

Pervaporation Characteristics and Solution–Diffusion Behaviors Through Sodium Alginate Dense Membrane

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SYNOPSIS

A sodium alginate dense membrane was prepared for water-selective separation by pervaporation (PV). In this study, alcohols and other organic liquids such as THF, 1,4-dioxane, and acetone were dehydrated through a membrane made of this polyelectrolyte. By changing the operating conditions, including feed concentration and temperature, the PV characteristics were investigated in detail. The results demonstrate that sodium alginate was an exceptional membrane material with large values of both flux and selectivity. Furthermore, the pervaporation mechanism was elucidated by making an investigation into the solution–diffusion behaviors of penetrants. It was found that the solution process makes much more of a contribution on permselectivity than does the diffusion step.

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INTRODUCTION

Sodium alginate is a membrane material with potential application in dehydrating organic aqueous solutions. As known, its performances exceed those of poly(vinyl alcohol) (PVA),¹ ion-exchange resins,² and some other polysaccharides with similar chemical structure such as chitosan³ and cellulose.⁴ It stands to reason that sodium alginate is a prospective membrane material that can be applied in treating expensive organic solvents, e.g., THF, dioxane, and glycerin, that have many needs and are of great economic value for medical and agrochemical industries. A series of organic liquid/water mixtures is herein employed to understand the definite relationship between properties and structures and the influence of some other factors as well. The mechanism of the pervaporation (PV) process was studied by carefully comparing characteristics of feed mixtures (such as molecular size and solubility parameters) and checking the diffusion and solution behaviors.

THEORETICAL TREATMENT

In Lee's opinion, the mass transfer of a binary liquid mixture through a nonporous dense membrane is generally described by the diffusion–solution mechanism.⁵ Penetrant migration is controlled by diffusion since a fast distribution equilibrium can be established between the bulk feed and the upstream surface of a membrane.^{6–8} The local diffusion rate, J_i , of penetrant i in a membrane can generally be depicted by Fick's first law. Under steady-state conditions, this law takes the following form for one-dimensional diffusion:

$$J_i = D_i(C_{i,m}) \frac{dC_{i,m}}{dz} \quad (1)$$

where D_i , strongly influenced by the concentration, is the local mutual diffusion coefficient of the penetrant/polymer system. Due to the immobilization of the membrane, D_i can be regarded as the self-diffusion coefficient. $C_{i,m}$ is the local penetrant concentration in the membrane at the position of coordinate z . J_i is taken per unit of cross-sectional area of a membrane.

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For a planar membrane, the permeation rate is achieved by integrating eq. (1) from upstream to downstream across the membrane:

$$Q_i = \int_0^\delta J_i dz = \int_{C_{i,p,m}}^{C_{i,f,m}} D_i(C_{i,m}) dC_{i,m} \quad (2)$$

where $C_{i,f,m}$ (g/cm^3) and $C_{i,p,m}$ are the weight concentration of component i at the membrane surfaces of the feed side (f) and the permeate side (p), respectively. Q_i ($\text{g m}/\text{m}^2 \text{h}$) is the specific permeation rate of component i . Since the concentration dependence of D_i is often not known, it is convenient to define a mean diffusion coefficient \bar{D}_i with the following relation:

$$\bar{D}_i = \int_{C_{i,p,m}}^{C_{i,f,m}} D_i(C_{i,m}) dC_{i,m} / (C_{i,f,m} - C_{i,p,m}) \quad (3)$$

Under steady-state conditions (J_i is constant),

$$Q_i = J_i \delta = \bar{D}_i (C_{i,f,m} - C_{i,p,m}) \quad (4)$$

Because of the low downstream pressure,

$$\begin{aligned} C_{i,p,m} &\approx 0 \\ C_{i,p} &\approx 0 \end{aligned} \quad (5)$$

We can approximately estimate the mean values of the self-diffusion coefficient:

$$\bar{D}_i = \frac{J_i \delta}{C_{i,f,m}} \quad (6)$$

The mean permeate coefficient is defined as follows:

