

Relationship between the Separation Performances and Free Volume Distributions of Polyimide/Ag₃O₄ Composite Membranes

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ABSTRACT: First, water, methanol, ethanol, acetone, and methyl *t*-butyl ether were used as molecular probes to measure the free volume distribution of a type of polyimide membrane material (HQDEA–DMMDA). The methods were equilibrium swelling and separation membrane technologies. From the Kirchheim theory of free volume distribution, a Gaussian distribution function was determined. The Gaussian distribution function was confirmed with tensile testing and wide-angle X-ray diffraction of the polyimide

films. Second, polyimide/Ag₃O₄ composite hollow-fiber membranes were prepared by dry/wet phase inversion. The separation performances of the composite membranes were characterized with a methanol/methyl *t*-butyl ether mixture. The change in the separation performances was explained by the free volume distribution function very well. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 871–879, 2005

Key words: composites; membranes; polyimides; swelling

INTRODUCTION

Membrane separation technology is an important field for polymer materials.¹ Polymer membranes have been widely applied to gas separation (e.g., N₂/H₂, CO₂/CH₄, and N₂/O₂), the separation of organic mixtures, and the dehumidification of compressed air.^{2–4} The separation mechanism is very significant for the design of new polymer materials. For gas separation, there are solution–diffusion and dual-mode sorption models.^{5,6} For the separation of organic mixtures, the mechanisms are often based on the Flory theory, UNI-FAC model, or Maxwell–Stefan equation.^{7,8}

One important peculiarity of polymer materials is that large free volumes exist in polymers. When small molecules permeate polymer membranes, they must enter the free volume. The fraction of free volume (FFV) is an important parameter in free volume theory. It describes the difference in the free volume for different polymers. Free volume theory has often been used to explain gas permeation in polymer membranes or combined with other separation mechanisms.^{9,10} FFV can be measured through experimental

tion or calculated from the polymer structure with Bondi's¹¹ or Park and Paul's¹² methods.

In fact, the free volume is composed of many microcavities of different sizes. As the molecular mass has a distribution, the number of free volume cavities with different sizes also has a distribution in probability. The distribution function generally is a Gaussian function according to the Kirchheim theory:¹³

$$n(V_h) = \frac{1}{\sigma_v \sqrt{\pi}} \exp[-(V_h - V_h^0)^2 / \sigma_v^2] \quad (1)$$

where V_h^0 is the central or average cavity volume, V_h is the cavity volume, and σ_v is the width of distribution. The free volume distribution can be measured with positron annihilation lifetime spectroscopy technology directly.¹⁴ The V_h range for different polymers, such as polycarbonate (PC), poly(vinyl alcohol) (PVA), and tetramethylpolycarbonate (TMPC), changes from 30 to 300 Å³.^{15–17} However, under certain conditions, the positron lifetime data might provide distorted free volume distributions.¹⁸

The free volume has a distribution. We think that, to permeating small molecules with different sizes, the available free volume is different. For some polymer materials with very rigid polymer segments, it is very difficult for large molecules to enter small free volume cavities under general operating conditions because the permeating molecules need to overcome a very large energy obstacle to edge into the small cavities.

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Therefore, the separation performance may be explained by the free volume distribution. We can assume that inserting some inorganic molecules into the free volume cavities will change the free volume distribution, and then the separation performance can be enhanced. For example, to a gas mixtures made up of large molecules and small molecules, when we plug up large free volume cavities that permit the large molecules to enter some inorganic crystals, the separation performance of the composite membrane should become higher than that of the pure polymer membrane.

In this study, we used five liquids [water, methanol, ethanol, acetone, and methyl *t*-butyl ether (MTBE)] as molecular probes to measure the free volume distribution of a kind of polyimide membrane material by the Kirchheim theory. The measuring method was a combination of equilibrium swelling and membrane separation technologies. In the first part, the free volume distribution of the polyimide was measured and tested with two types of experimentation [tensile testing and wide-angle X-ray diffraction (WAXD)]. A methanol/MTBE mixture was separated with the polyimide hollow-fiber membrane. In the second part, we prepared polyimide/Ag₃O₄ composite hollow-fiber membranes by inserting some Ag₃O₄ crystals into the separation dense skin layers of the polyimide hollow-fiber membranes to change the free volume distribution. The separation performances of the polyimide/Ag₃O₄ composite membranes was characterized with the methanol/MTBE mixture. The change in the separation performances of the composite membranes was analyzed from the free volume distribution function acquired in the first part of the study.

