Polymer Membranes for Separating Organic Mixtures

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ABSTRACT: Polyvinyl alcohol (PVA), polyacrylonitrile (PAN), and cellulose ester were respectively chosen as the separation layer and the support in the composite membranes based on the concept of the solubility parameter and the permselectivities for separating ethanol/water mixture, isopropanol/water mixture, and caprolactam/water mixture. The effects of the membrane materials and the construction of the composite membrane on the separation performance were preliminary discussed. The separation performance of the membranes prepared by several making-membrane techniques, i.e., the polymer solution making-membrane technique, and the membrane treatment technique (heat treatment, organic solvent modification) were presented. The composite membranes of PVA/PAN and PVA/cellulose acetate, and cellulose triacetate hollow fiber membrane modified, which possess good performance in separating the organic systems, were developed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1160–1164, 2006

Key words: membrane; permselectivity; organic/water mixture; pervaporation; reverse osmosis

INTRODUCTION

Since a pervaporation (PV) membrane separation device with a daily capacity of 150,000 L anhydrous ethanol was successfully put into industrial operation in 1988,[1] development of the membranes and their modules for separating a mixture of organic system has been listed as the preferential topics in the seven membrane processes by the world's experts in the field.[2]

As other membrane separation techniques, the suitable membrane material and its membrane-forming technique should be firstly found out for the study of separating organic system with PV process to obtain the separation membrane with good separation performance. The separation of the alcohol/ether system by polyimide membrane[3,4] and the separation of methanol (MeOH) and C_4 and C_5 mixture by cellulose acetate (CA) membrane and polyacrylic acid membrane[5] have achieved the results of industrial values.

The development of separation membranes and application techniques for organic system has been respectively listed the key projects of the National Natural Science Foundation of China, Zhejiang Provincial Natural Science Foundation (ZJPNSF) of China. This article describes some main progress in the key projects of ZJPNSF in recent years by author.

In this article, the permeation behavior of the homogenous membranes (polyvinyl alcohol (PVA) membrane and cellulose triacetate (CTA) hollow fiber membrane modified) and the composite membrane of PVA as separation layer and cellulose ester membranes and polyacrylonitrile (PAN) membrane respectively, as supporting layer under the experiment conditions is studied, and the influences of the membrane-forming techniques of homogeneous, composite, and CTA hollow fiber membrane modified by organic solvent on the PV performance are investigated.

General principle of choosing membrane material

Generally, the solubility parameter would be a guide[6] for the choice of the PV membrane materials being suitable for separating organic mixture, and the membrane materials with different chemical and physical structures should be selected for different separation systems. When a mixture with two-component (i, j) and a membrane (m) constitute a ternary system with $i/j/m$, the separation performance of PV will be affected by the system's solvate reaction.[7]

Table I lists the solubility parameter (δ_h)[8] of various components in three organic systems and five polymers. From the solubility parameter of the hydrogen bonding term (δ_h) in Table I, δ_h value of H_2O is respectively higher than that of the relative components, i.e. ethanol (EtOH), isopropanol (IPA), and caprolactam

TABLE I
Solubility Parameter (δ_h) of Various Components in Organic/Membrane System

Separation system	Component in the system	δ_h [(MPa)$^{1/2}$]
Organic/water	Isopropanol (IPA)	16.4
	Alcohol (EtOH)	19.4
	Caprolactam (CL)	26.0[a]
	Water (H$_2$O)	42.4
Membrane material	Polyacrylonitrile (PAN)	6.8
	Cellulose triacetate (CTA)	10.6
	Cellulose acetate (CA)	11.9
	Polyvinyl alcohol (PVA)	23.9

[a] δ value [(MPa)$^{1/2}$].

(CL) in two-component system of the EtOH/H$_2$O mixture, the IPA/H$_2$O mixture, and the CL/H$_2$O mixture, and the compatibility of PAN, CTA, CA, and PVA to H$_2$O increases in sequence. Thus, one would conclude that the membrane made from the polymers with high δ_h values would give high permselectivity for the component in the mixture that has high δ_h value.

