

# Preparation of a Water-Permselective Composite Membrane by the Concentrated Emulsion Method: Its Swelling and Permselectivity Characteristics

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## SYNOPSIS

A water-permselective composite membrane was prepared by the concentrated emulsion polymerization method. A large volume fraction of an aqueous sodium acrylate solution was dispersed in a small amount of divinyl benzene. Each of the two phases contained a suitable initiator and the continuous phase contained an appropriate surfactant. The concentrated emulsion thus obtained has the appearance and behavior of a gel. The gel was sandwiched between two glass plates and subjected to polymerization via heating at 45°C for 24 h. The resulting membrane was dried and further employed in several kinds of experiments. The swelling of the membrane in water depends on the pH of water and can be as large as 86. At low pH values, the swelling was very small. The permeation rate of a water-ethanol mixture was in the range of 96–560 g/m<sup>2</sup> h and decreased with increasing alcohol concentration and increasing poly(sodium acrylate) fraction in the membrane. The permselectivity varied between 32 and 235, increasing with increasing poly(sodium acrylate) fraction in the membrane and with increasing or decreasing ethanol concentration (depending upon the composition of the membrane). The activation energy for pervaporation varied between 6.58 and 8.14 kcal/mol, depending upon the composition of the feed. The permselectivity decreased slightly with increasing temperature.

## INTRODUCTION

Two types of membranes have been employed for the separation of water–alcohol mixture by pervaporation: the water and the ethanol-permselective membranes. In water-permselective membranes, hydrophilic groups such as vinyl alcohol, maleimide, and acrylic acid were mostly used as the permselective moieties. To prevent their dissolution in water, they were either crosslinked<sup>1,2</sup> or copolymerized with other monomers.<sup>3,4</sup> Membranes consisting of polyethylene films irradiation-grafted with acrylic acid,<sup>5</sup> or of polytetrafluorethylene (PTFE) films irradiation-grafted with *n*-vinyl pyrrolidone,<sup>6</sup> and, more recently, polypropylene films plasma-grafted with acrylic acid and acrylamide<sup>7</sup> have been reported.

A new kind of composite membranes prepared from concentrated emulsions has been developed

recently in this laboratory.<sup>8,9</sup> In a concentrated emulsion, the volume fraction of the dispersed phase is greater than 0.74 (which represents the volume fraction of the most compact arrangement of spheres of equal radius) and can be as large as 0.99. In this type of emulsion, which has the appearance of a gel, the dispersed phase is composed of polyhedral droplets separated among them by thin films of the continuous phase. Membranes prepared by the polymerization of concentrated emulsions have a large wt % of permselective moiety dispersed in the continuous phase, the latter ensuring the integrity of the membrane. In a previous paper, a composite membrane containing polyacrylamide as the dispersed phase and crosslinked polystyrene as the continuous phase, prepared by the concentrated emulsion method, exhibited high permselectivity to water from a water–ethanol mixture.<sup>10</sup>

In the present paper, another water-permselective membrane, also prepared via the concentrated emulsion method, is presented and its performance investigated. In this membrane poly(sodium

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acrylate) constitutes the dispersed phase and poly(divinyl benzene) the continuous phase. Sodium acrylate is selected because its ability to be ionized in water suggests a high permselectivity for water. Divinyl benzene was chosen as the continuous phase because it is insoluble in both components and because experiment has demonstrated that the concentrated emulsion prepared with divinyl benzene as the continuous phase leads to a better membrane than that in which styrene is the continuous phase. The swelling characteristics of this membrane as well as the rate of permeation and selectivity of the membrane in the separation of water from ethanol were investigated.

## EXPERIMENTAL

### Materials

The initiators azo bisisobutyronitrile (AIBN, Alfa Chemical Co.) and potassium persulfate ( $K_2S_2O_8$ , Aldrich Chemical Co.) were purified by recrystallization in methanol and water, respectively. Divinyl benzene and acrylic acid (Aldrich) were distilled under reduced pressure. Sorbitane monooleate (Span 80, Fluka), sodium hydroxide (97+%, Aldrich), and ethanol (HPLC grade, Aldrich) were used as received. Water was deionized and distilled.