MEASUREMENT OF THE FREE VOLUME DISTRIBUTION OF A POLYIMIDE MATERIAL

Theory

Measurement of the cavity number of the free volume and calculation of the distribution function

Equilibrium swelling is always used to measure the Flory–Huggins interaction parameters of polymer–nonsolvent systems.^{19–21} However, from another viewpoint, if we take different nonsolvents as molecular probes with different sizes, the increasing weight of the swelled polymer by nonsolvents may reveal the number of free volume cavities in the polymer. We can even calculate the numbers of cavities with a fixed volume by a series of molecular probes. Then, the distribution function of the free volume can be decided.

To a swelled polymer membrane, when the volume change (swelling degree) of the membrane is not large, the free volume distribution function should be the same as that of the original polymer. The absorbed

molecules occupy the free volume cavities. If one cavity holds only one probe molecule in the equilibrium state, the total number of cavities (N_i) occupied by i absorbed nonsolvent molecules can be calculated as follows:

$$N_i = A \frac{\Delta m_i}{M_i} \quad (2)$$

where Δm_i is the increasing weight of the swelled polymer, M_i is the molecular mass of probe molecule i , and A is Avogadro's number (6.022×10^{22}). N_i includes the number of cavities (n_i) whose volumes are near the molecular volume of probe molecule i and the number of cavities whose volumes are larger than the molecular volume of the probe molecule. However, the total number does not include the number of cavities whose volumes are smaller than the molecular volume of the probe molecule because the probe molecules cannot edge into small cavities (especially for the polymer with rigid chains), unless the pressure is very high. There are different values of N_i for different probes, for the molecular volumes are different. Then, n_i can be calculated as follows:

$$n_i = N_i - N_j \quad (3)$$

where N_j is the number of probe molecule j , which has a larger volume than probe molecule i .

When we take the molecular or cavity volume (V_i) as the molecular volume of the probe molecule, we acquire the probability density for the free volume cavities. When the free volume distribution function is taken as a Gaussian function from the Kirchheim theory, the parameters in the Gaussian function can be decided with a computer program from the values of V_i of probe molecule i and the corresponding values of n_i .

However, for the probe molecule with a relative large molecular volume, Δm_i may be very small, and it should be difficult to measure. In this experiment, the increasing weights of water, methanol, ethanol, and acetone could be accurately measured. The increasing weight of MTBE was very small. We used vapor permeation from membrane separation technology to solve the problem. A hollow-fiber membrane prepared from the polyimide was used to separate a mixture of methanol and MTBE via vapor permeation. When the mass concentrations of the feed vapor and permeation vapor were measured, the number of cavities with the molecular volume of MTBE could be calculated from the separation data and the cavity information about the methanol probe.

Testing of the distribution function with the bulk modulus (B) and average spacing (d)

We used two methods to confirm the free volume distribution function. One was mechanical experimen-

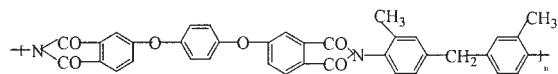


Figure 1 Chemical structure of HQDEA-DMMDA.

tation. According to the Kirchheim theory,²³ the free volume distribution function is

$$f(V_h) = f_0 \exp[-B(V_h - V_h^0)^2 / (2V_h^0 RT)] \quad (4)$$

where f_0 is a prefactor and T is near the glass temperature. When we compare the experimental Gaussian distribution function with eq. (4), B can be calculated. The calculated value of B can be tested with experimental B values.

Another method is WAXD. For the distribution of the free volume, V_h^0 is decided by d . When we measure d of polyimide and calculate the average volume from d , we can compare the two average volumes to test the distribution function. d was measured with WAXD.