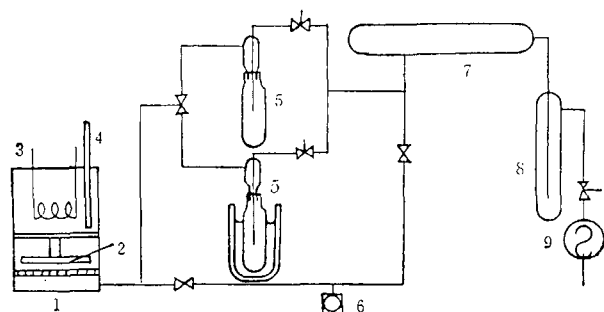


Figure 1 Schematic diagram of PV apparatus: (1) permeate cell; (2) stirrer; (3) heater; (4) thermometer; (5) permeate collector; (6) vacuumeter; (7) tube for safety; (8) cold trap; (9) vacuum pump.

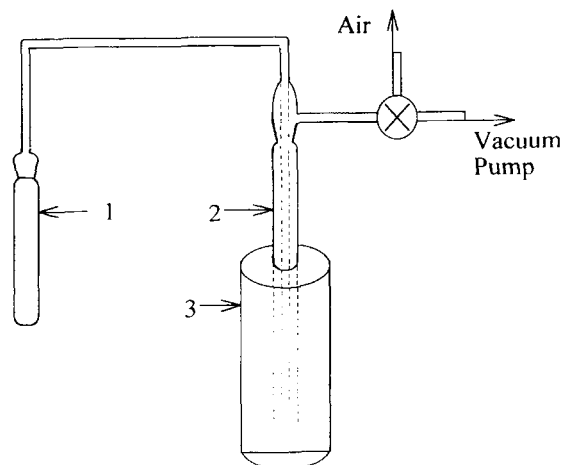


Figure 2 Schematic apparatus for equilibrium composition measurement of penetrants in the membrane: (1) heating tube; (2) collecting tube; (3) cold trap.

$$\bar{P}_i = \frac{Q_i}{C_{i,f} - C_{i,p}} \approx \frac{Q_i}{C_{i,f}} = \frac{J_i \delta}{C_{i,f}} \quad (7)$$

By defining a mean distribution coefficient as the following expression:

$$\bar{K}_i = \frac{C_{i,f,m}}{C_{i,f}} \quad (8)$$

and combining eqs. (6) and (8), we simplify expression (7) into

$$\bar{P}_i = \bar{D}_i \bar{K}_i \quad (9)$$

If the vapor pressure difference is used to substitute the liquid concentration difference as the driving force of the permeation,⁹ it is possible to describe the dependence of P_i , D_i , and K_i on the temperature with the Arrhenius formula to some degree in a short range of temperature:

$$\begin{aligned} P_i &= P_{i,0} \exp(-E_p/RT) \\ D_i &= D_{i,0} \exp(-E_d/RT) \\ K_i &= K_{i,0} \exp(-\Delta H_s/RT) \end{aligned} \quad (10)$$

Hence,

$$E_p = E_d + \Delta H_s \quad (11)$$

E_p and E_d are the apparent activation energy relevant to the total permeation and diffusion process and ΔH_s is the corresponding heat of solution. $P_{i,0}$, $D_{i,0}$, and $K_{i,0}$ are constants, R is the universal gas

Table I Effect of Water Content in Feed on $\alpha_{w/org}$. Through the Sodium Alginate Membrane

Water Content in Feed (Wt %)	Ethanol/Water ^a		THF/Water ^a		1,4-Dioxane/Water ^a	
	Q^b	$\alpha_{w/e}$	Q	$\alpha_{w/t}$	Q	$\alpha_{w/d}$
5	45	931	900	∞	763	1898
10	183	∞	1433	∞	1502	4491
15	286	∞	1926	∞	2465	11,327
20	703	∞	2489	∞	2862	39,996

^a Operating temperature was 70, 55, and 60°C for the ethanol/water, THF/water, and 1,4-dioxane/water solutions, respectively.

