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Pervaporation Properties of Polyimide Membranes for Separation of Ethanol + Water Mixtures

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Twelve kinds of polyimide membranes have been prepared using three dianhydrides (including 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA), 3,3′4,4′-benzophenonetetracarboxylic dianhydride (BTDA), and 3,3′4,4′-biphenyltetracarboxylic dianhydride (ODPA)) and four diamines (including benzidine (BZD), bis(4-aminophenyl)phenyl phosphate (BAPP), 4,4′-diaminodiphenylmethane (MDA), and 4,4′-diaminodiphenyl ether (ODA)) via a two-step method. The polyimides were characterized by FT-IR, DSC, and wide-angle X-ray diffraction (WAXD). The permeation experiments of water + ethanol mixtures through 12 polyimide membranes were carried out at 333 K. The temperature dependence of pervaporation performances of ODA-based polyimide membranes is also investigated. The flux of ethanol + water mixtures through the polyimide membranes with the same dianhydrides increases following the order of BZD < ODA < MDA < BAPP. The permeation flux increases with increase in temperature and the relationships between the flux and temperature can be described by the Arrhenius equation. According to the Arrhenius equation, the active energies of water + ethanol mixtures in BTDA + ODA, BPADA + ODA, and ODPA + ODA membranes are (19.3, 26.0, and 30.6) $kJ\cdot mol^{-1}$, respectively. However, the relationship between the separation factor and the temperature is not so clear. In addition, the natural logarithm of flux J ($\ln J$) increases linearly with the mean interchain distance.

Introduction

Pervaporation (PV) is one of the membrane-separation process involving the partial vaporization of a liquid mixture through a dense membrane whose downstream side is usually kept under vacuum.[1] In general, separation by PV can be performed using membranes based on the solution-diffusion mechanism of transport. The mass transport across the permselective membranes involves three successive steps, that is, (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.[2] The steady-state mass transport regime depends on several parameters such as upstream pressure, downstream pressure, temperature, film thickness, properties of solvent molecule, and membrane materials. Consequently, the mass transport through a dense polymer membrane is a complex process.

Polyimides are a class of thermally stable polymers that are often prepared from dianhydride and diamine monomers. They are usually prepared by the so-called two-step method in which a dianhydride and a diamine are allowed to undergo condensation polymerization to form a polyamic acid precursor. Subsequently, the precursor is converted thermally or chemically to the final polyimide. They have a number of outstanding properties such as high thermal resistance, dimension stability, excellent electrical, and mechanical properties[3,4] and have been widely used in applications such as aircraft parts, electronic packaging, adhesives, and membranes, especially the vapor separation membranes.[5,6] In the development of polyimides as vapor separation membranes, particularly for dehumidification of gases, air, and organic vapors, polyimide membranes with high water vapor permeability have attracted great interest. In contrast, there have been a few reports on the use of aromatic polyimide membranes in pervaporation.[7]

In the present work, 12 kinds of polyimide membranes have been prepared using three dianhydrides (including 2,2-bis[4-(3,4-dicarboxyphenoxy)-phenyl]propane dianhydride (BPADA), 3,3′4,4′-benzophenonetetracarboxylic dianhydride (BTDA), and 3,3′4,4′-biphenyltetracarboxylic dianhydride (ODPA)) and four diamines (including benzidine (BZD), bis(4-aminophenyl)phenyl phosphate (BAPP), 4,4′-diaminodiphenylmethane (MDA), and 4,4′-diaminodiphenyl ether (ODA)) via a two-step method. The polyimides were characterized by FT-IR, DSC, and wide-angle X-ray diffraction (WAXD). We also carry out the PV experiments of ethanol + water mixtures through 12 kinds of dense polyimide membranes at 333 K to study the influence of polymer structure on the PV performances of membranes. In addition, the temperature dependence of PV performances of some polyimide membranes is investigated.