Experimental

Materials

The polyimide was organic and soluble (HQDEA-DMMDA). Figure 1 presents the chemical structure. It was soluble in *N,N*-dimethylformamide, chloroform (CHCl₃), *N*-methylpyrrolidone (NMP), and dichloromethane (CH₂Cl₂). Polyimide materials are generally amorphous. They have rigid molecular segments and large FFVs. They can resist many organic solvents, and the swelling degrees are small. Some polyimides have been prepared as separation membranes.²⁻⁴ HQDEA-DMMDA is an excellent separation membrane material.⁴ It was synthesized at the Changchun Institute of Applied Chemistry (Changchun, China). The synthetic method was described by Ding et al.²² The density was 1.296 g/cm³, the glass-transition temperature (T_g) was 541 K, and the weight-average molecular weight was about 100,000.

Probe molecules

Water, methanol, ethanol, acetone, and MTBE were chosen as probe molecules. The reason was that the difference in the apparent molecular volume was al-

most equal between the adjacent probe molecules (water, methanol, ethanol, and acetone). The shape of the free volume cavities was taken to be a sphere, and the probe molecules were taken to be stiff spheres. V_i was calculated from its molar volume (V_m) with the following equation:

$$V_i = \frac{V_m}{A} \quad (5)$$

The diameter of the molecule (D_i) and free volume cavity were calculated with V_i by a sphere formula. If one cavity can hold only one molecule, the diameter of the largest cavities should be smaller than two times the diameter of the smallest cavities. In this experiment, water was the smallest probe, and MTBE was the largest probe. The properties of the probe molecules are listed at Table I. Methanol, ethanol, acetone, and MTBE were analytical reagents and were purchased from Beijing Chemical Plant (Beijing, China).

Equilibrium swelling

Homogeneous polyimide membranes were measured by equilibrium swelling. First, the polyimide was dissolved in NMP (Beijing Chemical Plant). The mass concentration of the polymer solution was 30%. Then, the polymer solution was cast onto glass plates at 80°C to make the solvent volatilize slowly. The thickness of the homogeneous membranes was 0.5–0.8 mm. After being placed in an oven at a temperature of about 120°C for 10 h to maintain constant weights (they were kept flat with glass plates), these homogeneous membranes were cut into rectangle membranes about 140 mm long and about 15 mm wide. An analytical balance (TG328A, Shanghai Balance Instrumental Plant, Shanghai, China) was used to weight the homogeneous membranes. A vernier caliper (0.02-mm precision and 150-mm length) was used to measure the length changes of the swelled polymer membranes to test the swelling degrees.

Four pieces of homogeneous membranes were placed in four conical flasks containing water, methanol, ethanol, and acetone, respectively. The flasks were placed in a thermostated bath at 20°C for 5 days until the weights did not increase anymore. Then, they were taken out, rapidly wiped, and measured. The

TABLE I
Properties of the Probe Molecules at 20°C

Probe	Water	Methanol	Ethanol	Acetone	MTBE
M_i (g/mol)	18.015	32.027	46.043	58.080	88.150
V_m (mL/mol)	18.11	40.55	58.33	73.61	116.30
V_i (Å ³)	30.1	67.2	98.5	122.2	193.1
D_i (Å)	3.9	5.0	5.7	6.2	7.2

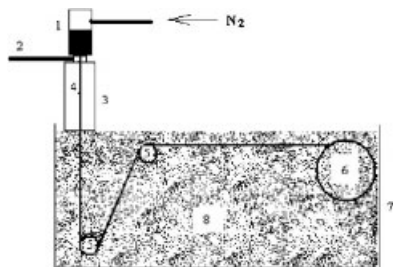


Figure 2 Sketch of the spinning of a hollow fiber: (1) the polymer solution reservoir, (2) the internal coagulant (distilled water), (3) the air gap, (4) the hollow fiber, (5) the guiding wheel, (6) the pulling wheel, (7) the tank, and (8) the external coagulant.

percentage of increasing weight ($P_m = \Delta m/m_0$) and the percentage of increasing length ($P_l = \Delta L/L_0$) were calculated.

Preparation of the polyimide hollow-fiber membranes

Generally, a polyimide can be prepared as a defect-free and ultrathin-skin-layered asymmetric hollow-fiber membrane by dry/wet phase inversion technology.² With this method, a polymer solution is made from a solvent, a nonsolvent, and the polymer material. During the spinning process, the nonsolvent volatilizes in the air gap, and a very thin (0.1–5- μm) dense separation skin layer forms after the fiber enters the external coagulant. The dense skin layer has the same property as its homogeneous polymer membrane. HQDEA–DMMDA can also be prepared as a hollow-fiber membrane by this method. Figure 2 presents a sketch of the spinning of hollow fibers.

