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Transport Phenomena of Chitosan Membrane in Pervaporation of Water–Ethanol Mixture

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ABSTRACT

The pervaporation transport process of H_2O–EtOH solution was studied on a chitosan membrane and on a H_2SO_4 crosslinked chitosan membrane. The influence of concentration, temperature, and crosslinking was also studied. The dependence of permeation fluxes on feed concentration showed strong coupling effects existed in the permeation process. That the thermodynamic swelling–distribution relationship changed with the feed concentration also showed that a strong coupling effect existed in the thermodynamic swelling process. The permeation fluxes and thermodynamic swelling processes showed analogous relationships versus the concentration in the feed. The high swelling ratio and the high selectivity of the membrane in the thermodynamic swelling distribution process was the basis of high flux and high permselectivity of pervaporation. With an increase of temperature, the permeation fluxes increased quickly, but the swelling ratio of water and EtOH in the membrane scarcely changed. This showed that an increase of temperature promoted the diffusion process but had little influence on permselectivity. The permselectivity of pervaporation depended strongly on the thermodynamic swelling process.

Key Words. Pervaporation; Chitosan membrane; H_2SO_4 crosslinking chitosan membrane; Water–ethanol mixture; Membrane separation; Temperature; Thermodynamic swelling process; Transport phenomena

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INTRODUCTION

Since pervaporation was first studied by Binning et al. (1), much work has been done in understanding the phenomenon of pervaporation (2–4). In pervaporation a liquid mixture contracts one side of a membrane and the permeate is removed as a vapor from the other side. Permeation through the membrane is induced by maintaining the vapor pressure on the permeate side lower than that on the feed side (5). Pervaporation is now recognized as an effective process for separating azeotropic mixtures, close-boiling point compounds, and heat-sensitive compounds (6). Because of the commercial applications of this new technique, it is important to study the transport phenomena in pervaporation.

The description of transport phenomena in the pervaporation process is quite complicated. According to the interaction between components and polymer transport processes in a dense membrane can be divided into three aspects: I, ideal transport process (such as H_2/N_2 separation); II, weak interaction transport process (such as organic gas separation); and III, strong interaction transport process (such as pervaporation). For the ideal transport process, the interaction between components and polymers is not considered. The sorption of low molecular weight penetrants is typically described by Henry's law and the diffusion coefficient is also a constant. The selectivity of a membrane can be known from the pure component's permeation experiments because one component cannot affect the other component's transport. For the weak interaction transport process, the sorption of penetrants cannot be described by Henry's law because of the interaction between polymer and components, the transport characteristic of one component changes with the nature of the other component. Some theories, such as the Dual-Mode Model (7), can describe this kind of transport process.

According to solution-diffusion, Dual-Mode Model, and plasticizing effect, the ideal transport process and the weak interaction transport process can be successfully described. Transport phenomena in pervaporation is not completely understood compared with gas separation because of the strong coupling effects in the thermodynamic swelling process and the diffusion process.

With the development of membrane materials for pervaporation, various polyion membranes (8, 9) have been prepared, and high separation factors and high fluxes have been obtained. Representatives of this kind of polyion membrane are chitosan and its derivative membranes (10–12, 16). How to describe their high separation factor and high flux is becoming more and more significant.

For a pervaporation membrane with a high separation factor, there exist strong interaction between polymer and components, especially in the thermodynamic swelling process. How to describe the strong coupling effect in the thermodynamic swelling process and the diffusion process is also essential to the pervaporation separation process (13–15).

Figure 1 describes the transport process of pervaporation in a ternary phase diagram. *A* and *A′* are the concentrations of the components in the feed and in the permeate. Two ways are used to study the transport process in pervaporation. 1) The membrane is considered to be a "black box" and the transport characteristics inside the membrane are not studied; this is usually called the permeation process. According to studies of the permeation process, the total transport phenomena can be understood and the total transport characteristics can be found. 2) The transport process is divided into three parts as shown in Fig. 1:

1. The thermodynamic swelling process mainly describes the relationship between thermodynamic swelling curve *OO′* and feed composition.
2. The transport process mainly describes the components' composition distribution along the membrane thickness. The shape of the transport curve displays the influence of diffusion coupling.
3. The desorption process. Because the permeation pressure is very low, study of the desorption process is usually neglected.