### Preparation of the Concentrated Emulsion

A small amount of divinyl benzene containing sorbitane monooleate and AIBN was placed in a round-bottom flask (100 mL capacity) equipped with a mechanical stirrer and an addition funnel. An aqueous solution of sodium acrylate prepared by titrating acrylic acid with a solution of sodium hydroxide to a pH slightly above 7 was introduced in the addition funnel, and a potassium persulfate solution in water was added as initiator. The concentrated emulsions were prepared at room temperature by the dropwise addition of the sodium acrylate solution to the stirred divinyl benzene mixture. The addition process lasted about 25 min. Three sets of amounts (M1, M2, and M3) of the components involved are listed in Table I.

### Preparation of the Membrane

The concentrated emulsions were transferred into a syringe (10 mL capacity) for M1, M2, or a test tube (15 mL capacity) for the less viscous M3. Different centrifugation conditions, dependent upon the viscosity of the concentrated emulsion, were em-

**Table I** Amounts of Components Used in the Preparation of the Concentrated Emulsion

	M1	M2	M3
Dispersed phase			
Aqueous solution of sodium acrylate	30 g	30 g	30 g
	(containing 8 g acrylic acid)		
Initiator ( $K_2S_2O_8$ )	$1.7 \times 10^{-4}$ g/g of acrylic acid for all emulsions		
Continuous phase			
Divinyl benzene	2 g	4 g	6 g
Initiator (AIBN)	$2.0 \times 10^{-4}$ g/g of monomer for all emulsions		
Surfactant (sorbitane monooleate)	1 g	1 g	1 g

ployed to eliminate the minute air bubbles (M3: 1800 rpm, 30 s; M2: 2000 rpm, 5 min; M1: 2500 rpm, 10 min). Two well-cleaned and dried glass plates (10 × 15 cm) were used to prepare the membrane. A small amount of glycerol was placed as a lubricant on the surface of the glass plates. The packed concentrated emulsions were located between the two glass plates and squeezed slowly to avoid trapping air bubbles. For polymerization to occur, the glass plates sandwiching the concentrated emulsion were placed in a temperature-controlled oven at 45°C for 24 h. After preparation, the membranes were dried at the relatively low temperature of 45°C in an oven under vacuum for 24 h. The drying temperature of 45°C was selected in order to prevent crosslinking in the dispersed phase. The membranes employed in the experiments involving low concentrations of ethanol (25 wt %), for which the swelling is very large, were additionally dried at 70°C for 12 h in order to achieve some crosslinking and thus to avoid the dissolution of the dispersed phase. The thickness of the membrane was 0.15–0.20 mm. The membrane was brittle at room temperature and in dry air; it became softer and elastic in a high-humidity environment.

### The Swelling Test

The change in weight of the membrane produced by swelling was determined as follows: Membrane strips of about 0.5 g were placed in flasks filled with different mixtures of ethanol and water. After different periods of time, the weight was determined. The

swollen membrane was then dried in an oven to determine the weight of the dried membrane. The swelling of the membrane is defined as

$$S = \frac{W_s - W_0}{W_0}$$

where  $W_0$  and  $W_s$  represent the weights of the dry and swollen membrane, respectively.

### Pervaporation Experiments

Pervaporation studies of water-ethanol mixtures were carried out by employing the apparatus used in a previous paper.<sup>9</sup> The upper compartment of the pervaporation cell had a capacity of 250 mL, and the membrane area in contact with the feed solution was of about 9 cm<sup>2</sup>. The membranes were swollen (for 60 min in the mixtures with more than 50 wt % ethanol concentration because for them  $S$  is lower, and for 15 min in the mixtures with less than 50 wt % concentration because for them  $S$  is relatively high) before being inserted into the pervaporation cell. The permeated vapor was collected in a liquid-nitrogen cold trap after 5 h of running the apparatus at room temperature. This blank run was carried out to ensure the complete removal of the water-ethanol mixture soaked during the initial swelling, in the lower part of the membrane, which otherwise will be evacuated to the cold trap. During the experiments, the portion of the membrane which does not contact the feed solution contracted, because of drying. Experiments were conducted at room temperature (23°C) and also between 30 and 50°C in order to investigate the temperature dependence. The products were analyzed with a gas chromatograph (Varian 3700), equipped with a Porapak T column (Alltech) heated at 150°C. The permselectivity  $\alpha$  is defined by the relation

$$\alpha = \frac{X_W/X_E}{Y_W/Y_E}$$

where  $X_W$  and  $X_E$  represent the weight fractions of water and ethanol in the permeate and  $Y_W$  and  $Y_E$  those in the feed, respectively.

