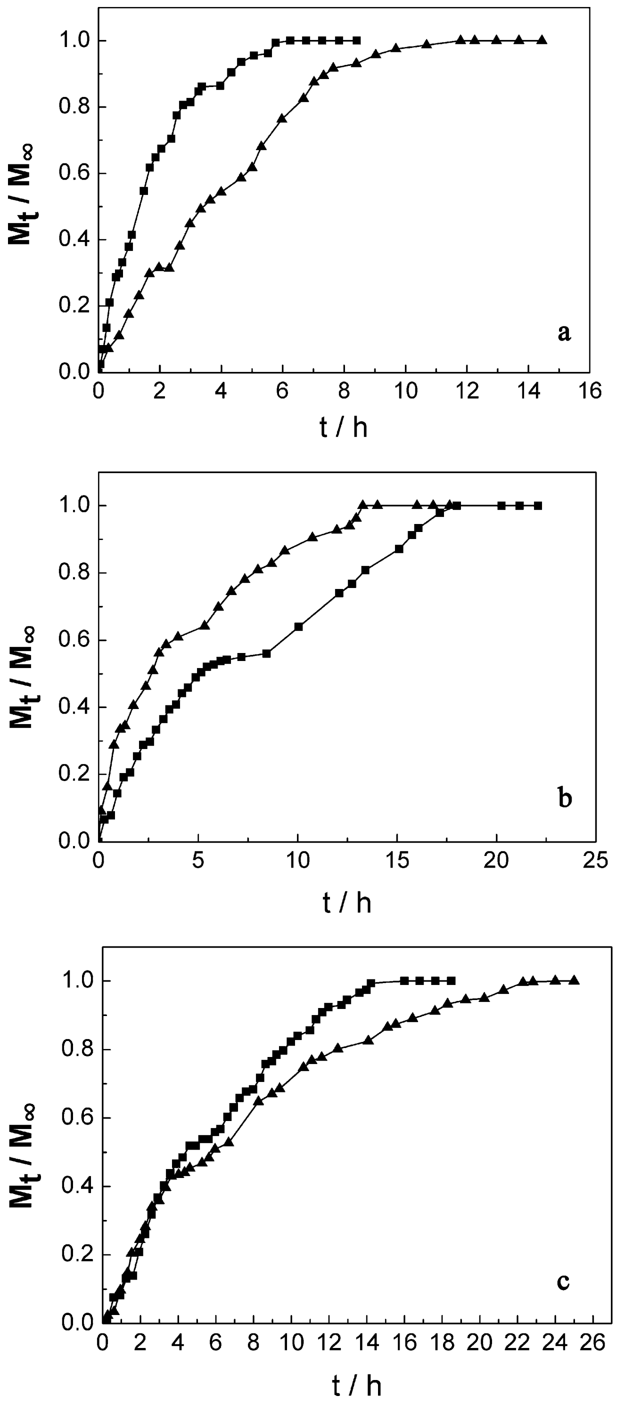

Figure 5. (a) Dynamic sorption curves of polyimide membranes in methanol: ■, methanol/PI2; ▲, methanol/PI3. (b) Dynamic sorption curves of polyimide membranes in ethanol: ■, ethanol/PI4; ▲, ethanol/PI3. (c) Dynamic sorption curves of polyimide membranes in dichloromethane: ■, dichloromethane/PI2; ▲, dichloromethane/PI3.

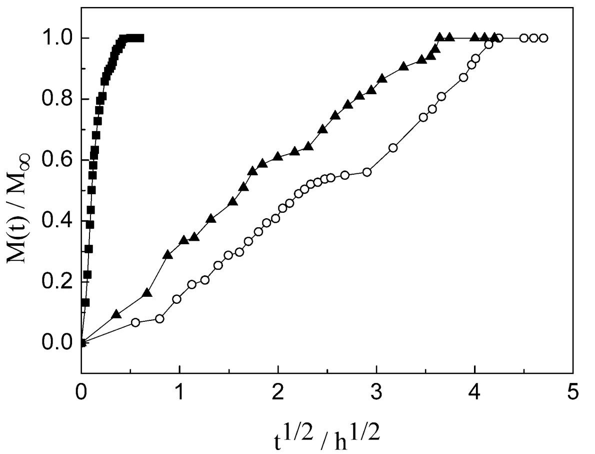

Figure 6. Relationships between the percentage mass gain $M(t)/M_\infty$ and the square root of time $t^{1/2}$ of water and ethanol in polyimide membranes: ■, water/PI4; ▲, ethanol/PI3; ○, ethanol/PI4.