First, the polyimide was dissolved in a blending solvent (composed of NMP and acetone). The mass ratio of the polyimide to NMP to acetone was 5:8:5. The total polymer mass concentration was kept at 27%. After filtration, the solution was kept in the reservoir overnight to remove the dissolved gas. The

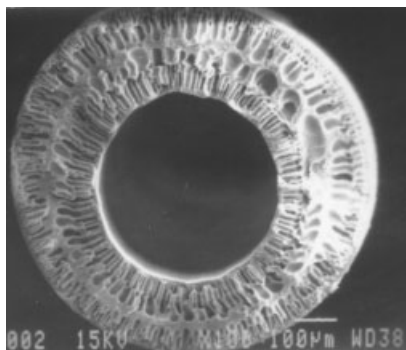


Figure 3 SEM image of a section of an asymmetric polyimide hollow fiber.

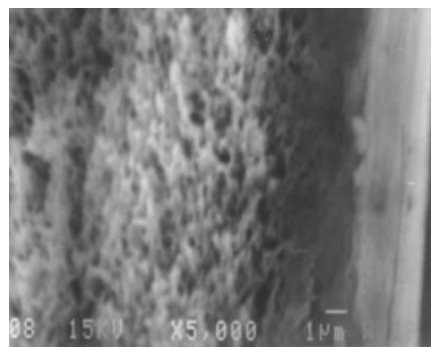


Figure 4 SEM image of a section of the outer skin layer.

solution was spun into hollow fibers with double skin layers by the dry/wet phase inversion method. The temperature of the polymer solution was 40°C. The air gap was about 100 cm, and the temperature of the air gap was about 40°C. The spinning speed was 300 cm/min. Distilled water was used for both the internal and external coagulant. The flow rate of the internal coagulant water was 25 mL/h. The hollow fiber had double skin layers with an inner diameter of 0.4 mm and an outer diameter of 0.6 mm. Figure 3 presents a scanning electron microscopy (SEM) image of a section of a hollow fiber. Figure 4 presents the section of the outer skin layer of a hollow fiber.

Preparation of the membrane module of hollow fibers and vapor permeation equipment

Figure 5 shows the membrane module and separation equipment. A bundle of 20 fibers (50 cm long and 8 mm in diameter) bent into a U-shape was installed in a distillation column. The module was labeled A0. The effective separation area of A0 was 100 cm², which was calculated from the outer surface of the fibers.

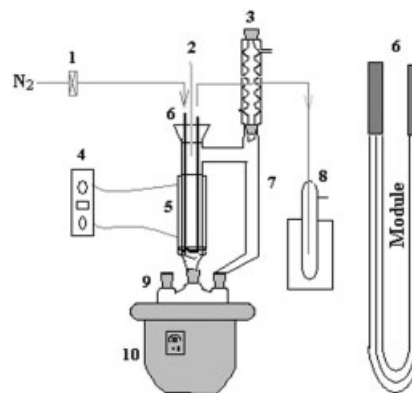


Figure 5 Sketch of the vapor permeation process: (1) the flow meter, (2) the thermometer, (3) the condenser, (4) the electrical source, (5) the heater, (6) the module, (7) the circulator, (8) the cold trap, (9) the distillation flask, and (10) the heater.

TABLE II
P_l and *P_m* of Homogeneous Polyimide Membranes in Probe Liquids

Probe	Water	Methanol	Ethanol	Acetone
<i>P_l</i> (%)	1.156	1.141	0.377	0.267
<i>P_m</i> (%)	3.81	6.02	2.59	2.13

A vapor permeation process was adopted to separate a methanol/MTBE mixture with the hollow-fiber-membrane module. The mass concentration of methanol in the feed vapor was 13%. The vapor was in equilibrium with the liquid mixture in the flask, passing along the outer surface of the hollow fibers, and was condensed with a condenser. A heater was used to heat the feed vapor above the boiling point. High-purity nitrogen entered the lumen side of the hollow fibers from one end, swept through the hollow fibers, and exited from the other end. The vapor permeation was carried away by a nitrogen stream and condensed in a semiconductor cold trap. A gas chromatograph (GC-8A, Shimadzu Corp., Kyoto, Japan) was used to analyze the components of the permeation.

