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POLY(ACRYLATE-CO-ACRYLIC ACID)/POLYSULFONE COMPOSITE MEMBRANES FOR PERVAPORATION OF VOLATILE ORGANIC COMPOUNDS FROM WATER

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ABSTRACT

Novel cross-linked poly(acrylate-co-acrylic acid)/polysulfone membranes were prepared for pervaporation of aqueous solutions of 1,1,2-trichloroethane (TCA), trichloroethylene (TCE), and tetrachloromethane. Among 6 copolymers, the poly(BA-AA-MMA)/PS composite membrane showed the highest selectivity as well as the highest permeation flux. The separation factor was around 6000 and the flux was around 0.20 kg/m^{2}h for pervaporation of TCE-water through the poly(BA-AA-MMA)/PS membrane at 60°C.

Key Words: Pervaporation; Volatile organic compounds; Composite membrane; Polyacrylate; Polyacrylic acid

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INTRODUCTION

The major contaminants in industrial wastewater and ground water are the volatile organic compounds (VOCs). VOCs have long been regarded as a potential threat to the biosphere, and most of these compounds are classified as priority pollutants. Of the commonly occurring VOCs, chlorinated compounds are carcinogenic. Conventional treatments such as air stripping, distillation, and extraction are used for the treatment of wastewater containing trace VOCs. Pervaporation has established itself as one of the most promising membrane technologies. Pervaporation is regarded as an energy-saving separation process compared to the conventional distillation process, especially for removal of VOCs from aqueous solutions. The attractiveness of pervaporation lies in the flexibility of its design, the low energy cost, and the possibility of selectively removing the polluting compounds and recycling them for reuse (1,2).

In accordance with aqueous solutions of different VOCs, various kinds of suitable membranes should be used for pervaporation. Many researchers have tested a great many membrane materials for the pervaporation of chlorinated VOCs from aqueous solutions. In their studies, the polymeric membranes used included those of silicone rubber (3,4,5), composite materials (6), and a filling-polymerized variety (7,8,9).

The basic requirement for the pervaporation membranes is that it must provide both high flux and high selectivity for VOCs. The desired membrane has low cost for industrial application. However, both high flux and high selectivity for one-particulate membranes are not always available. This can be seen from the data presented in Table 1 for the pervaporation of trichloroethylene (TCE)-water. The highest selectivity can only be obtained for a hollow fiber contained liquid

Table 1. Pervaporation Results of TCE/Water in Literatures

Membrane	Temperature (°C)	TCE Concentration in Feed (wt%)	Flux (kg/m^2h)	Separation Factor α	Reference
Poly(BAA-AA-MMA)/PS	60	0.0014	0.2	6000	This work
BA-AA	25	0.0529	0.0213	804	(6)
HFCLM	25	0.1525	0.00438	4050	(10)
SRHF	25	0.0525	0.00451	1201	(10)
Silicon tubing	20	0.05	0.014		(17)
PDMS grafting HDFNMA	25	0.042	0.112	407	(11)

BA is *n*-butylacrylate; AA is acrylic acid; SRHF is single fiber-set system contained silicon rubber hollow fiber; HDFNMA, 1H,1H,9H-hexadecafluorononyl methacrylate.

membrane (HFCLM), which simultaneously combined a membrane extraction process with a pervaporation process in one membrane module (10).

Separation by pervaporation is fundamentally dependent on the solubility and diffusivity of the components in the membrane. In the previous reports of composite membranes, a polyacrylate dense layer showed certain affinity to chlorinated hydrocarbons, and the porous substrate was completely inert to organic liquid (5,12,14). The solubility difference of the polymer to the feed components exhibits permselectivity, and the substrate matrix restrains the swelling of the polymer.

The search for new polymeric materials with improved pervaporation properties amenable to industrial applications has not produced any good membrane candidates and has continued to be the focus of intensive investigation. In response to this challenge, we synthesized the new poly(acrylate-co-acrylic acid) materials and prepared the novel composite membranes for removal of dissolved VOCs from water. VOCs, 1,1,2-trichloroethane (TCA) and trichloroethylene (TCE), CCl_4, and $CHCl_3$ were used as examples of halogenated hydrocarbon contaminants in water.