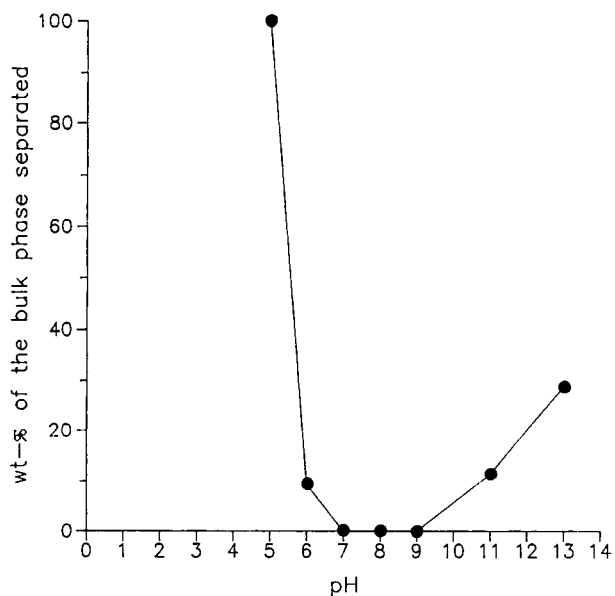
## RESULTS AND DISCUSSION

Before discussing the results obtained concerning the performance of the membrane, it is important

to examine the stability of the concentrated emulsions from which the membranes were prepared. Acrylic acid was the monomer selected as the dispersed phase of the emulsion. Neither this monomer alone nor its aqueous solution could lead to concentrated emulsions with divinyl benzene as the continuous phase. However, if the aqueous solution of acrylic acid was treated with an appropriate amount of sodium hydroxide, it could generate a concentrated emulsion with divinyl benzene. Experiment has shown that a concentrated emulsion with the composition M1 forms at room temperature for pH > 5. The stability of the formed concentrated emulsion, expressed as wt % of bulk phases separated from the concentrated emulsion during heating for 24 h at 60°C, is plotted against pH in Figure 1, which shows that the most stable concentrated emulsions lie in the pH range 7–9. The partial phase separation beyond pH 9 is probably due to the hydrolysis of the surfactant by the alkali (the surfactant sorbitane monooleate being an ester).

### The Swelling Test

The polymerized sodium acrylate is a polyelectrolyte. High swelling of the membrane in water is therefore expected to occur. Indeed, membrane (M1)



**Figure 1** Weight percent of the bulk phases separated from the concentrated emulsion (M1), in the absence of initiators, after heating for 24 h, at 60°C in a water bath, as a function of the pH of the aqueous solution of acrylic acid.

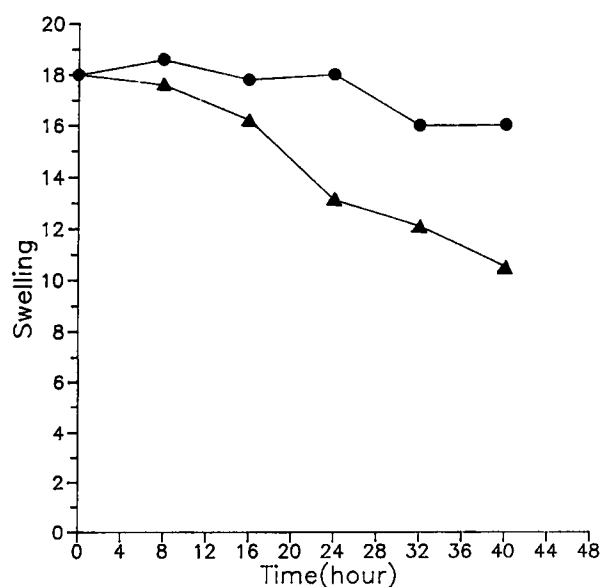
**Table II** The Swelling of Membranes M1, M2, and M3 at Various Concentrations of Ethanol (wt %)<sup>a</sup>