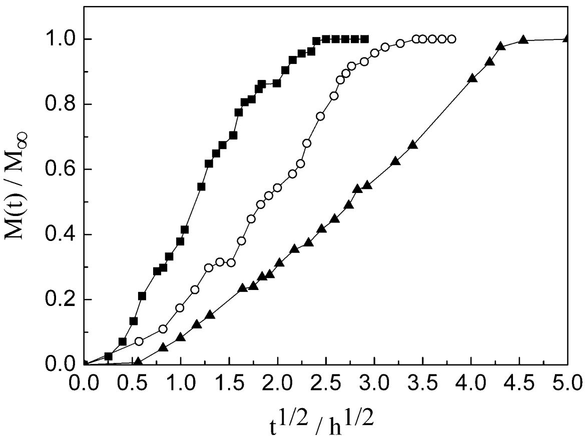

Figure 7. Relationships between the percentage mass gain $M(t)/M_\infty$ and the square root of time $t^{1/2}$ of methanol in polyimide membranes: ■, methanol/PI2; ▲, methanol/PI4; ○, methanol/PI3.

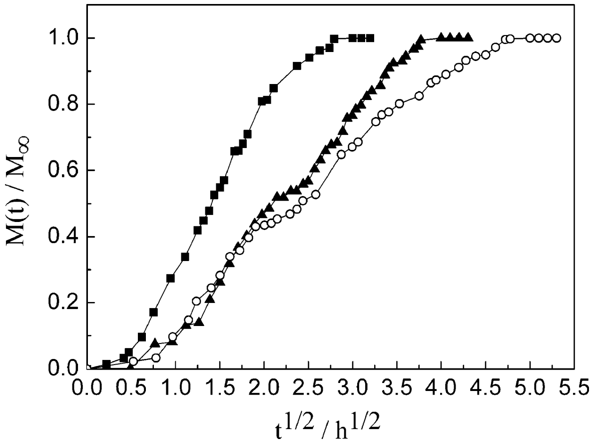

Figure 8. Relationships between the percentage mass gain $M(t)/M_\infty$ and the square root of time $t^{1/2}$ of dichloromethane in polyimide membranes: ■, dichloromethane/PI1; ▲, dichloromethane/PI2; ○, dichloromethane/PI3.

because of the complexity of the diffusion process. The diffusion processes of small molecules into dense polymer membranes may be related to a number of factors such as the shape and polarity of the penetrant molecule, the size of the hole required accommodating the molecule, and the interaction between the penetrant molecules and the polymer; all of these factors make the phenomena become complicated.

However, it is apparent that the values of flux decrease as those of the membrane thickness increase for the same penetrants in different polyimide membranes. However, there is not an evident linear relationship between the flux J and the reciprocal of membrane thickness L^{-1} as shown in Figure 9 (take the diffusion of dichloromethane as an example). This also implies that the diffusion behaviors of these penetrants do not obey the Fickian diffusion law, all having anomalous diffusion.

The steady permeation experiment of binary penetrants dichloromethane/methanol was carried out, and the results are presented in Table 4. The mass fraction of methanol in the mixture is 50 %. The mass fraction of each penetrant in permeate

Table 3. Steady Permeation Flux (*J*) of Dichloromethane, Methanol, and Ethanol in PI Membranes[a]

polyimide membrane	membrane thickness/μm	J/g·m^{-2}·h^{-1}		
		dichloromethane	methanol	ethanol
PI1	25.4	398.17	18.39	0.75
PI2	50.8	119.11	9.86	0.27
PI3	76.2	66.13	4.84	0.13
PI4	127	50.88	3.12	0.12

[a] $T = 303.2$ K and the pressure in the permeate compartment was 665 Pa.