EXPERIMENTAL

Chemicals

TCA, TCE, trichloromethane and tetrachloromethane (purity 99.5%) were obtained from the Tianjin Reagent Factory; liquid N_2 was from Nankai University; the PS (polysulfone) membrane (trapped wt 20 000) was from the Nuclear Energy Research Center in P.R. China.

Preparation of Copolymer

Poly(acrylate-co-acrylic acid)s were prepared from acrylate and acrylic acid (AA) by free radical solution polymerization in a mixture of toluene and ethyl acetate with an initiator azobisisobutyronitrile at 70°C for approximately 5–7 hours. The acrylate monomers and AA were purified by vacuum distillation. Other regents were used without further purification.

Membrane Preparation

The synthesis copolymer after polymerization was diluted by ethyl acetate. Epoxy resin used as a cross-linker was added to the polymer solution. The cast solution was coated on the flat PS film support at 25°C. The membrane was put into triethylamine solution and then exposed to the air at room temperature for 15 minutes. After it was dried, the flat composite membrane was heated at 40°C for 1 hour. Thickness of the thin layer on the composite membrane was measured to be 3–5 μm.

Experimental Unit

Membranes with an effective area of $0.019 m^2$ were evaluated with a laboratory-scale pervaporation test system. Figure 1 shows the experimental unit. The pervaporation was performed at a constant temperature with an error of ± 0.1°C and at an absolute pressure of approximately 6–10 mm Hg on the permeate side.

A gas chromatography (GC) HP 4890GC was used for the analysis of the feed and permeate compositions. Aqueous halogen concentrations were measured in a HP 4890 series GC equipped with a flame ionization detector and a HP-5 capillary column (cross-linked with 5% Ph Me siloxane) of 15 m length, 0.53 mm diameter, and 0.15 m film thickness (Hewlett Packard). Ultrapure nitrogen was used as the carrier gas. The optimum operation conditions were determined by varying GC parameters independently at different times. The sample volume was 1 μl; the sample equilibration time was 2 minutes; oven temperature was set at 100°C for 2.5 minutes to get clear separation of halogen and methanol.

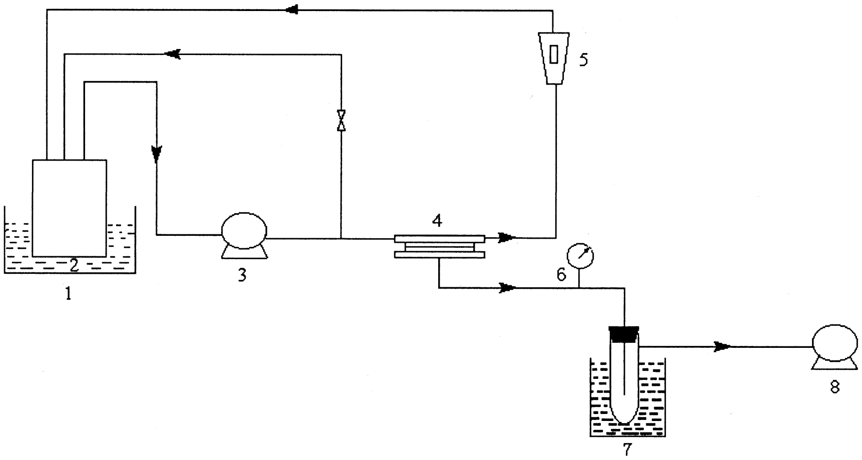


Figure 1. Pervaporation test unit for removal of VOCs from water. 1) Thermostatic bath, 2) feed reservoir, 3) Pump, 4) pervaporation cell, 5) flow meter, 6) vacuum gauge, 7) liquid N_2 cold trap, 8) vacuum pump.

The separation performances are expressed in terms of the flux J and separation factor α.

$$J = \frac{Q}{A\theta}\ \text{kg/m}^2\text{h} \tag{1}$$

where Q is the amount of the permeate during a time interval θ, and A is the effective membrane area.

$$\alpha = \frac{Y(1 - X)}{(1 - Y)X} \tag{2}$$

where X and Y denote the concentration (by molar percentage) of a VOC (TCA or TCE) in the feed and the permeate, respectively.