Results and discussion

Equilibrium swelling results of the homogeneous polyimide membranes

Table II lists the *P_l* and *P_m* values of homogeneous polyimide membranes in the four probe liquids. The percentages of increasing volume of the swollen polyimide membranes were all less than 4% (*3P_l*). This meant that the swelling degrees were all small in the four probe liquids. Therefore, the free volume distribution function of the swollen membranes could be taken as the distribution function of the polyimide membranes.

Table III presents *N_i*, which was calculated according to eq. (2).

Vapor permeation results for the hollow-fiber membrane (A0)

Table IV presents the vapor permeation results and calculated number of cavities occupied by the MTBE probe. As discussed earlier, for the large MTBE probe molecules, the increasing weight of the swollen polyimide was very small and difficult to measure. We used the vapor permeation method to measure the

TABLE III
N_i of the Polyimide Membranes

Probe	Water	Methanol	Ethanol	Acetone
<i>N_i</i> (10 ²¹ /cm ³)	1.65	1.47	0.44	0.29

TABLE IV
N_i (10²¹/cm³) for the MTBE Molecules

<i>C₁</i> (%)	<i>C₂</i> (%)	<i>R₁</i>	<i>R₂</i>	<i>N_{methanol}</i> / <i>N_{MTBE}</i>	<i>N_{methanol}</i>	<i>N_{MTBE}</i>
13.0	91.4	0.41:1	29.2:1	71.2:1	1.47	0.02

mass concentrations in the feed and permeation, and we calculated the number of cavities from the data. First, the molar ratios of methanol to MTBE in the feed and permeation (*R₁* and *R₂*, respectively) were calculated from the vapor permeation results: the mass concentration of methanol in the feed (*C₁*) and the mass concentration of methanol in the permeation (*C₂*). Then, the value of *N_{methanol}*/*N_{MTBE}* for the polyimide was calculated as *R₂*/*R₁*. With the number of cavities of methanol in Table III, the number of cavities occupied by MTBE was calculated.

Calculation of *n_i*

n_i was calculated with eq. (3). Figure 6 presents a sketch of the calculation with the data listed in Tables I, III, and IV. Here the hypothesis that one cavity could hold only one molecule and that the diameter of the largest cavities should be smaller than two times the diameter of the smallest cavities was needed to decide the largest *V_h* value, whose number of cavities was taken to be zero. Of the five probe molecules, the smallest molecule was water. Table I shows that its diameter was 3.9 Å. Two times that was 7.8 Å, corresponding to a *V_h* value of approximately 250 Å³. Therefore, cavities with a volume of approximately 250 Å³ did not exist in the polyimide.

Table V lists the last calculated values of *n_i*. The calculation was performed as follows. From Tables I, III, and IV, according to eq. (3), *n_{30.1}* (*V_h*, taken as the molecular water volume, was 30.1 Å³) was equal to *N_{water}* - *N_{methanol}*. Similarly, *n_{67.2}* was equal to *N_{methanol}* - *N_{ethanol}*, *n_{98.5}* was equal to *N_{ethanol}* - *N_{acetone}*, and *n₁₉₃* was equal to *N_{MTBE}* - *N₂₅₀* = *N_{MTBE}* - 0. Figure 6 shows that there was not a suitable molecule with a volume of approximately 150 Å³ for calculating the data of *n₁₂₂*. Therefore, the value of *n₁₂₂* in Table V is blank.

Calculation of the free volume distribution function with the Kirchheim theory

According to the Kirchheim theory, the free volume distribution function is a Gaussian function. Therefore, a general Gaussian function was used to fit *n_i* (Table V) with a data processing program (Origin 6.0). The expression is

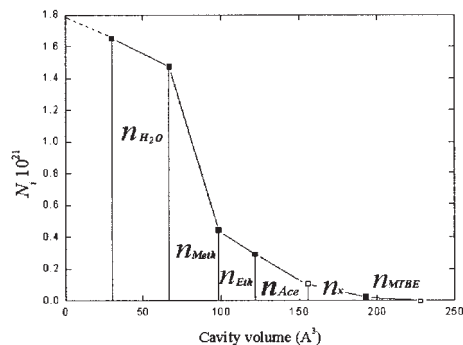


Figure 6 Relationship between n_i and N_i .