EXPERIMENTAL

Membrane materials and chemicals

Membrane materials of separating layer

PVA with alcoholysis degree 98.0–99.0% (batch number: PVA-124, made in Japan) and CA with acetylizing degree 39.8% were separately used as the materials of separation membrane to prepare homogeneous PVA membrane and CA membrane. PVA and CA were the membrane materials used to prepare the composite membrane respectively. CTA hollow fiber reverse osmosis (RO) membrane[9] (made in China) was used for modification.

Membrane materials of supporting layer in composite membrane

The porous membranes used as the supporting layer in PVA composite membrane were those of PAN and CA.[10] These porous membranes (made in China) are the ultrafiltration membranes with various cut-off molecular weights (cut-off MW).

Chemicals

Acetone, EtOH, IPA, CL, and acetic acid (made in China) are of analytical grade. The chemicals were used in this study without further purification.

Preparation of membranes and modification of RO membrane

Preparation of membrane-forming solutions

CA powder dried in the dry oven was dissolved respectively in acetone and dioxane at 25°C to make 8–15 wt % casting solution. Weigh PVA and place it into a vessel with hot water; after stirring and dissolving, add a certain amount of crosslinking agent (e.g., polyacids or aldehydes) to the solution; continue to slowly stir the solution at room temperature for 4 h, then rest for debubbling, and await use. The crosslinking agent is the maleic acid unless another specification.

Preparation of membranes of homogenous and composite

Preparation of the composite membrane is that, first, drip–dry the supporting membrane, which has been immersed in water at least 1 day and night, and then cast the PVA solution by a stainless steel kind on the supporting membrane fixed onto glass plate. When the homogenous membrane was cast, the casting solution of CA and PVA was directly cast onto glass plate. Finally, PVA membranes in the gelatinizing state were been placed into a dry oven for more than 3 h at 100–150°C.

Modification of RO membrane—solvent treatment technique

CTA hollow fiber RO membrane for the desalination of brackish water with high salinity[9] was immersed in the organic solvents with different organic radicals (for example acetone) for 8–24 h at the room temperature. Then, the CTA hollow fiber membrane treated by organic radical was drip-dried.
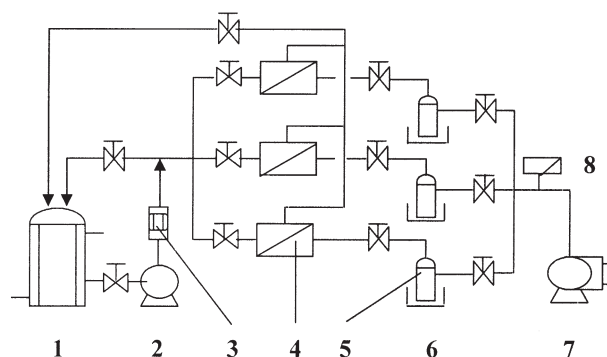

Figure 1 Schematic diagram of PV test. (1) Feed vessel; (2) Feed pump; (3) Flow meter; (4) Membrane; (5) Permeate collector; (6) Liquid N$_2$ cold trap; (7) Vacuum pump; (8) Vacuum meter.

PV test

The PV apparatus and test procedure have been reported in the previous work.[10–14] The schematic diagram of PV test is shown in Figure 1. The PV experiments were carried out with the organic mixture (EtOH/H_2O mixture: 6 wt % H_2O; IPA/H_2O mixture: 13.0 wt % H_2O; CL/H_2O mixture: 33.32 wt % H_2O) at 25°C under a downstream pressure less than 1000 Pa. The permeate through the membrane was collected in cold traps cooled with liquid nitrogen. The concentration of the feed and the permeate was analyzed with a gas chromatograph with thermal conductivity detector. The membranes were characterized respectively by the total permeation flux, J (g/m^2 h), and the separation factor ($\alpha_{H2O/Organic}$), as follows.

$$J_{PV} = Q/At, \text{ and}$$

$$\alpha_{H_2O/Organic} = (Y_{H_2O}/Y_{Organic})/(X_{H_2O}/X_{Organic})$$

where $Y_{H_2O}/Y_{Organic}$ is the weight ratio of H_2O to organic in the permeate (Y); $X_{H_2O}/X_{Organic}$ is the weight ratio of H_2O to organic in the feed mixture (X); Q, A, and t are the weight of permeate (g), effective membrane area (m^2), and test time (h), respectively.