Sorption Measurement

The dried and weighed membrane (W_0) was immersed in halogen solution and sealed at 25°C until equilibrium was reached. The membrane was then taken out of the vessel, wiped quickly with filter paper, and weighed (W_1). The degree of sorption of halogen solution into the membranes was measured as follows:

$$S(\text{degree of sorption}) = \frac{W_1 - W_0}{W_0} \times 100 \tag{3}$$

The membrane was then frozen in a glass vessel under a vacuum. The glass vessel was heated, and vaporized adsorbate was collected in the cold trap with liquid nitrogen. The concentrations of organic solvent and water were determined in the same way as the pervaporation was measured. The separation factor, α was calculated as

$$\alpha_s = \frac{Y'(1 - X)}{(1 - Y')X} \tag{4}$$

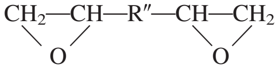
where X and Y' denote the concentration of a VOC (TCA or TCE) in the feed solution and the swollen membranes, respectively.

RESULTS AND DISCUSSION

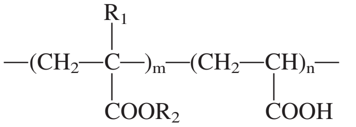
Effect of Chemical Structure of the Membrane Materials

Chemical structures of polyacrylate and the cross-linking agents are summarized in Table 2. Effect of the chemical structure on pervaporation and sorption of the TCA-water mixture through polyacrylate is shown in Table 3. As can be seen, the separation factor is the highest for poly(BA-AA-MMA) (which contains

Table 2. Chemical Structure of Monomers and Cross-linking Agent

Monomer	R_1	R_2
Butyl Acrylate (BA)	—H	$—C_4H_9$
Ethyl acrylate (EA)	—H	$—C_2H_7$
Methyl methacrylate (MMA)	—H	$—C_2H_7$
Octyl acrylate (OA)	—H	$—C_8H_{17}$
Epoxy resin	 $CH_2—CH—R''—CH—CH_2$ (O bridging each $CH_2—CH$ pair)	

1.



$$—(CH_2—\underset{COOR_2}{\overset{R_1}{C}}—)_m—(CH_2—\underset{COOH}{CH})_n—$$

2. R″: $—(CH_2—CH)_m—$

5% MMA), because of the better solubility of TCA, which is based on the affinity of TCA to the hydrocarbon side chain of the polymer. This result is supported by the sorption data shown in Table 3. However, the highest flux was obtained for poly(BA-AA) membranes. The greater flux is attributed to the high diffusion coefficient because BA has not only relatively small side chains but also lower glass transition temperature, T_g, which favors side chain movements. This copolymer experiences low filling effects in the intersegmental spaces. However, T_g of these copolymers was measured, and the order of T_g values did not coincide with the order of permeation flux. The copolymer membrane with a relatively high T_g shows a relatively low permeation flux in this series. Among the copolymers tested, poly(BA-AA-MMA)/PS (5% MMA) membrane was found to be the most promising.

Table 3. Pervaporation and Sorption of TCA-Water Mixture Through Poly(acrylate-co-acrylic acid)/PS Composite Membrane

	Pervaporation (30°C)							Sorption (20°C)		
Membrane	Polymer Composition (wt%)			TCA in Feed (wt%)	J kg/hm^2	α	T_g°C	TCA in Feed (wt%)	S	α_s
BA-AA-EA	20 AA	50 BA	30 EA	0.174	0.1130	17.65	−4.73	2.4457	0.3091	125.13
OA-AA	20 AA	80 OA	—	0.346	0.103	1.320	−23.83	2.4457	0.264	116.47
BA-AA	15 AA	85 BA	—	0.134	0.121	34.72	−16.35	0.058	0.3115	134.19
BA-AA-MMA	15 AA	5 MMA	80 BA	0.148	0.083	201.5	−9.84	0.058	0.3152	153.21
BA-AA-MMA	15 AA	10 MMA	75 BA	0.083	0.063	69.46	−5.34	—	—	—
BA-AA-MMA	15 AA	25 MMA	60 BA	0.822	0.035	10.56	13.4	2.4457	0.3182	89.36

Effect of Organic Compound Solutes

The data of sorption and pervaporation for some VOCs with poly(BA-AA-MMA)/PS (5% MMA) membrane are listed in Table 4. The optimum observed for TCE was striking and may be explained by two effects: first, though a high polarity implies an increase sorption in the polarity of the minor membrane material, TCE′ α_s is highest in this series due to its molecular structure. TCE has an unsaturated double bond between the 2 carbon atoms, which leads to an increase electron cloud density and improved nucleophilic power compared with other solvents. Therefore TCE has higher sorption than others. Second, a comparison of the separation data by pervaporation with that of sorption suggests that diffusion selectivity is higher than 1. This result can be attributed to the double bond because these molecules exhibit a plane geometry that favors transport without steric hindrance (14,15,16).