Ethanol (wt %)	0	25	50	75
M1	18.0	1.60	1.17	0.78
M2	19.6	1.56	1.14	0.76
M3	22.2	1.49	1.10	0.71

<sup>a</sup> Time of swelling was 10 min for 0%; 0.5 h for 25%; and 24 h for 50 and 75%.

has swollen 86-fold in water after soaking for 24 h. The swelling was so high that the membrane had lost its mechanical strength. To avoid this, the swelling test was carried out for short times at low-ethanol concentrations. Table II summarizes some results. The swelling decreases rapidly as the concentration of ethanol increases in the mixture.

Two other swelling characteristics of the membranes were also investigated. Sodium acrylate molecules crosslink among themselves at higher temperatures. The drying of the membrane in the oven promotes some crosslinking in the dispersed phase and this can affect the swelling behavior. Figure 2 depicts the dependence of the swelling of membrane M1 on the drying time and temperature when the membrane was dried in an oven under vacuum. Although there was little difference in swelling after the membrane was dried at 45°C, the drying at 70°C



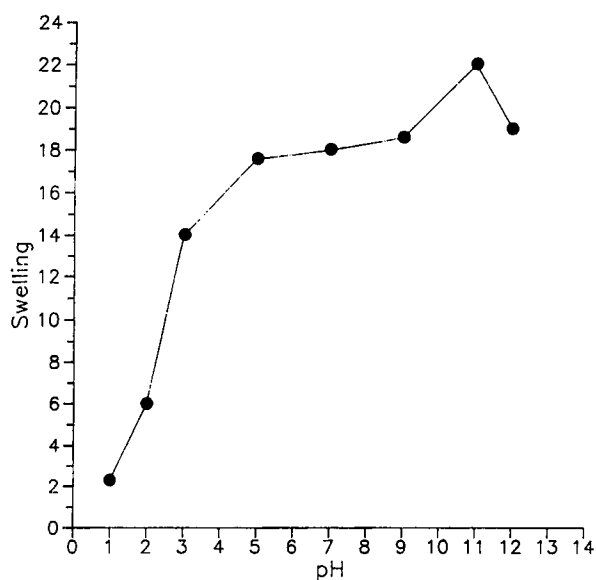
**Figure 2** Swelling of membrane M1 as a function of the drying time in an oven under vacuum at 45°C (●) and 75°C (▲) (time of swelling = 10 min).

was expected to reduce swelling because of the crosslinking of the sodium acrylate. This was indeed observed. It was also noted that the membrane dried at 70°C was translucent compared to the milky white appearance of the membrane dried at 45°C. It should be noted that extended drying at 70°C decreased the mechanical strength of the membrane.

Further, in Figure 3 the dependence of the swelling of membrane M1 on the pH of water is plotted. The swelling of this membrane is small below pH 2, a range in which the poly(sodium acrylate) is transformed to poly(acrylic acid). The difference in the swelling behavior between poly(sodium acrylate) and poly(acrylic acid) is a result of their different affinities for water.

### Pervaporation Experiments

The membranes prepared via the concentrated emulsion pathway are dense (nonporous) and relatively thick. Those prepared by solvent casting are also dense but much thinner. A dense and thicker membrane is expected to have a higher permselectivity and a lower permeation rate. However, the larger wt % of the permselective moiety (dispersed phase) in the membrane offsets at least partially the disadvantages caused by their greater thickness. Table III summarizes the permeation rate and permselectivity at various ethanol concentrations, at room temperature, for the membranes M1, M2, and M3.