Experimental Section

Materials. All monomers were purchased from Acros Organics Inc. and Fluka Chemical Corp. BTDA, BPADA, ODPA, ODA, MDA, BAPP, and BZD were purified before polymerization. The BPADA, BTDA, and BAPP monomers were purified in a vacuum oven at different temperatures. The ODPA, BZD, MDA, and ODA monomers were purified by recrystallization. *N*,*N*-Dimethylformamide (DMF) was obtained from Beijing Yili Chemicals Co. Ltd., purified on distillation under reduced pressure over calcium hydride, and stored over molecular sieves (4 Å). Two penetrants (i.e., water and ethanol) were also obtained from the Beijing Yili Chemicals Co. Ltd.,

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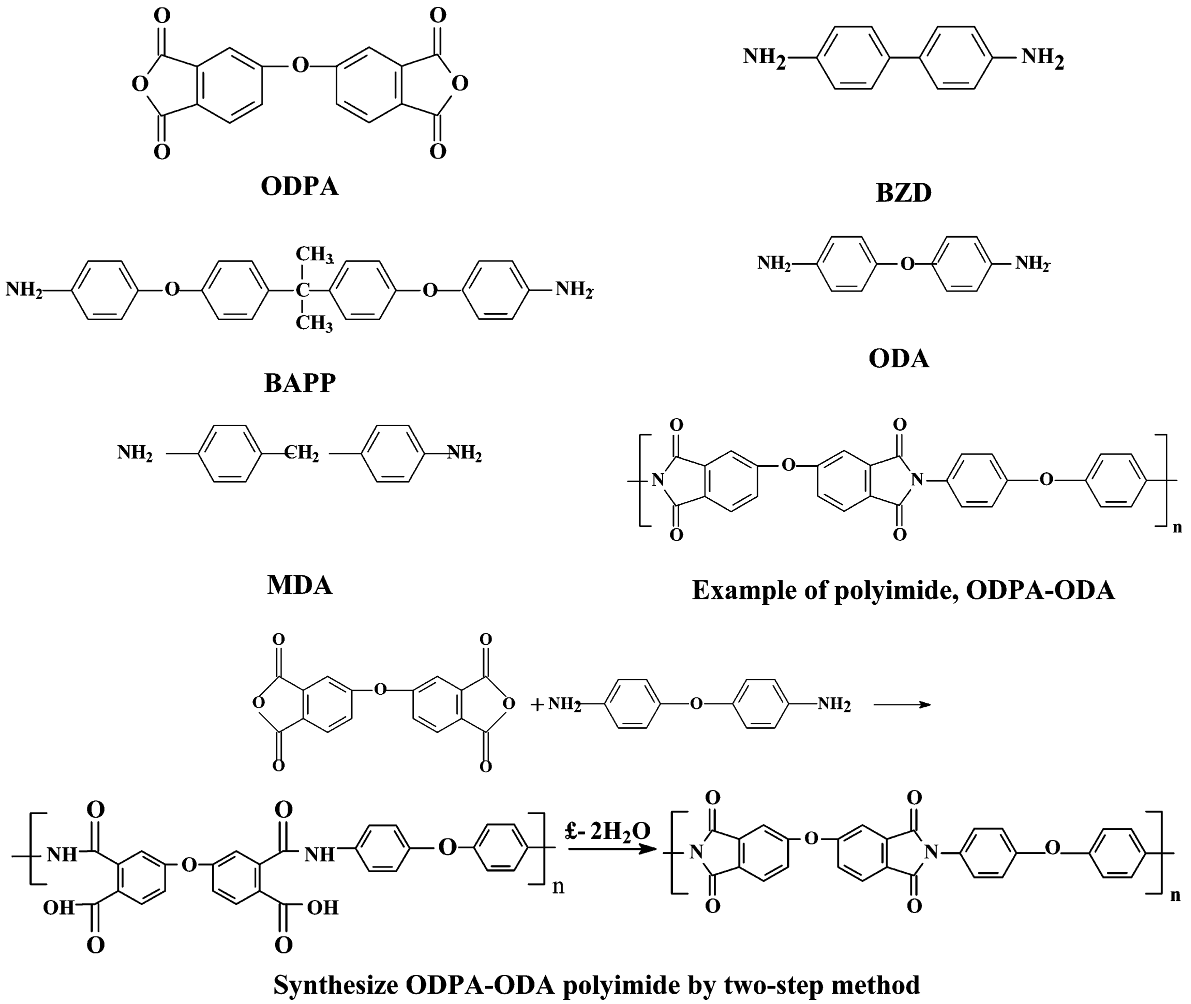

Figure 1. Structures of polyimide monomers.

and they were of reagent grade. All the monomers of polyimides are shown in Figure 1. The structure of ODPA + ODA as an example polyimide is also shown there.