Effect of Temperature on *J* and α

Temperature dependence of permeation rates and separation factor of TCA-water and TCE-water through the poly(BA-AA-MMA)/PS (5% MMA) composite membrane are shown in Figs. 2(a) and 2(b), respectively.

The separation factor and permeation flux increase remarkably with increasing temperature. In the high temperature region, molecular motion of the polymer side chains becomes easier and so does diffusion of the molecules. TCE is a more volatile compound than that of water and its vapor pressure increases more rapidly than water with increasing temperature, leading to promotion of

Table 4. Sorption and Pervaporation Data for Different Solute with Poly(BA-AA-MMA)/PS Composite Membrane

			Sorption (20°C)		Pervaporation (30°C)		
Solvent	MV cm^3/mol	μ, D (20°C)	Concentration in feed (wt % of solv.) $\times 10^3$	α_s	Concentration in feed (wt % of solv.) $\times 10^3$	*J*, kg/m^{2}h	α
TCA	93.00	1.25	58.0000	153.21	55.9000	0.1280	258.58
TCE	90.30	1.01	0.4000	250.13	0.4000	0.1190	474.81
CCl_4	97.15	0.00	0.0068	135.75	0.0068	0.0836	186.29
$CHCl_3$	80.66	1.01	0.7650	142.51	2.2700	0.0770	—

MV = molar volume; μ = dipole moment (14).

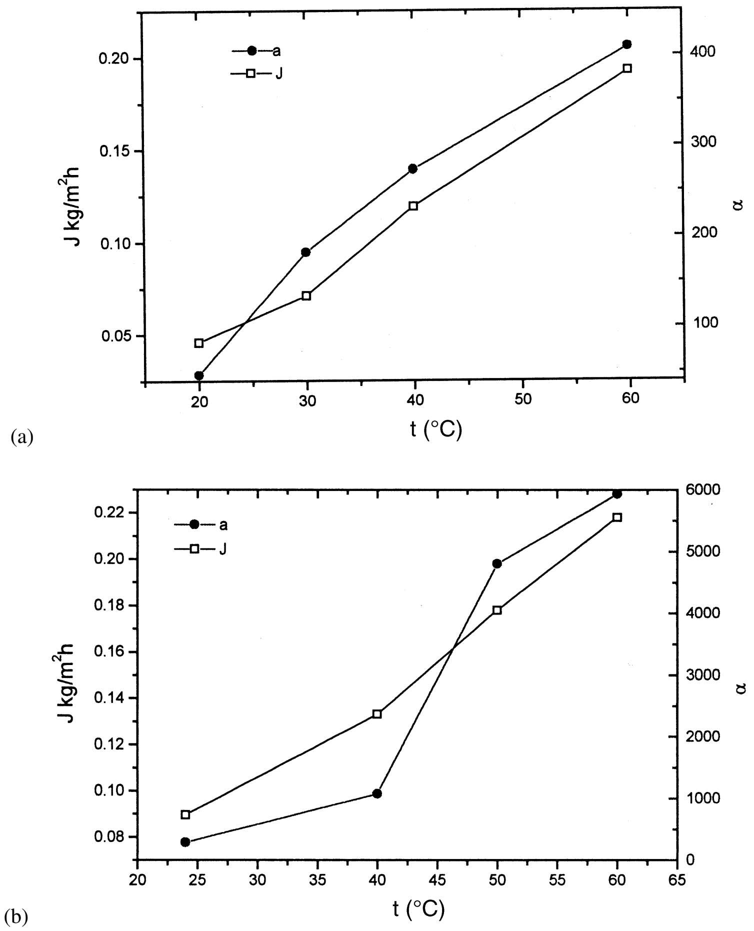


Figure 2. Flux and selectivity versus temperature.

mass transfer. The pervaporation of TCE-water differs with other membranes . In our work, a rise in temperature was usually correlated with an increased flux and decreased selectivity α because the solubility and diffusion increased with temperature. We assumed that the membrane swelled more rapidly at high temperature.