^b Q : g/m² h.

constant, and T means the absolute temperature. The permselectivity is defined below¹⁰:

$$\alpha_{i/j} = \frac{P_i}{P_j} = \frac{D_i K_i}{D_j K_j} = S_d S_k \quad (12)$$

Here,

$$S_d = \frac{D_i}{D_j}$$

$$S_k = \frac{K_i}{K_j} \quad (13)$$

S_k implies the relative affinity of penetrants to polymer, and S_d reflects the relative ability of penetrants to pass through a membrane by diffusion:

$$\text{Swelling degree} = \frac{W_2 - W_1}{W_1} \times 100\% \quad (14)$$

where W_2 is the weight of the swelling polymer (g), and W_1 , the weight of the dry polymer (g).

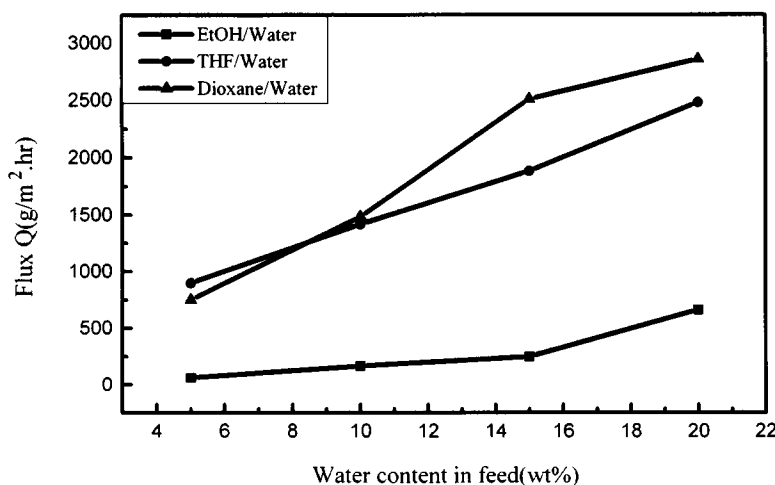
EXPERIMENTAL

Membrane Preparation

Membrane material was supplied by Kimitsu Chemical Industries, Japan. The sodium alginate was an M (homopolymeric block of D-mannuronic acid)-rich polymer. An aqueous solution, 2.0 wt %, was cast onto a glass plate after being filtered and degassed and then dried at room temperature for 48 h. The membrane thickness was 20 μm .

PV Measurement

The pervaporation mode is sketched in Figure 1. A membrane with 25 cm² of the PV area was laid on a metal-support porous plate and then sealed with a rubber ring. At the downstream side, a vacuum pump was used to maintain a low pressure less than 200 Pa. At the liquid nitrogen temperature, the permeate vapor was collected in a trap. The composition was determined by a GC-8810 gas chromatograph (Kechuan Instruments Ltd., Shanghai).


Figure 3 Concentration dependence of flux through sodium alginate dense membrane.

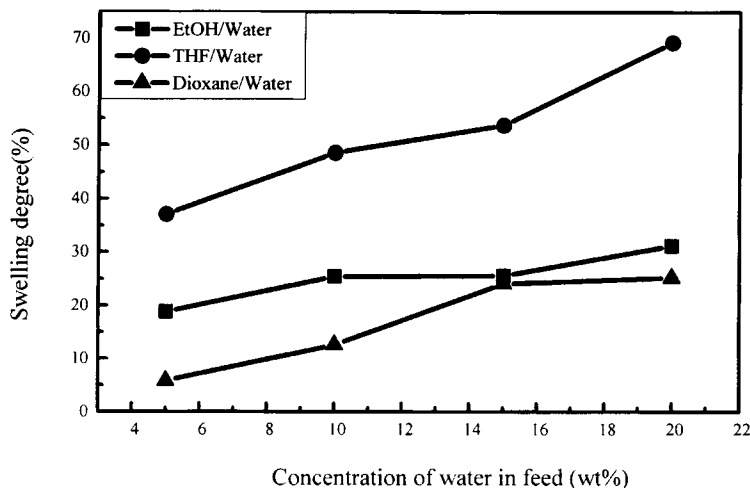


Figure 4 Effect of water content on swollen properties of membrane. (operating temperature is 70, 55, and 60°C for ethanol/water, THF/water, and 1,4-dioxane/water, respectively).