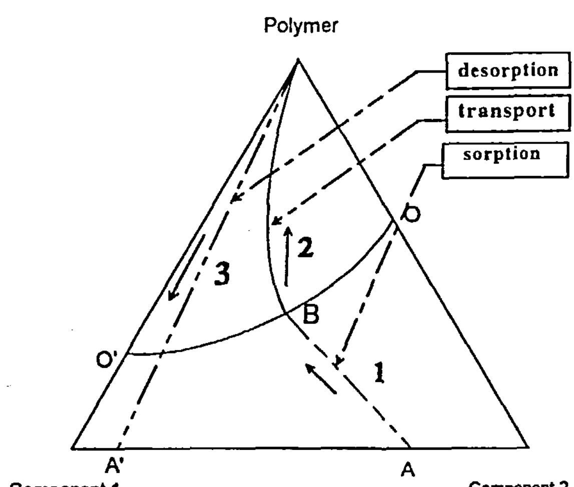


FIG. 1 A description of the transport process of pervaporation in a ternary phase diagram.

Based on above description, in this paper the transport characteristics of pervaporation are studied with a chitosan membrane and a H_2SO_4 crosslinking chitosan membrane. The dependence of the thermodynamic swelling distribution relationship on feed concentration is studied in order to illustrate the contribution of the thermodynamic swelling process to the permeation process. And the dependence of the permeation process and the thermodynamic swelling process on temperature is also studied in order to understand the contribution of temperature to permeation fluxes and membrane permselectivity.

EXPERIMENTAL

Materials

Chitosan was purified in our laboratory. The acetic acid, sodium hydrate, ethanol, and sulfur acid used were analytically pure reagents. Water was deionized and filtered through an ultrafiltration membrane before use.

Preparation of Membrane

The casting solution was prepared by dissolved chitosan (8 g) in about 1 N acetic acid (800 mL) at 25°C. The chitosan acetate salt membrane was made by pouring the casting solution onto a rimmed glass plate and allowing the casting solution to evaporation at room temperature. The chitosan membrane was made by immersing the chitosan acetate membrane into 3 wt% NaOH solution for 2 days and washing with about 70 wt% EtOH solution. The chitosan membrane crosslinked with H_2SO_4 was prepared by immersing the chitosan membrane into about 0.075 N H_2SO_4 solution for 2 days, after which the H_2SO_4 crosslinking chitosan membrane can be obtained by washing with 70 wt% EtOH solution. The thicknesses of the chitosan membrane and the H_2SO_4 crosslinking chitosan membrane were 57 and 70 μm, respectively. The difference in thickness did not influence the permselectivity.

Apparatus and Measurements

Permeation experiments were performed with the apparatus shown in Fig. 2. The temperature was controlled by a thermostatic bath. The vacuum on the downstream side was maintained at <200 Pa by a vacuum pump. The permeate was condensed and collected in a cold trap immersed in liquid nitrogen. The permeate composition was analyzed by gas chromatography (GC-8810A). When the flux and permeate composition did not change with time, steady-state conditions had been reached. The separa-

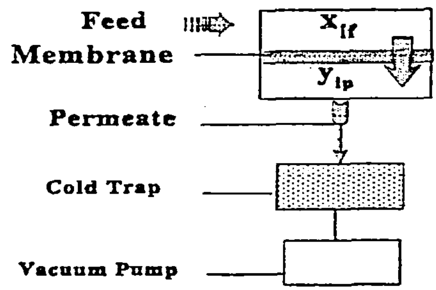


FIG. 2 Schematic diagram of PV through a membrane.

tion factor, α, was calculated by

$$\alpha = \frac{Y_{H_2O}}{Y_{EtOH}} \cdot \frac{X_{EtOH}}{X_{H_2O}}$$

where Y_{H_2O}, Y_{EtOH}, X_{H_2O}, and X_{EtOH} denote the concentrations of water and ethanol in permeate and feed, respectively.

The swelling ratio of the membrane (SR) was calculated as follows:

$$SR = \frac{W_1 - W_2}{W_2} \times 100\%$$

where W_1 and W_2 are the weights of the swollen and dry membrane. The liquid adsorbed in the membrane was evaporated and collected in a cold trap immersed in liquid nitrogen. The composition of EtOH in the collected liquid (free of the membrane) was analyzed by gas chromatography.