Preparation of Polyimide Membrane. The polyimide membrane was prepared by the so-called two-step method (Figure 1). The polyamic acid (PAA) precursors of polyimides were prepared by solution condensation polymerization at ambient temperature and at a composition of 12 % solids by mass DMF. The aromatic dianhydride monomer was added to an equimolar amount of aromatic diamine dissolved in the solvent all at once.

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. After cooling, the membranes were removed from the glass plates. Finally, the homogeneous polyimide membranes with uniform thickness were obtained. In this study, the thicknesses of polyimide membranes were all (14 to 16) μm.

Characterization. The physical property parameters of polyimide membranes are presented in Table 1. The density of polyimide membrane at 298 K was measured by flotation in a mixed solution. The solution was prepared by ethanol ($\rho = 0.79$ g·cm^{-3}) and carbon tetrachloride ($\rho = 1.599$ 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. WAXD patterns were measured by a Bruker D8 wide-angle X-ray diffractometer using Cu Kα radiation wavelength, and the WAXD pattern of the BTDA + ODA polyimide is displayed in Figure 2. 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 as the mean interchain distance (*d*-spacing). The *d*-spacing can be calculated from Bragg's equation.[8] Free volumes are calculated by Bondi's model of group contribution, and the parameters and the details have been described elsewhere.[9]

Table 1. Physical Property Parameters of Polyimide Membranes

	ρ	T_g	M^a	*d*-spacing	$V_m{}^b$
polyimide	g·cm^{-3}	K	g·mol^{-1}	Å	cm^3·mol^{-1}
BTDA + BZD	1.386	558	470.39	4.1	237.10
BTDA + ODA	1.373	544	486.39	4.3	242.60
BTDA + MDA	1.337	531	484.39	4.9	247.33
BTDA + BAPP	1.308	522	690.61	5.2	446.30
ODPA + BZD	1.374	558	458.37	4.9	230.90
ODPA + ODA	1.348	538	474.37	5.0	236.00
ODPA + MDA	1.306	534	472.43	5.1	241.13
ODPA + BAPP	1.307	531	678.60	5.3	440.10
BPADA + BZD	1.339	525	662.65	5.7	403.90
BPADA + ODA	1.325	506	678.66	6.1	409.40
BPADA + MDA	1.297	502	676.64	6.4	414.13
BPADA + BAPP	1.279	488	870.82	6.9	532.20

[a] *M* is the molar weight of the repeat unit. [b] V_m is the molar van der Waals volume of the repeat unit calculated from the group-contribution method.[9]

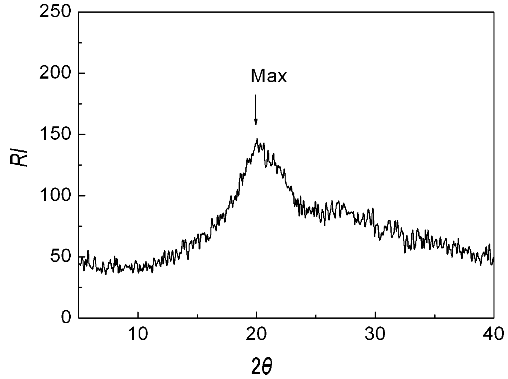

Figure 2. WAXD pattern of BTDA + ODA polyimide (RI denotes the relative intensity).