The relationship between flux and temperature for the pervaporation by poly(BA-AA-MMA) membrane is shown in Fig. 3. The relationship of the 2 parameters is related to the Arrhenius function (18), $J = J_0 \exp^{(-E/RT)}$.

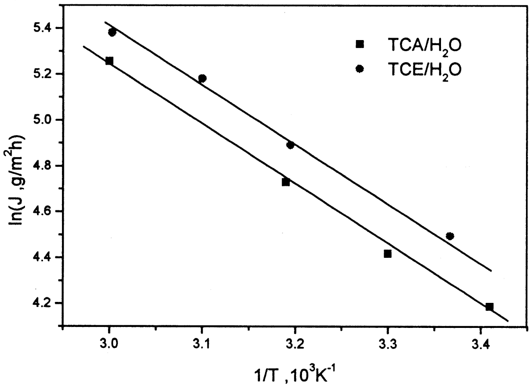


Figure 3. ln *J* vs. 1/T.

Membrane Structure

The cross-section structure of the poly(BA-AA-MMA)/PS composite membrane is shown in the scanning electron micrograph (SEM) (Fig. 4).

A typical asymmetric pore structure with a skin layer and underneath fingerlike cavities of the composite membrane can be seen. In fact, the membrane contains 2 layers, a homogenous unporous surface layer made of poly(BA-AA-

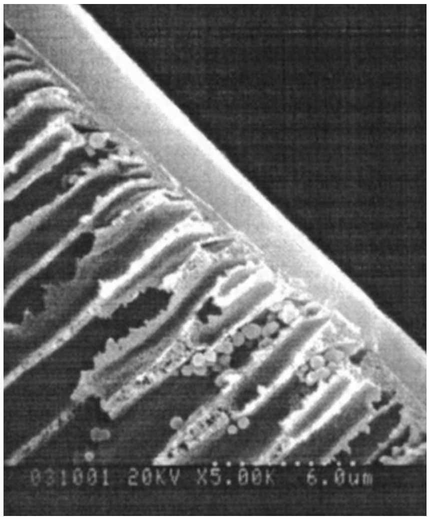


Figure 4. SEM picture of the poly(BA-AA-MMA)/PS composite membrane.

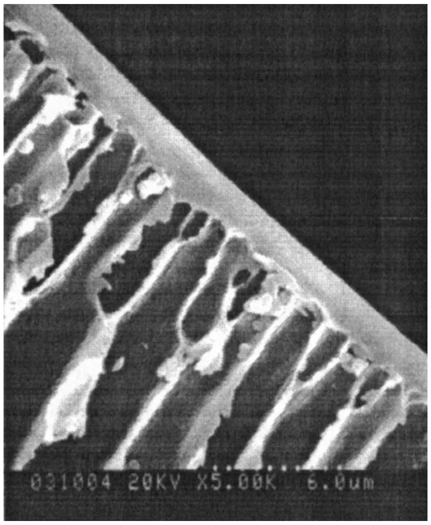


Figure 5. Cross-section of the support membrane (PS).

MMA) and a porous support made of PS. Figure 5 shows the cross-section of the support membrane (PS) only. No linking exists on the top layer of the membrane.

The joint of the top layer of the support and the linking coat is a compact and hydrophobic barrier that functions as an active layer for resisting water and transiting VOCs through the composite membrane.

CONCLUSIONS

1. Poly(BA-AA-MMA)/PS composite membranes with cross-linked structure show a high selectivity and permeation flux for removal of VOCs from water;
2. These composite membranes can be used at room or higher temperatures. Both permeation flux and selectivity for TCE and TCA increased with increasing temperature in our experiments. The separation factor reached 6000 while the flux achieved was 0.21 kg/m^{2}h when a TCE-water feed was used at 60°C.
3. SEM images of poly(BA-AA-MMA)/PS composite membranes identify that the support tightly integrates with the surface linking layer, which is a compact and homogenous hydrophobic polymer layer.
4. We believe that the removal of VOCs from water with pervaporation through the use of the poly(BA-AA-MMA)/PS composite membrane has good potential because of its low energy consumption and low membrane cost.

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