**Figure 3** The swelling of membrane M1 against the pH of water (time of swelling = 10 min).

**Table III Permeation Rate and Permselectivity of the Membranes**

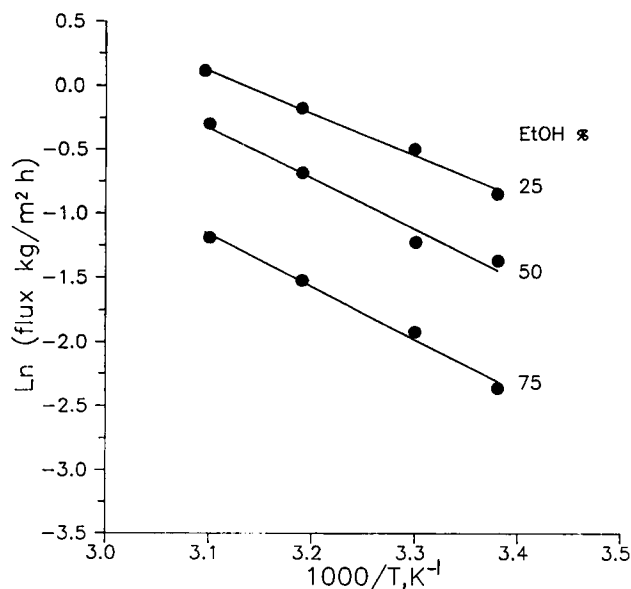
Ethanol (wt %)	Permeation Rate (kg/m <sup>2</sup> h)			Permselectivity $\alpha$		
	25	50	75	25	50	75
M1	0.43	0.26	0.094	65	78	235
M2	0.54	0.33	0.111	50	60	78
M3	0.56	0.34	0.111	42	40	32

The permeation rate decreases as the ethanol concentration in the feed increases. This constitutes a common characteristic of the water-permselective membranes. The permeation rate decreases as the poly(sodium acrylate) fraction increases in the membrane. A possible explanation is that micropores form in the membranes with a higher continuous phase content. During the drying of the membranes, the dispersed phase contracts because of the loss of water. However, compared to membrane M1 which shrinks considerably, membranes M2 and M3 change much less because of the larger fraction of the rigid continuous phase in these membranes. The micropores are, thus, responsible for the higher permeation rate in membranes M2 and M3. One can see from Table III that the permselectivity is not much decreased by the pores, especially in the low-ethanol concentration range.

The temperature dependence of pervaporation for membrane M1 in the range of 30–50°C is presented in Table IV. Naturally, the permeation rate increases with the temperature of the feed. The permselectivity becomes only slightly smaller when the temperature increases. An Arrhenius relationship exists between the permeation rate and temperature (Fig. 4), and the activation energy is 6.58, 7.91, and 8.14

**Table IV Temperature Dependence of Permeation Rate and Permselectivity for Membrane M1**

Ethanol (wt %)	Permeation Rate (kg/m <sup>2</sup> h)			Permselectivity $\alpha$		
	25	50	75	25	50	75
30°C	0.61	0.29	0.14	64	70	222
40°C	0.83	0.50	0.22	60	72	222
50°C	1.11	0.74	0.30	60	62	172

**Figure 4** Arrhenius plots of the permeation rate through membrane M1.

kcal/mol for the 25, 50, and 75 wt % ethanol concentrations, respectively.

One final comment: Even though the use of divinyl benzene as the continuous phase ensures the stability of the concentrated emulsion, the resulting polymeric membrane, which contains poly(sodium acrylate) as the dispersed phase, is brittle in dry air. The membrane becomes much softer and even somewhat elastic in ethanol–water mixtures due to the strong solvation of the dispersed phase by water. One possible pathway to prepare a more elastic membrane is to select a monomer for the continuous phase whose hydrophobicity ensures the stability of the concentrated emulsion, but whose resulting polymer has a sufficiently low glass transition temperature to improve the mechanical properties of the membrane. Sodium acrylate having a high affinity for water is still the favorite monomer for the dispersed phase.

## CONCLUSION

A water-permselective membrane, prepared by the concentrated emulsion polymerization method, and containing poly(sodium acrylate) as the dispersed phase and poly(divinyl benzene) as the continuous phase, exhibits high permselectivity to water because of the ionic groups of poly(sodium acrylate) in the membrane.

The swelling behavior of this membrane depends on the pH of water and is affected by the extent of crosslinking of the dispersed phase caused by the drying at high temperatures. The permeation rate through the membrane is in the range of 96–560 g/m<sup>2</sup> h and depends on the ethanol concentration in the mixture and on the composition of the membrane. The permselectivity is between 32 and 235, depending on the compositions of the mixture and membrane. The permeation rate is temperature-sensitive (the activation energy is between 6.58 and 8.14 kcal/mol); however, the permselectivity only slightly decreases with increasing temperature.

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