The membrane of homogenous or composite was mounted in a PV cell (effective membrane area: 22.8 cm^2). Two ends of the CTA hollow fiber membranes were adhered with the 504 type adhesion agent in a stainless steel tube after they were drip-dried. The characteristics of the CTA hollow fiber membranes and the module used in the test were as follows: inner diameter 0.13 mm, outer diameter 0.38 mm for hollow fiber membrane, inner diameter 0.010 m, outer diameter 0.014 m, length 0.4 m for the membrane module, effective area of CTA membrane module: (9.7 × 10^{-2}) m^2.

RESULTS AND DISCUSSION

Casting solution of making-membrane

PVA is a polymer with a large quantity of strongly hydrophilic hydroxyl groups and its solubility to water is, to quite great degree, governed by polymerization degree, especially alcoholysis degree. Fully alcoholytic PVA dissolves in water in an extremely little quantity, and it can be completely dissolved in water when heated to over 80°C. Under the condition of stirring, slowly add PVA with 98.0–99.0% alcoholysis degree to hot water of 90°C. After stirring for at least 2 h continuously, cool it to room temperature, again stir it while adding PVA crosslinking agent such as organic polyprotic acid or aldehyde; finally, the PVA casting solution with ternary constituents is generated.

When laying the PVA aqueous solution at ambient temperature, its viscosity will increase with time lapsing, especially long-term storage of PVA with full alcoholysis or with additive crosslinking agent will lead to gelatination. This trend will be more obvious as the concentration of PVA or crosslinking agent increases. For the PVA aqueous solution without crosslinking agent, the cause of viscosity increase is because the interaction between PVA molecules is an entanglement between hydrated molecular balls rather than solid binding of hydrogen bond in interaction between PVA molecules, but this entanglement is very weak and can be easily broken.[15]

For the purpose of desalination, water treatment, etc., cellulose ester membrane of CA or CTA must be prepared with the casting solution with multi-constituent formulation, but in the case of homogeneous membrane for separating organic system, cellulose ester is dissolved only in a good solvent, for example acetone, having no any additive constituents. For the cellulose ester membrane with excellent performance of separating organics, cellulose ester concentration in casting solution should be far lower than the concentration of casting solution for preparing porous desalination membrane.

Preparation technique of separation membrane

Complete evaporation of solvents in casting solution

The complete evaporation method of the solvent system for preparing RO membrane[16] can be successfully applied to the preparation of PV membrane. Its technological process is that the casting solution is cast into gel-state membrane, and then let solvents such as water and acetone fully evaporate in gel state membrane, finally, homogeneous PVA membrane and cellulose ester membrane are obtained. If the casting solution is cast on porous supporting membrane and then solvent fully evaporating, the composite membrane will be obtained.

Heat treatment of PVA membrane

PVA membrane, which was prepared by complete evaporation method, was placed in a dry oven at over 100°C to heat, within a certain time. PVA reacts chemically with crosslinking agent, when drying temperature reaching to over PVA glass-transition temperature (T_g 71°C), crystallization happens in amorphous zone, at that time, hygroscopic quantity decreases, resistance to water and mechanical strength heightens; and PVA crystallization quickens with the rise of heat treatment temperature, but when rising to 200°C, the heat decomposition of PVA appears. Thus, the heat treatment temperature of PVA membrane was experimentally determined at 100–150°C.