RESULTS AND DISCUSSION

Influence of Feed Concentration on Separation Factor and Fluxes

Figure 3 shows the separation characteristics of EtOH–H_2O mixtures for the chitosan membrane and the H_2SO_4 crosslinking chitosan membrane in pervaporation. The separation factor of the H_2SO_4 crosslinking chitosan membrane increased from $\sim 10^2$ to $\sim 10^4$ compared with the chitosan membrane. The concentration of EtOH in the permeate changed with the concentration of EtOH in the feed. This was the result of competition between the thermodynamic swelling process and the diffusion process of H_2O and EtOH.

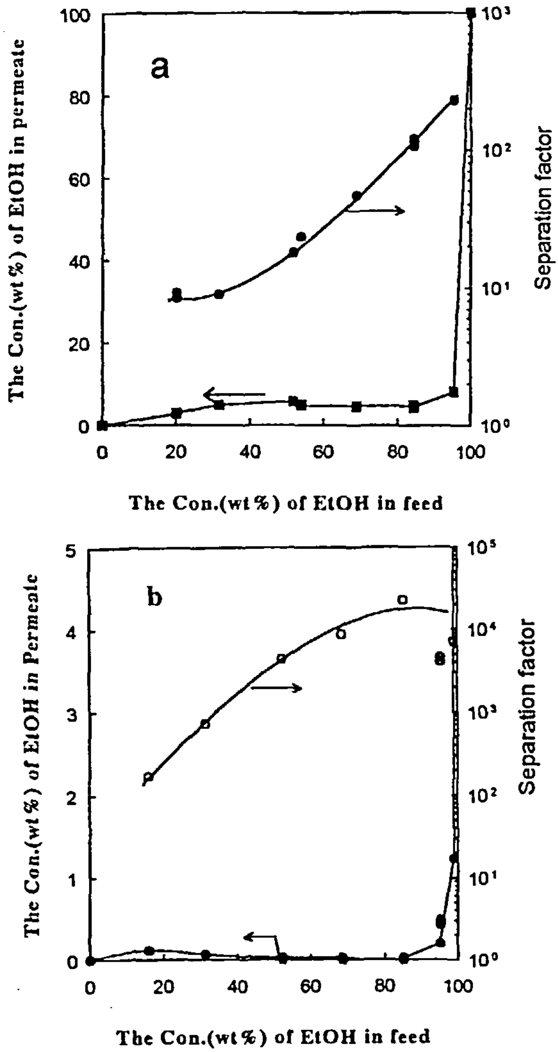


FIG. 3 The concentration of EtOH and selectivity in the permeate versus the concentration of EtOH in the feed: (a) chitosan membrane (membrane thickness: 57 μm) and (b) H_2SO_4 crosslinking chitosan membrane (membrane thickness: 70 μm). Temperature: 30°C.

The dependence of permeation fluxes of H_2O and EtOH on feed concentration are shown in Fig. 4. With an increase of EtOH concentration, the total permeation fluxes decreased quickly and the permeation flux of water was lower than for the ideal transport process. In the ideal transport pro-

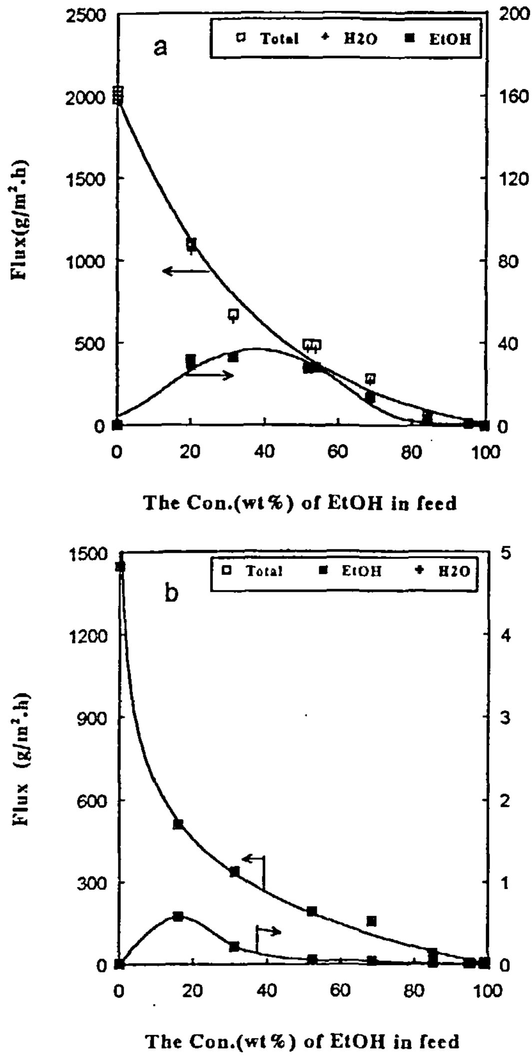


FIG. 4 The partial permeation flux of H_2O and EtOH versus the concentration of EtOH in the feed: (a) chitosan membrane (membrane thickness: 57 μm) and (b) H_2SO_4 crosslinking chitosan membrane (membrane thickness: 70 μm). Temperature: 30°C.