$$y = y_0 + \frac{A}{w\sqrt{\pi/2}} \exp\left[-2\frac{(V_h - V_h^0)^2}{w^2}\right] \quad (6)$$

where y is the probability density of free volume cavity numbers, y_0 is the offset, A is the area, and w is the width. The fitted parameters are listed in Table VI. Figure 7 presents a plot of the free volume distribution function of the polyimide. The corresponding Gaussian function is

$$y = 0.01 + \frac{45.78}{34.99\sqrt{\pi/2}} \exp\left[-2\frac{(V_h - 63.43)^2}{34.99^2}\right] \quad (7)$$

Tensile test results for the homogeneous polyimide membranes

As discussed earlier, the tensile testing of homogeneous polyimide membranes was used to test the calculated free volume distribution function with the Kirchheim theory. When we compared eqs. (4) and (6), we determined a new formula:

$$B = \frac{4V_h^0 RT}{w^2} \quad (8)$$

For the polyimide membrane, we inputted eq. (8) with the data from Table VI: $V_h^0 = 3.82 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ (63.43 \AA^3), $w = 2.11 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ (34.99 \AA^3), $T = 541 \text{ K}$ (T_g), and $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. B was calculated to be 1544 MPa.

Five pieces of homogeneous polyimide membranes were tested at 20°C with an Instron 1121 instrument (Instron Corp., Canton, MA). The rate was 50 mm/min. The values of B are listed in Table VII. The calculated B value agreed with the experimental results very well.

WAXD results for the homogeneous polyimide membrane

Figure 8 presents the WAXD results for a homogeneous polyimide membrane from a PX-010X diffrac-

TABLE V
 n_i of Polyimide

Cavity volume (\AA^3)	30.1	67.2	98.5	122.2	193.1	250
n_i ($10^{21}/\text{cm}^3$)	0.18	1.03	0.15	—	0.02	0

tion instrument (Japan; Cu, 40 kV, 200 mA, $2^\circ/\text{min}$). d was 4.8445 \AA . According to the formula $V = (\pi/6)D^3$, the corresponding V_h^0 value for the polyimide was about 60 \AA^3 . Table VI shows that the center volume of the distribution function was 63.4 \AA^3 . Comparing the two values, we believe that the Gaussian distribution function of eq. (7) is reasonable.

CHANGING THE FREE VOLUME DISTRIBUTION TO ENHANCE THE SEPARATION PERFORMANCES

As discussed in the first part of this article, molecules permeating a polymer membrane need the free volume cavities to be larger than the molecules. For separation membrane materials, we always manage to enhance the separation performance by synthesizing new polymer materials or changing the properties of old polymer materials through simple methods.

Now, according to the theory of free volume distribution, when we reduce the number of large free volume cavities by some methods, the separation performance must change. In this part, we inserted Ag_3O_4 into the separating skin layers of polyimide hollow-fiber membranes and measured the separation performances of the composite membranes for the methanol/MTBE mixture described in the first part. The separation performances were quantitatively discussed with the free volume distribution function of eq. (7).

Preparation of the composite membranes

In the first part of this study, dry/wet phase inversion technology was used to prepare polyimide hollow-fiber membranes. In our earlier work, we found that AgNO_3 could blend with NMP very well. When AgNO_3 was added to the polymer solution, Ag^+ dispersed in the polymer solution equably. If Br^- existed in the external coagulant water, when the original hollow fiber entered the external coagulant water, Br^- had to permeate the outer skin layer of the fibers and react with Ag^+ rapidly. According to the mechanism

TABLE VI
Gaussian Parameters of Polyimide

A	V_h^0	w	y_0
45.78	63.43	34.99	0.01

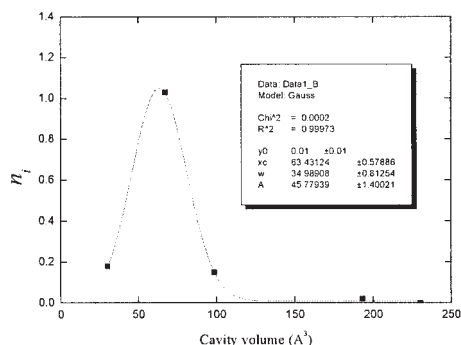


Figure 7 Free volume Gaussian distribution function.

of dry/wet phase inversion, the polymer chains in the outer skin layer of the fibers were frozen quickly after the fiber entered the external coagulant water. Therefore, AgBr mainly existed in the outer skin layer of the hollow fiber.