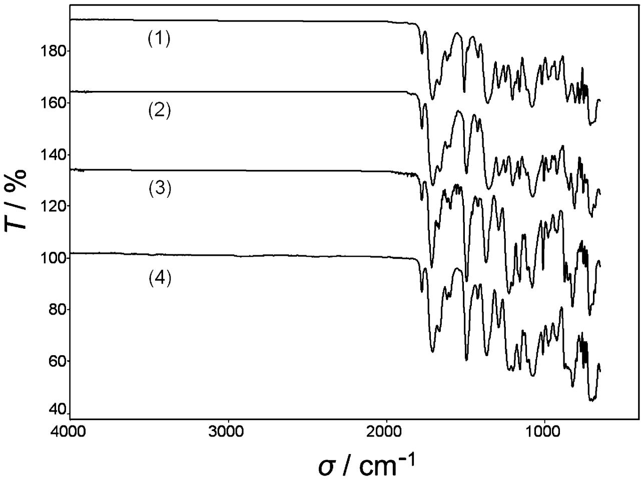

Figure 3. IR spectra of BTDA-based polyimide membranes (T denotes the transmittance): 1, BTDA + MDA; 2, BTDA + BZD; 3, BTDA + BAPP; 4, BTDA + ODA.

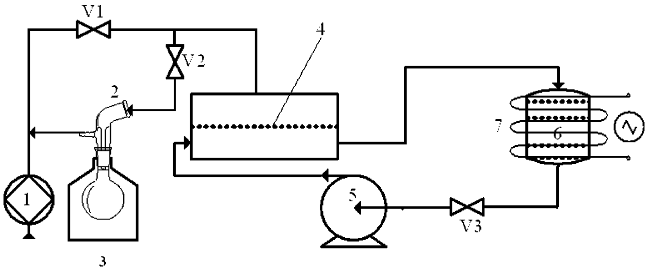

Figure 4. Flowsheet of steady permeation experiments. 1, vacuum pump; 2, permeate collector; 3, cold trap; 4, polyimide membrane; 5, feed pump; 6, feed; 7, thermostat (V1−3, valves).

The polyimides were analyzed by Fourier transform infared (FT-IR) spectra and were recorded on a Nicolet IR560 spectrometer with polymer membrane. Spectra in the optical range of (400 to 4000) cm^{-1} were obtained by averaging 32 scans at a resolution of 4 cm^{-1}. The IR spectra of BTDA-based polyimide membranes as examples are shown in Figure 3. Polyimide membranes showed representative imide carbonyl peaks, but no distinct amide groups. This indicated that the polyimides had been fully imidized.

Permeation Experiments. The permeation apparatus of liquid feeds through flat-sheet membranes is shown schematically in Figure 4. In the membrane cell, the membrane sample was supported on a porous sintered stainless plate, and its active surface area is 21.35 cm^2. Vacuum was 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 was circulated between the membrane cell and a large feed vessel of about 3.5 L, which kept the feed at a constant temperature. The steady state of the permeation experiment was reached after 3 h. Then the permeate sample was drawn out by the vacuum pump and collected by a cold trap cooled with liquid nitrogen once an hour and then analyzed by the gas chromatogram (GC-14CPTF, SHIMADZU Co., Japan) to obtain the mass fraction of each penetrant component. The PV performances were evaluated by the separation factor (α) and the permeation flux (J). The separation factor is defined by

$$\alpha = \frac{Y_w \cdot X_0}{X_w \cdot Y_0} \tag{1}$$

where Y_0 and Y_w represent the weight fractions of organic solvent and water in the permeate, and X_0 and X_w are those in the feed, respectively. The permeation flux (J) was calculated using the expression:

$$J = \frac{Q}{A \times T} \tag{2}$$

where Q is the total mass of permeate collected through the effective area of membrane (A) during time T after the steady state has been reached.

In this study, the liquid feed is the ethanol + water mixtures, and the mass fraction of ethanol is 88.9 %. The permeation experiments of all membranes at 333 K are carried out to investigate the influence of polyimide structure on the PV performance of membranes. Moreover, the permeation experiments of ODA-based polyimide membranes are carried out at (323, 333, 338, and 343) K, respectively, to study the temperature dependence of pervaporation performance of membranes. The permeation experiment of a polyimide membrane at each temperature is repeated three times, and pressure in the permeation compartment is 450 Pa.