cess there is no interaction between the components and polymer, and the permeation flux of a component is assumed to be proportional to its concentration in the feed (9):

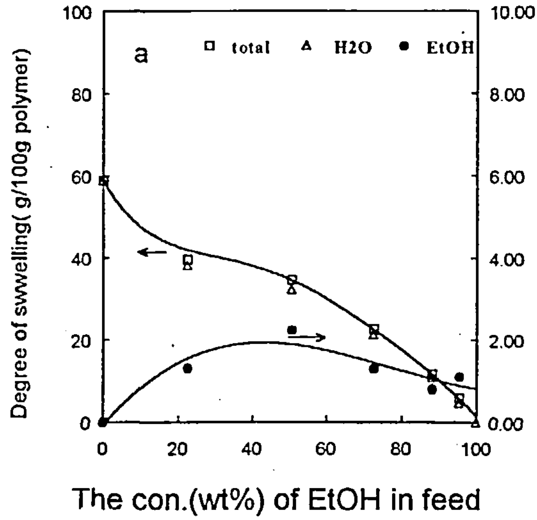
$$j_i = x_i J_i$$

where J_i is the flux of pure component i, x_i is the concentration of component i in the feed, and j_i is the ideal permeation flux of component i. The EtOH permeation flux showed a positive deviation from the ideal transport process, reaching a maximum at some concentration. That is, the existence of H_2O in the membrane enhanced the permeation flux of EtOH. Because of the effect of H_2SO_4 crosslinking, the EtOH permeation flux decreased very quickly compared with the chitosan membrane, but the permeation flux of H_2O changed only a little. The result was that the permselectivity of the H_2SO_4 crosslinking chitosan membrane was up to $\sim 10^4$ and the total permeation flux for the H_2SO_4 crosslinking chitosan membrane changed only a little compared with the chitosan membrane.

Influence of Feed Concentration on Thermodynamic Swelling Process

The thermodynamic swelling distribution relationship is shown in Fig. 5. With an increase of EtOH concentration in the feed, the total swelling ratio of the membrane decreases. The EtOH swelling ratio showed maximum points at some concentration, which showed that strong coupling effects exist between components and polymer in the thermodynamic swelling process. The fact that the high total swelling ratio of the H_2SO_4 crosslinking chitosan membrane was almost the same as that of the chitosan membrane determined that the H_2SO_4 crosslinking chitosan membrane had a flux almost as high as that of the chitosan membrane. The fact that the EtOH swelling ratio of the H_2SO_4 crosslinking chitosan membrane was less than that of the chitosan membrane shows that the swelling process of EtOH was retarded greatly by the effect of ionized crosslinking. The notable difference of the EtOH swelling ratio between the H_2SO_4 crosslinking chitosan membrane and the chitosan membrane determined that the H_2SO_4 crosslinking chitosan membrane had a very high permselectivity. The concentration of EtOH in the membrane changed with the feed concentration in Fig. 6, which directly determines the permselectivity in the thermodynamic swelling process. The concentration of EtOH is much less for the H_2SO_4 crosslinking chitosan membrane, which means the H_2SO_4 crosslinking chitosan membrane has a very high permselectivity.