Determination of Swelling Degree and Equilibrium Composition of Mixtures in the Membrane

The apparatus determining the equilibrium composition in a membrane was designed as in Figure 2. The whole system was sealed with organic silicone grease and then kept in an isolated vacuum. A membrane sample (70 × 20 mm) was immersed into the feed for 6 h to reach an equilibrium state, and then the swollen membrane was taken out and weighed quickly after the liquid remaining on the membrane surface was absorbed carefully with filter paper. The components were extracted from the membrane

which was put into the left tube and heated and then condensed in the right tube cooled with liquid nitrogen. After that, the dried membrane was also weighed to obtain the values of the swelling degree according to expression (14).

RESULTS AND DISCUSSION

Effect of Water Content in Feed

The change of PV characteristics against water content (C_w) is shown in Table I and Figure 3 as well. As an ionic polymer, sodium alginate is water-

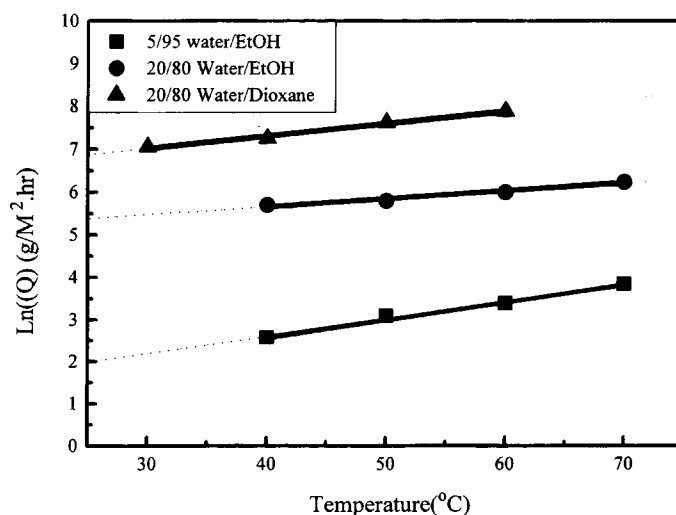


Figure 5 Dependence of flux on operating temperature through sodium alginate dense membrane.

Table II Dependence of Separation Factor on Temperature

Temp (°C)	20/80 Ethanol/Water	5/95 THF/water	20/80 1,4-Dioxane/Water
	$\alpha_{w/e}$	$\alpha_{w/t}$	$\alpha_{w/d}$
70	∞	981	—
60	∞	970	39,996
50	∞	975	13,000
40	∞	1019	7996
30	—	—	1996

soluble, so the water content in the feed should not exceed 50 wt % in the experiments or the membrane will resolve into the feed. The flux complies with the typical ascendance while increasing the water content in the feed, regardless of separating ethanol/water, THF/water, or 1,4-dioxane/water mixtures. As for the separation factor, its very high values are interesting. Furthermore, it does not show any descendent. In contrast, the selectivity increases and even approaches ∞ when water concentration in feed increases. For the water/ethanol solution ($C_w > 10\%$), herein, the permeate concentration of ethanol is so low (<0.01 wt %) that it is beyond the discernibility of the gas chromatograph and, hence, is considered to be ∞ ($>50,000$) in a mathematical treatment.

Conformations of polymer molecular chains change successively by the thermal motion, resulting in the fluctuation of the occupation volume of the chains and the formation of "holes," which are effective transport channels allowing the small molecules to permeate easily. The "holes" size will fluctuate with the conformation change driven by ionic repulsion and stereo hindrance.¹¹ Since swelling capacity often implies the expandability of the free volume, its marked increase means the expansion of the free volume and the "holes" size, and then components can permeate fast. In Figure 4, values of the swelling degree are cited to explain the dif-

ference of flux. For example, a feed containing 5 wt % water swells a membrane poorly; therefore, the permeation is slow. While the feed concentration of water increases, the swelling degree ascends, accompanied by increase of the flux. For different feed mixtures, due to different properties of organic solvents such as the molecular size, solubility parameter, and the variation of operating temperature, there is no comparability between them. Considering the complication of the concentration effect, it is not easy to give a concise expression to depict this phenomenon.