AgBr changed to stable crystals (e.g., Ag₃O₄, AgO, and Ag), which occupied the free volume cavities. From the standpoint of thermodynamics, these silver crystals should have been inclined to occupy the large free volume cavities during the formation of the composite hollow fibers. When the concentration of crystals increased, small free volume cavities were filled.

AgNO₃ (Beijing Chemical Plant) was added to the polymer solution, which was described earlier. Three composite hollow-fiber membrane modules were prepared by changes in the Ag⁺ concentration in the polymer solutions. The mass ratios of AgNO₃ to NMP were 1:100, 1:50, and 1:25 (separation membranes A1, A2, and A3, respectively). NaBr (Beijing Chemical Plant) was added to the external coagulant, distilled water. The mass ratio of NaBr to distilled water was 1:100. The spinning conditions, the methods of making the membrane modules, and the vapor permeation process were all the same as those for the pure polyimide hollow-fiber membrane (A0).

Vapor permeation separation results

Table VIII lists the vapor permeation results of the composite membranes and the pure polyimide membrane. The composite membranes had higher selectivity for methanol than the pure polyimide membrane. The selectivity of the composite membranes increased with the addition of AgNO₃ to the polymer solutions.

TABLE VII
B of Polyimide from Tensile Tests

	Sample				
	1	2	3	4	5
B (MPa)	1460	1600	1390	1570	1510

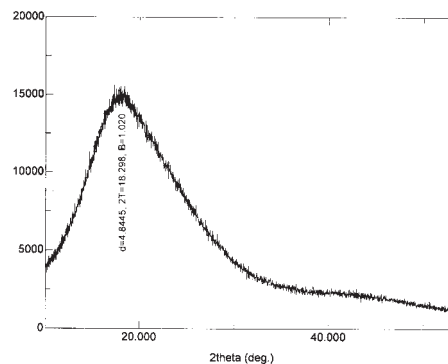


Figure 8 WAXD of a polyimide membrane.

However, when the mass ratio of AgNO₃ to NMP was 1:50 (A2), the selectivity reached a maximum. Adding more AgNO₃ (A3) induced the depression of the selectivity.

Characterization of the composite hollow fibers with WAXD

Because the silver crystals were very small (maybe <1 nm) and were only distributed in the thin skin layers of the composite hollow fibers, it was difficult to characterize them with SEM. Moreover, because the crystals only formed in the asymmetric hollow fibers, we could not use transmission electron microscopy to characterize them either. Therefore, their formation was confirmed with WAXD. Figure 9 presents WAXD of pure polyimide hollow fibers, and Figure 10 presents WAXD of composite hollow fibers.

Through a comparison with the powder diffraction file of the Joint Committee on Powder Diffraction Standards, the crystals in the composite membrane (A2) were determined. Table IX lists the crystallographic data.

Explanation of the separation performance of the composite membranes with the free volume distribution

According to the vapor permeation results of Table VIII, the inorganic crystals in the composite membranes certainly prevented MTBE molecules from permeating the membranes, and this enhanced the selectivity to methanol. For the free volume cavities, if the crystals existed in the free volume cavities in the shape

TABLE VIII
C₂

	Membrane			
	A0	A1	A2	A3
C ₂ (%)	91.4	93.8	96.0	95.4

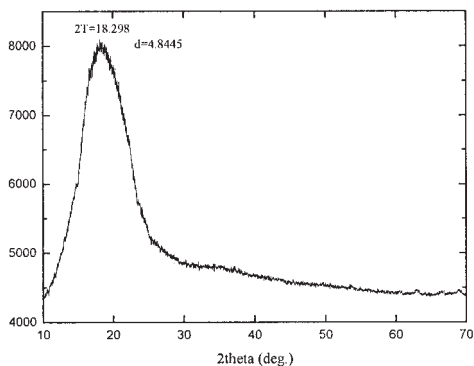


Figure 9 WAXD of a polyimide hollow fiber (A0).

of single crystals, the volume changes could be estimated from the volume of the crystals. In combination with the free volume distribution function, the separation performance could be calculated and compared with the experimental results.