Comparison of the permeation fluxes and thermodynamic swelling process of Figs. 4 and 5 shows the analogous relationship versus the concentration in the feed. Comparison of the H_2SO_4 crosslinking chitosan membrane with the chitosan membrane shows the separation factor of the permeation process increases with a decrease of the EtOH swelling ratio in the membrane. The thermodynamic swelling distribution relationship



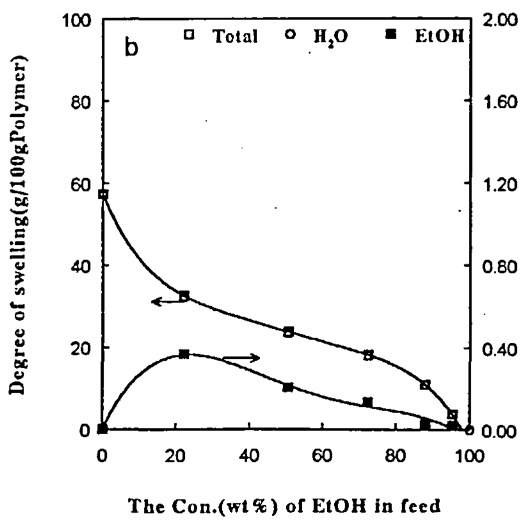


FIG. 5 Swelling ratio of H_2O and EtOH versus the concentration of EtOH in feed; (a) chitosan membrane and (b) H_2SO_4 crosslinking chitosan membrane. Temperature: 30°C.

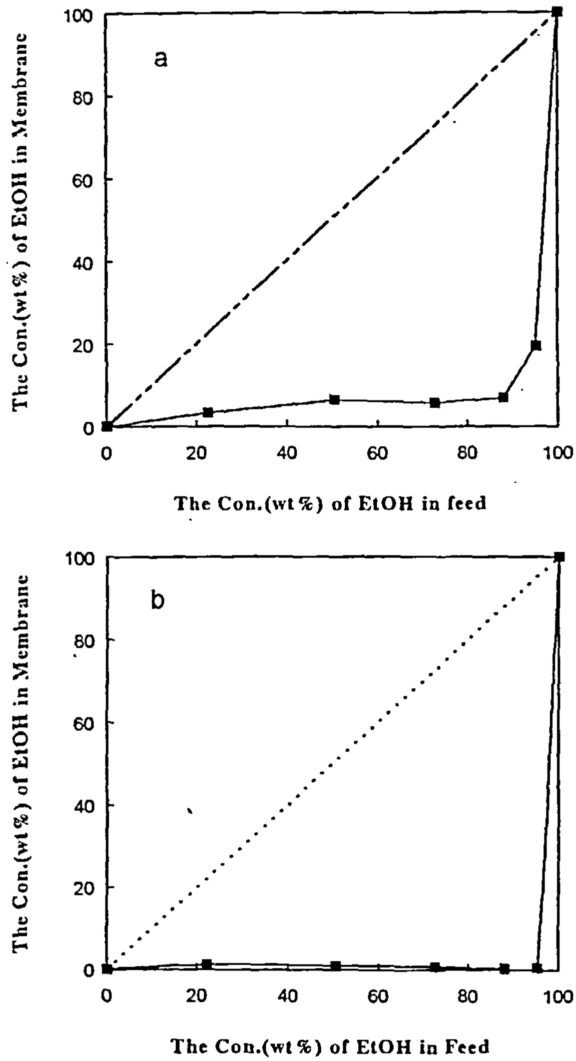


FIG. 6 The concentration of EtOH in the thermodynamic swelling process versus the concentration in the feed: (a) chitosan membrane and (b) H_2SO_4 crosslinking chitosan membrane. Temperature: 30°C.

directly controls the permselectivity of the permeation process. This can be seen from Figs. 3 and 6. The high swelling ratio and the high selectivity of the membrane in the thermodynamic swelling distribution process is the basis of the high flux and high perselectivity of the permeation process.