TABLE II
Permeation Behavior of PVA Homogenous Membrane and CTA Hollow Fiber
Membrane Modified in Different Separation Systems

Membrane	Organic system	H_2O concentration (wt %)		Permeate flux (g/m² h)
		Feed	Permeate	
PVA	CL/H_2O	33.32	99.99	419
CTA modified	IPA/H_2O	13.0	99.96	364

Modification effect of CTA RO membranes

The CTA hollow fiber RO membrane modified in several organic solvents possesses good performance for separating EtOH/H_2O mixture. The PV performance of CTA hollow fiber RO membrane modified through dipping processing with acetone or alcohol aqueous solution is the most superior. The CTA hollow fiber RO membranes turn into a meaningful PV separation membrane. It was shown that the solvent treatment process of the asymmetric RO membranes is the "defects" reparation of the membrane skin layer.[17]

Permselectivity through homogenous membrane

Table II shows the data of separating organic mixtures of the homogenous membranes of PVA and CTA hollow fiber membrane modified, respectively.

It can be seen from Table II that when organic/water system is separated with PVA homogenous membrane and CTA hollow fiber membrane modified, water rather than organics preferentially penetrates the membrane. The homogenous membranes have preferential permselectivity for water and have higher retention performance for organics (EtOH, CL, and IPA).

Separation performance of PVA composite membrane with various supports

It was found that better separation performance of the composite membrane of PVA/PAN and PVA/CA can be obtained when being compounded on PAN and CA porous supports for separating EtOH/H_2O mixture. The test results are shown in Table III.

It can be seen from Table III that when the porous membranes with 50,000 cut-off MW is used as supporting layer, the separation performance of the composite membrane made of CA as supporting layer is nearly the same as PAN membrane in PV separating IPA (81.5 wt %)/H_2O mixture. But, when the material of the supporting membrane is identical, because of the difference between cut-off MW of CA membranes being 10 times, the permeate flux of PVA/CA composite membrane with smaller cut-off MW is nearly 1 time higher than that with larger cut-off MW. These results show that not only the material types of supporting membrane have obvious influence on the PV performance, but pore size of supporting membrane also exerts influence on separation performance.[14] Because the permeate flux is affected by five structural parameters of composite membrane,[18] i.e., thickness of composite separation layer (l_1), thickness of skin in supporting layer (l_2), depth of polymer solution intrusion into the pores of porous supporting membrane when casting the composite membrane (l_3), thickness (l_4), and porosity of porous supporting layer (ξ_1). For the composite membrane at given l_1, l_2, l_4, and ξ_1, coating the casting solution on porous membrane with large pores will lead to the increase of l_3,[19] showing obvious decreases of permeate flux when separating; thus, the porous membrane with smaller cut-off MW should be selected as the supporting layer of the composite membrane.

The experimental results in Table IV show that when taking the same PAN porous membrane as the supporting layer, separating performance of the composite membrane with PVA separating layer is superior to that with CA separating layer for separating IPA/H_2O mixture. The performance of homogeneous CA membrane is superior to that of CA composite membrane. No matter whether the CA membrane has

TABLE III
Effect of Supporting Layers on Performance of PVA Composite Membranes

Supporting layer		PV performance	
Polymer	Cut-off MW (×10⁴)	Flux (g/m² h)	H_2O concentration in permeate (wt %)
PAN	5	352	99.5
CA	0.5	675	99.6
CA	5	340	99.4

TABLE IV
Performance Comparison of Composite Membranes and Homogeneous Membrane

Membranes	Flux (g/m² h)	$\alpha_{H_2O/IPA}$
CA	518	81
CA/PAN	360	32
PVA/PAN	350	7860

the supporting layer or not, the separating performance is inferior to the PVA composite membrane, the variety of the separating performance of CA membrane is in conformity with the literature[18] reported.

It can be seen from Table II–IV that two kinds of membrane materials, through which the identical constituent in organic mixture can preferentially permeate, were used as separating layer and supporting layer respectively, and then, the composite membrane with such separating layer and supporting layer is sure to generate excellent permselectivity.

CONCLUSIONS

1. The optimum selection scheme of the composite membrane materials is to select these membrane materials having preferential permeability against the identical constituent in the organic mixture respectively as the separating layer material and the supporting layer material of the composite membrane.
2. The preparation of homogeneous membrane or composite membrane by the complete evaporation method of solvents, and the modification of the CTA membrane for RO desalination of high salinity brackish water into the PV membrane by dipping processing with organic solvents, i.e. solvent treatment technique, is the effective making-membrane techniques for PV separation of the organic mixture.

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