Effect of Operating Temperature

The dependence of the flux of water on the operating temperature (the flux of organic solvent is too low to be noticed when compared with that of water) can be expressed by an Arrhenius equation. As plotted in Figure 5, the apparent activation energy of the permeation is found to be 17.7 kJ/mol for water in a 20/80 water/ethanol mixture, 34.1 kJ/mol in a 5/95 water/ethanol solution, and 27.9 kJ/mol in a 20/80 water/1,4-dioxane mixture. The membrane shows a higher permeate flux of the feed containing dioxane than that of ethanol; it is not suitable to use swelling properties to explain this, since there is no apparent difference between these values. However, the diffusion coefficient of the components

Table III PV Characteristics of Sodium Alginate Membrane Used for Separating Organic Liquid/Water Mixtures

Organic Solvent	Temp (°C)	Q (g/m ² h)	$\alpha_{w/e}$	Molecular Size (Å ³)	δh (MPa ^{1/2})
MeOH	60	163	567	67.60	22.3
EtOH	60	436	∞	97.12	19.4
iso-PrOH	70	2970	∞	127.6	16.4
Acetone	50	2105	∞	122.9	7.0
Water	—	—	—	29.9	42.3

Water content in the feed was 20 wt % for all feed mixtures.

Table IV Effect of Temperature on Distribution Selectivity and Diffusion Selectivity

Temp (°C)	20/80 (H ₂ O/EtOH)		20/80 (H ₂ O/Dioxane)	
	<i>Sk</i>	<i>Sd</i>	<i>Sk</i>	<i>Sd</i>
70	23,000	1.7	—	—
60	8600	4.5	7999	5.0
50	1800	22	3939	3.3
40	770	50	2665	3.0
30	—	—	998	2.0

may bring about the distinction, as will be illustrated below.

For ethanol aqueous solutions (including $C_w = 5\%$ and 20%), there is no marked variation of the separation factor; However, dioxane/water mixtures show great variation against operating temperature, i.e., when temperature increases from 30 to 60°C, the separation factor increases quickly from 1996 to 39,996, as shown in Table II.

Effect of Properties of Feed on PV Characteristics

Since δh reflects the ability of combination through hydrogen bonds between two compounds, a high value of δh represents good affinity of the component to the ionic polymer and brings about at least dual effects. On the one hand, it increases the distribution coefficient of components from the feed into the membranes; On the other hand, it causes a strong coupling effect during mass migration.¹² The former will make a high distribution selectivity of water

toward organic compounds, and the latter induces low diffusion selectivity. Since there are more opportunities existing to form polymer-water-organic multimolecule groups in strong coupling effect systems, it also results in low flux. For example, the δh of methanol is the highest among alcohols and acetone in Table III then, low flux and low selectivity are expected. Of course, this does not repulse the active effect of molecular size on selectivity, but this effect is somewhat limited in the case. The permeate rate decreases according to the augmentation of carbon numbers of organic liquids, which actually reflects the variation of δh to some degree.

Solution and Diffusion

In terms of the permeation mechanism, the permeate process can be separated into three steps: first, solution of feed at the upstream surface of a membrane; second, diffusion of penetrants in the membrane; and last, desorption of penetrants from the

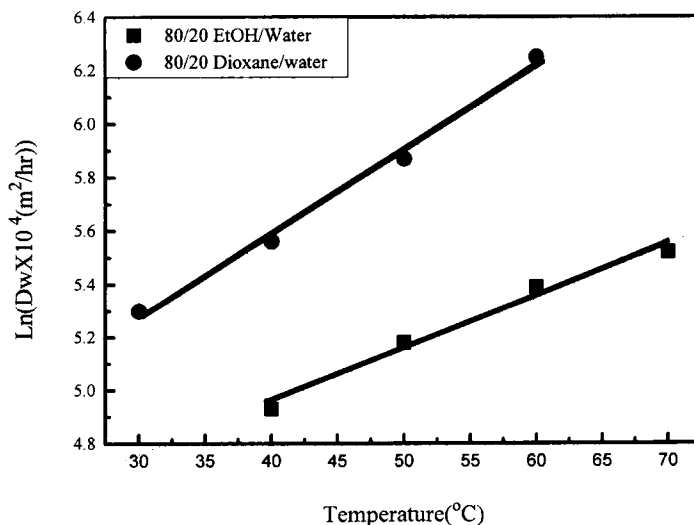
**Figure 6** Effect of temperature on diffusion coefficient of water (D_w) in membranes.