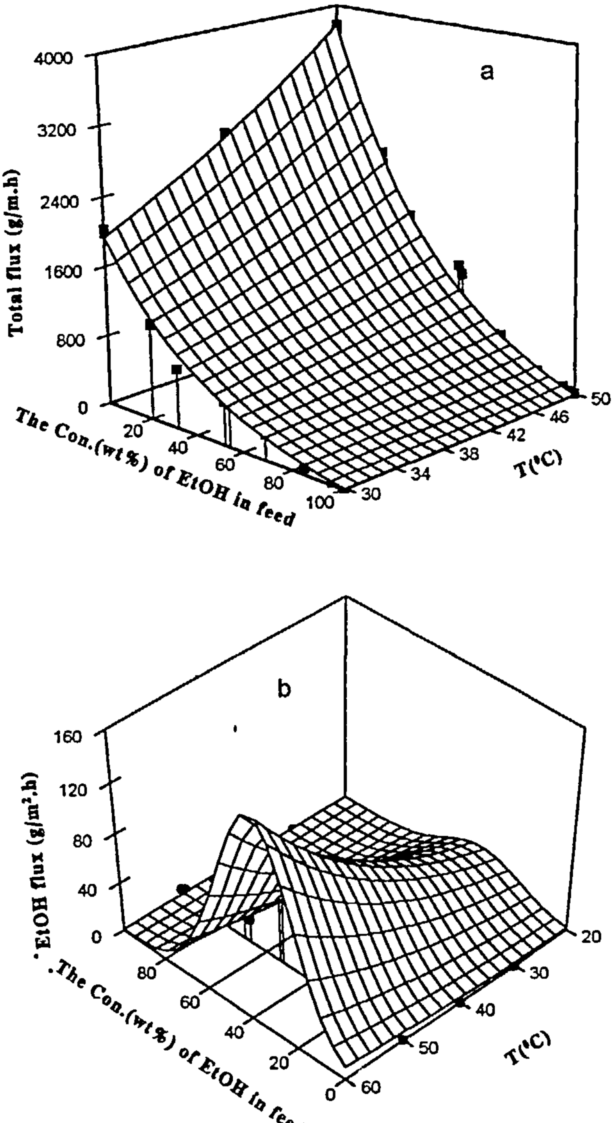


FIG. 7 The permeation fluxes versus the composition of EtOH in the feed, and the temperature of the chitosan membrane (membrane thickness: 57 μm). (a) Total flux and (b) EtOH flux.

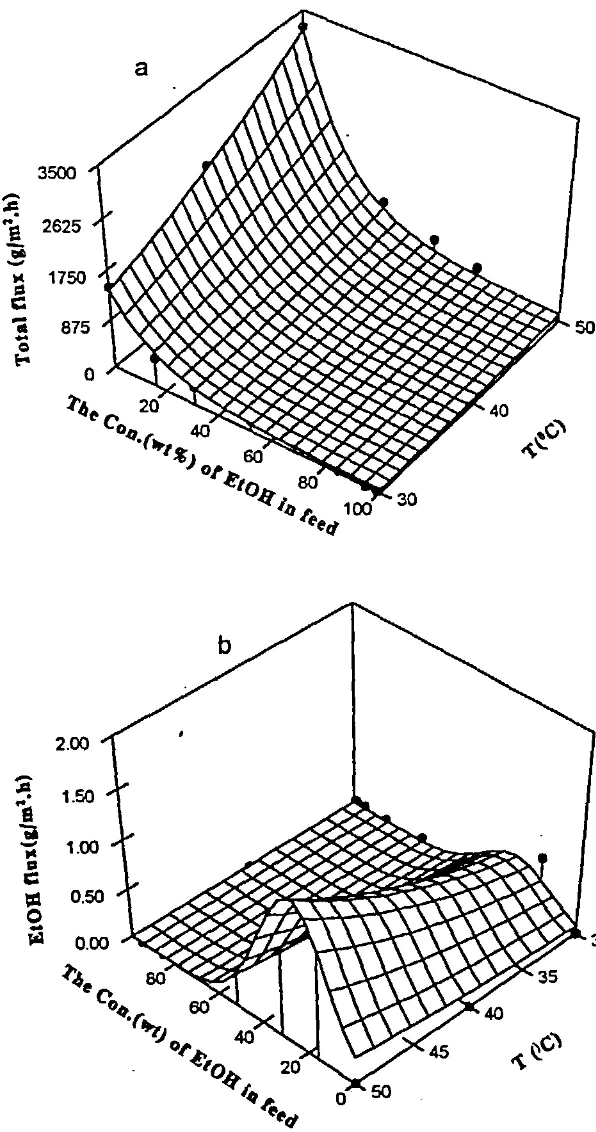


FIG. 8 The permeation fluxes versus the composition of EtOH in the feed, and the temperature of the H_2SO_4 crosslinking chitosan membrane (membrane thickness: 70 μm). (a) Total flux and (b) EtOH flux.