Results and Discussion

PV is a complex membrane-based separation process affected by many factors such as the physicochemical properties of the mixtures to be separated, the chemical nature of the macromolecules that comprise the membrane, and the physical structure of the membrane. Table 1 presents the physical properties of 12 polyimide membranes. It has been shown that the free volume values of polyimide with the same dianhydride increase in the following order: BZD < ODA < MDA < BAPP. It means that the free volume increases with the decreasing of density, and the higher the density, the lower the free volume is. This is probably due to the introduction of bridging atoms for diamines. Moreover, it also can be seen that with the same dianhydrides, the *d*-spacings of polyimide chains increase in the following order: BZD < ODA < MDA < BAPP, which agrees with the increase order of free volume values. In comparison of T_g of polyimides composed of the same dianhydride components and different diamine components, BZD-based polyimides show high T_g maybe because of their symmetric biphenyl structures.

The values of steady permeation flux and separation factor of water + ethanol mixtures in 12 kinds of polyimide membranes at 333 K are listed in Table 2. It can be seen that, with the same diahydrides, the flux of solvents increases following the order of BZD < ODA < MDA < BAPP for BTDA-, ODPA-, and BPADA-based polyimide membranes. However, the separation factor exhibits the opposite variation order for

Table 2. Values of J and α of Water + Ethanol Mixtures in Polyimide Membranes at 333 K

membrane	α	J / $g \cdot m^{-2} \cdot h^{-1}$
BTDA + BZD	2341	10.8
BTDA + ODA	703	18.9
BTDA + MDA	128	21.0
BTDA + BAPP	277	30.5
ODPA + BZD	1594	15.2
ODPA + ODA	299	20.4
ODPA + MDA	133	27.5
ODPA + BAPP	175	38.1
BPADA + BZD	1272	18.4
BPADA + ODA	586	26.6
BPADA + MDA	166	32.6
BPADA + BAPP	92	41.6

Table 3. Temperature Dependence of Pervaporation Performances of Polyimide Membranes

membrane	T / K	α	J / $g \cdot m^{-2} \cdot h^{-1}$
BTDA + ODA	323	1624	15.7
	333	703	18.9
	338	522	21.6
	343	608	23.8
ODPA + ODA	323	1011	15.1
	333	299	20.4
	338	285	25.8
	343	290	29.0
BPADA + ODA	323	380	20.8
	333	583	26.6
	338	338	32.5
	343	118	36.1

BPADA-based polyimides, and those of ethanol + water mixtures in BTDA- and ODPA-based polyimide membranes increase following the order: MDA < BAPP < ODA < BZD. This fact is probably attributed to the rigidity of polymer chains. Generally, strong rigidity and weak mobility of polymer chains will result in high selectivity, and loose packing of segment will be good for increasing the flux. The mobility and flexibility of BZD-based polyimide chains are weak because of the symmetric biphenyl group, so the polymer chains are difficult to rotate. BZD-based polyimides exhibit the highest T_g as shown in Table 1. All of these factors hinder the diffusion of small molecules through the polymer membranes and lead to the decrease of the flux. Consequently, the BTDA + BZD polyimide membrane with strong rigid chains shows the highest selectivity and the lowest flux as shown in Table 2.

Furthermore, the ODA-based polyimide membranes was chosen to carry out the permeation experiments of ethanol + water mixtures at different temperatures in order to investigate the temperature dependence of PV performances. As shown in Table 3, the flux through all the membranes increases with increase in the feed temperature, while the correlation between separation factor and temperature is not so clear. The mobility of polymer chain segment increases with increase in temperature, and it will increase the flexibility of polymer chains as well as the free volume of polymer. All of these will increase the diffusion of small molecules through the polymer membrane. In general, the relationship between the permeation flux and temperature can be described by an Arrhenius type relationship:

$$J = J_0 \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where J is the permeation flux, J_0 is a constant, T is the temperature of liquid feed, R denotes the universal gas constant, and E_a is the activation energy. Clearly, there is a linear relationship between ln J and $1/T$ as shown in Figure 5, and E_a can be obtained from the slope of the straight line. Table 4 lists the values of activation energy. It can be seen that the activation energy of solvents in ODPA-based polyimides is larger than that of solvents in BTDA- and BPADA-based polyimides. Consequently, the flux of solvents in ODPA-based polyimide membranes increases rapidly while that of solvents in BTDA- and BPADA-based polyimide membranes increases more slowly with an increase in temperature, as shown in Table 3 and Figure 5.