Of the crystals listed in Table IX, the biggest single crystal was Ag_3O_4 , and the content of Ag_3O_4 was the greatest in the composite membrane (Fig. 10). With the shape of Ag_3O_4 taken to be a sphere, the crystal volume was about 21 \AA^3 , as calculated with the formula of the sphere volume. As for the permeation of MTBE molecules, only the cavities with a volume of at least 193 \AA^3 (Table I) permitted MTBE to permeate the polymer membrane. When these cavities were all inserted with Ag_3O_4 (there were enough Ag_3O_4 crystals), the number of cavities that permitted MTBE to permeate became small. However, to the cavities with a volume larger than 214 \AA^3 ($21 + 193 \text{ \AA}^3$), they still permitted MTBE to permeate them.

According to the free volume distribution function [eq. (7)], the number of cavities whose volumes were larger than 214 \AA^3 was $0.01 \times 10^{21}/\text{cm}^3$. If the influence of Ag_3O_4 on the permeation of methanol was neglected (i.e., there were not enough crystals to be inserted into small cavities), the permeation of methanol would not be influenced by Ag_3O_4 . With the

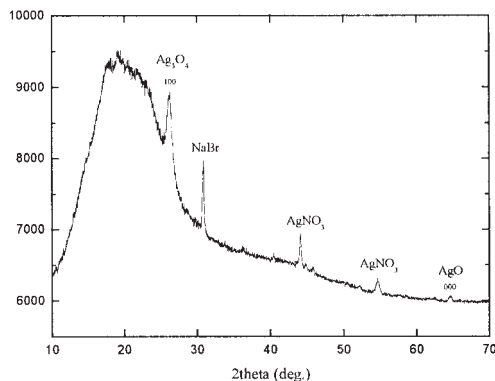


Figure 10 WAXD of a composite hollow fiber (A2).

TABLE IX
Parameters of the Crystals in a Composite Membrane (A2)

	Crystal				
	Ag_3O_4	NaBr	AgNO_3	AgNO_3	AgO
2θ ($^\circ$)	25.88	30.14	44.02	54.74	63.91
<i>hkl</i>	100	200	204	142	000
<i>d</i> (\AA)	3.437	2.960	2.050	1.674	1.453

value of N_{methanol} (Table IV), for the composite membrane (A2), $N_{\text{methanol}}/N_{\text{MTBE}}$ was $1.47/0.01 = 147$. The molar ratio of methanol to MTBE in the feed was 0.41:1 (Table IV), so the molar ratio of methanol to MTBE in permeation was $(0.41 \times 147):1 = 60.3:1$. This value shows that the mass concentration of methanol in permeation was 0.956 $[(60.3 \times 32)/(60.3 \times 32 + 88)]$. This agreed with the experimental value of 0.96 (Table VIII) very well.

CONCLUSIONS

For a polyimide material (HQDEA-DMMDA), the free volume distribution was measured with equilibrium swelling and separation membrane technologies with water, methanol, ethanol, acetone, and MTBE as molecular probes. A Gaussian function was calculated according to the Kirchheim theory. The distribution function was tested with tensile tests and WAXD. Polyimide/ Ag_3O_4 composite membranes were prepared from the standpoint of changing free volume distributions. The separation performance was characterized with a methanol/MTBE mixture. From the free volume distribution function [eq. (7)], for composite membrane A2, the calculated permeation concentration (0.956) agreed with the experimental result (0.960) very well.

In conclusion, for the permeation of large molecules (with respect to H_2 , N_2 , and O_2), the available free volume is different for each permeating molecule. FFV may not be enough to describe the separation performance of polymer membranes. The free volume distribution becomes important for the explanation of separation performance. With the free volume distribution function of a polymer membrane, the number of cavities with a chosen volume (e.g., 214 \AA^3) can be calculated, and the separation performance can be explained or forecast. Equilibrium swelling can be used to detect the free volume distribution. The precondition is that the swelling degree of the swelled polymer is not large, and so the distribution function of the swelled polymer can represent the distribution of the original polymer.

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