Table 4. Permeation Flux of Methanol/Dichloromethane Binary Penetrants[a] **in Polyimide Membranes**[b]

polyimide membrane	membrane thickness/μm	total flux/ g·m^{-2}·h^{-1}	mass fraction of methanol in permeate side/%
PI1	25.4	17.11	58
PI2	50.8	11.67	63
PI3	76.2	5.46	65
PI4	127	3.43	67

[a] The mass fraction of methanol in mixture is 50 %. [b] $T = 303.2$ K and the pressure in the permeate compartment was 665 Pa.

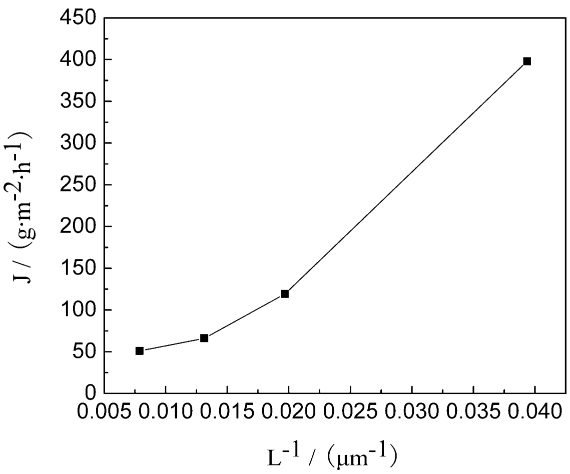

Figure 9. Relationship between the flux *J* of dichloromethane in PI1, PI2, PI3, and PI4 membranes and the reciprocal of corresponding membrane thickness L^{-1}.

side was analyzed by gas chromatography (GC-14CPTF, Shimadzu Co., Japan). It can be seen that the increase of the membrane thickness results in the decrease of the total flux. Moreover, the mass fraction of methanol in the permeate side increases as the membrane thickness increases. This is in conflict with the Fickian law, and it can be concluded that the separation factor of the dichloromethane/methanol binary system is influenced by membrane thickness because the diffusion behaviors of dichloromethane and methanol in polyimide membranes belong to the anomalous diffusion.

In summary, it can be concluded from all of the results above that the diffusion behaviors of methanol, ethanol, and dichloromethane in polyimide membranes belong to the anomalous diffusion. These are probably attributed to the polyimide materials and the solvents. Polyimides are a class of thermally stable polymers with excellent mechanical, electrical, and solvent-resistance properties. Because of the introduction of phenyl rings in the main chains, polyimide chains often exhibit high rigidity. The T_g of polyimides is usually up to 500 K, and the fraction of free volume of polyimides is usually very low, for example, the T_g and fraction of free volume of PMDA + ODA polyimides are 572 K and 0.1034, respectively. The temperature of study is below the T_g of polyimide, and the polymer chains are not sufficiently mobile to permit immediate penetration of the solvent in the polymer core. Moreover, the van der Waals volumes of methanol, ethanol, and dichloromethane are bigger than that of water. These factors will make the diffusion of small molecule penetrants in polyimide membranes often not obey the Fickian diffusion law.

Conclusion

Series of polyimide membranes with different thicknesses have been prepared using PMDA and ODA monomers, and the properties of polyimide membranes have been measured by experimental techniques. The dynamic sorption and steady permeation behaviors of water, methanol, ethanol, and dichloromethane as well as the steady permeation of the methanol/dichloromethane binary system in polyimide membranes were investigated.

The experimental results show that the diffusion of water in polyimide membranes is more rapid than other penetrants in this study, and the diffusion behavior of water exhibits the typical characteristics of Fickian diffusion. However, the sorption curves of methanol, ethanol, and dichloromethane are typical of a sigmoid shape. In addition, the steady permeation flux of all these penetrants decreases with an increase in the membrane thickness. However, there are no evident linear relationships between the flux and the reciprocal of membrane thickness. For the diffusion of the dichloromethane/methanol binary penetrants, the total flux of dichloromethane and methanol also decreases with an increase in the membrane thickness. Moreover, the mass fraction of methanol in the permeate side increases as the membrane thickness increases. This is in conflict with the Fickian diffusion law. In summary, it can be concluded from all of the results above that the diffusion behaviors of methanol, ethanol, and dichloromethane in polyimide membranes belong to the anomalous diffusion.

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