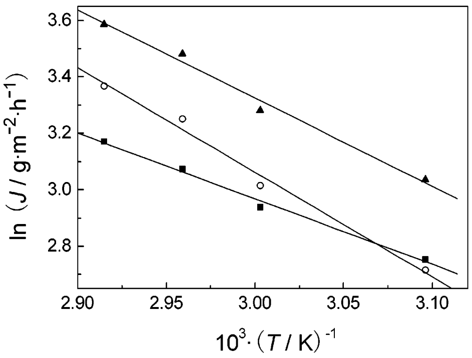

Figure 5. Temperature dependence of the flux J for water + ethanol mixtures in polyimide membranes: ■, BTDA-based polyimide; ■, BPADA-based polyimide; ▲, ODPA-based polyimide.

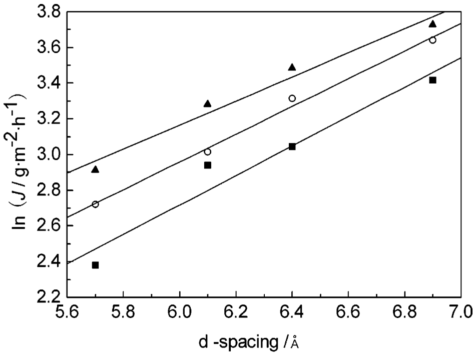

Figure 6. Relation of flux for water + ethanol and d-spacing of polyimide membranes at 333 K: ■, BTDA-based polyimide; ▲, BPADA-based polyimide; ○, ODPA-based polyimide.

Table 4. Values of Activation Energy

membrane	BTDA + ODA	ODPA + ODA	BPADA + ODA
E_a/kJ·mol^{-1}	19.3	30.6	26.0

In addition, the gas permeability of polymer membranes in gas separation process is influenced not only by the temperature but also by other properties such as the glass transition temperature, d-spacing, and the free volume of the polymers. Similarly, we investigated the relationship between the PV performance and d-spacing of polyimide membranes. In a glassy polymer, the d-spacing calculated from the data of WAXD offers an index of the distance between neighboring segments. In some polymers, gas permeability was discussed with the d-spacing. O'Brien et al.[10] and Charati et al.[11] discussed a correlation of d-spacing and diffusivities for CO_2 and CH_4 and suggested that d-spacing might correlate with diffusion coefficient and permeability of the penetrants in membranes. Values of d-spacing measured in this study are summarized in Table 1, and the correlation between ln J and d-spacing is shown in Figure 6. Clearly, ln J increases linearly with d-spacing. The result maybe implies that the enough distance between neighboring segments is the prerequisite for transport behavior of small molecules in polymer membranes. The d-spacing expresses the mean distance of the neighboring segments and can influence the PV performance of polymer membranes.

Conclusions

Twelve polyimide membranes have been prepared using three dianhydrides (including BPADA, BTDA, and ODPA) and four diamines (including BZD, BAPP, MDA, and ODA) via a two-step method, and the polyimides were characterized by FT-IR, DSC, and WAXD. The steady permeation experiments of water + ethanol mixtures through 12 polyimide membranes were carried out at 333 K. The temperature dependence of PV performances of ODA-based polyimide membranes is also investigated.

According to the experimental results, the flux of ethanol + water mixtures through the polyimide membranes with the same dianhydrides increases following the order of BZD < ODA < MDA < BAPP. Furthermore, the steady permeation flux increases with the temperature rising, and the relationships between the flux and temperature can be described by the Arrhenius equation. According to the Arrhenius equation, the active energies of water + ethanol mixtures in BTDA + ODA, BPADA + ODA, and ODPA + ODA membranes are (19.3, 26.0, and 30.6) $\text{kJ}\cdot\text{mol}^{-1}$, respectively. However, the relationship between the separation factor and temperature is not so clear. In addition, the natural logarithm of flux J, $\ln J$ increases linearly with d-spacing. All of these indicate that the PV separation process is governed by the chemical nature of the macromolecules that comprise the membrane, the physical structure of the membrane, and the physicochemical properties of the mixtures to be separated.

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