Table V Distribution Coefficients of Components and Swelling Degree Versus Temperature

Temp (°C)	20/80 (H ₂ O/EtOH)			20/80 (H ₂ O/Dioxane)		
	<i>Ke</i> (×10 ⁴)	<i>Kw</i>	<i>Sw</i>	<i>Ke</i> (×10 ⁴)	<i>Kw</i>	<i>Sw</i>
70	2.1	4.9	31.0	—	—	—
60	5.7	4.9	30.0	6.3	5.0	28.0
50	28	4.9	30.0	13	5.0	29.0
40	50	4.9	29.0	19	4.9	29.0
30	—	—	—	50	4.9	30.0

downstream surface of a membrane into a reduced vacuum. In the present discussion, the third step has no significant effect on mass transfer owing to a very low concentration of both penetrants. As proposed above, the separation factor can be divided into distribution selectivity (*Sk*) and diffusion selectivity (*Sd*). In this case, *Sk* is so high that *Sd* can be neglected as shown in Table IV, namely, diffusion makes little contribution on permselectivity.

The heat of the solution for the ethanol aqueous mixture is 0.66 kJ/mol, and for the dioxane/water mixture, 2.68 kJ/mol; these low values indicate that there is a fast establishment of mass balance between the feed and the membrane in the kinetics, so that the PV process is carried out under equilibrium¹³ but with a nonequilibrium mechanism. The activation energy of diffusion, as inferred below, is much higher than ΔH_s ; therefore, diffusion controls the permeation process. This coincides with the properties of glassy polymers.

At the upstream, water is condensed too high to consider the content of organic liquids, so the diffusion process primarily involves water. Although there are some disadvantages caused by organic molecules themselves on diffusion through the membrane, their effects can be neglected due to their low enrichment at the upstream surface of the membrane, which leads to a low driving force for organic liquid transport over a membrane. In fact, the permeation rate of water is much higher than that of ethanol. Therefore, increasing *Cw* in the feed to some extent induces the expansion of the free volume and "holes" size and just makes more water permeate through a membrane.

As shown in Figure 6, the dependence of the diffusion coefficient of water on temperature conforms to the Arrhenius relation. Values of \bar{D}_w (mean diffusion coefficient of water) increase at an exponential magnitude with increasing temperature. The apparent activation energy of the diffusion for water in the dioxane/water solution is 25.22 kJ/mol. In

the ethanol/water mixture, the value is 17.04 kJ/mol. \bar{D}_w in the ethanol solution is less than that in the dioxane/water system; this means that water more easily passes through the membrane in the latter than in the former. As temperature increases, the distribution coefficient of water (*Kw*) remains constant as shown in Table V, causing no perceptible change in the swelling degree; hence, it is reasonable to believe that the increase of the flux should only be attributed to the augmentation of \bar{D}_w . This explains the relative higher values of flux for the dehydration of dioxane depicted in Table II.

CONCLUSION

A dense membrane made from sodium alginate was prepared, and organic liquid/water solutions (such as alcohols, THF, and 1,4-dioxane) were used to characterize PV performances. Moreover, a mass-transfer mechanism was attempted to elucidate the results of diffusion and distribution.

1. Permeate rate increases as the concentration of water in feed increases; this mainly includes the contribution of both increase of the swelling degree, which conduces to the expansion of the free volume, and the active effect of the diffusion coefficient of water through a membrane. However, as concerns the influence of temperature on flux, the free volume has little distinction in the whole range of temperature; the variation of the flux mostly comes from the increasing diffusion coefficient caused only by temperature.
2. A high separation factor is determined mainly by high distribution selectivity; the diffusion process makes a quite small positive contribution on it.
3. The δh of various organic liquids influences both the permselectivity and flux, and a high

δh is disadvantageous to the PV characteristics.

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