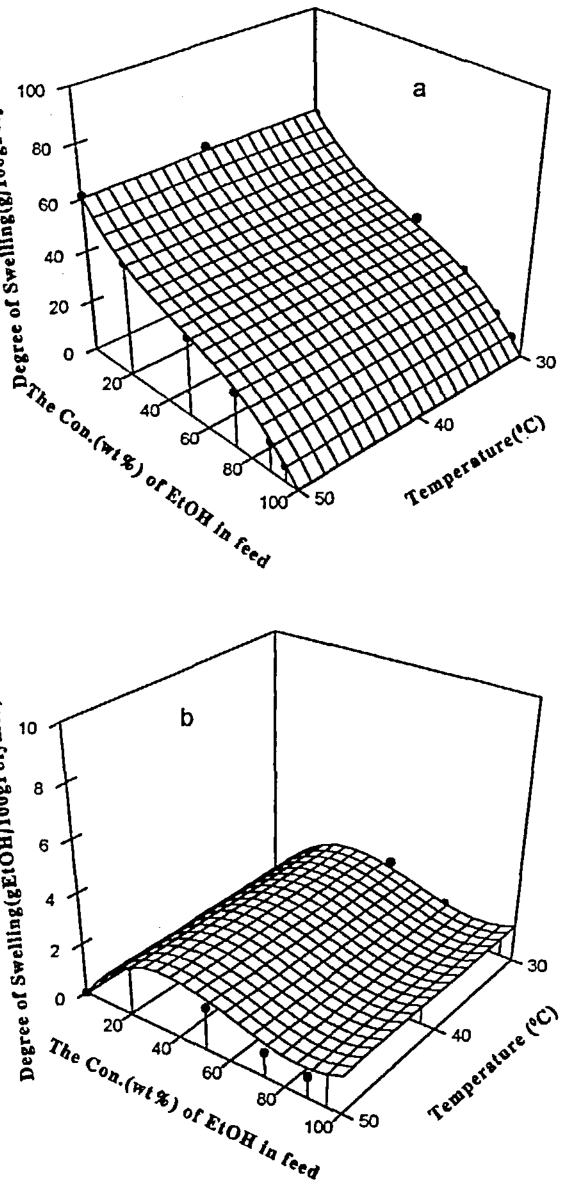
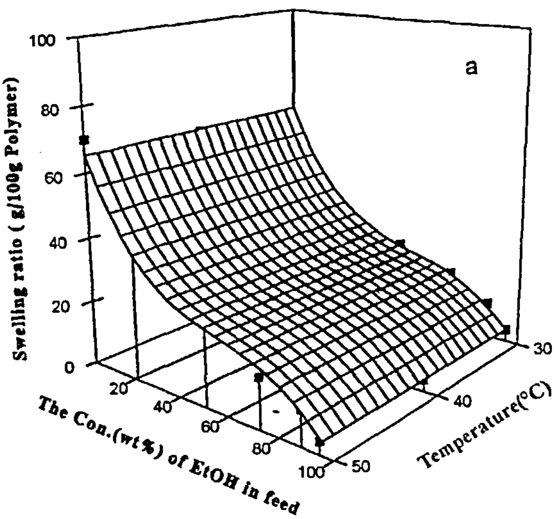


FIG. 9 The swelling ratio of H_2O and EtOH versus the temperature, and the concentration of EtOH in the feed for the chitosan membrane: (a) water and (b) EtOH.



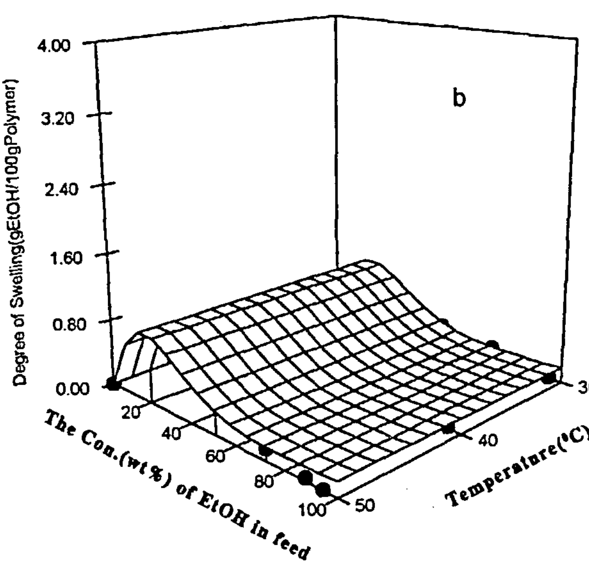


FIG. 10 The swelling ratio of H_2O and EtOH versus the temperature, and the concentration of EtOH in the feed for the H_2SO_4 crosslinking chitosan membrane: (a) water and (b) EtOH.

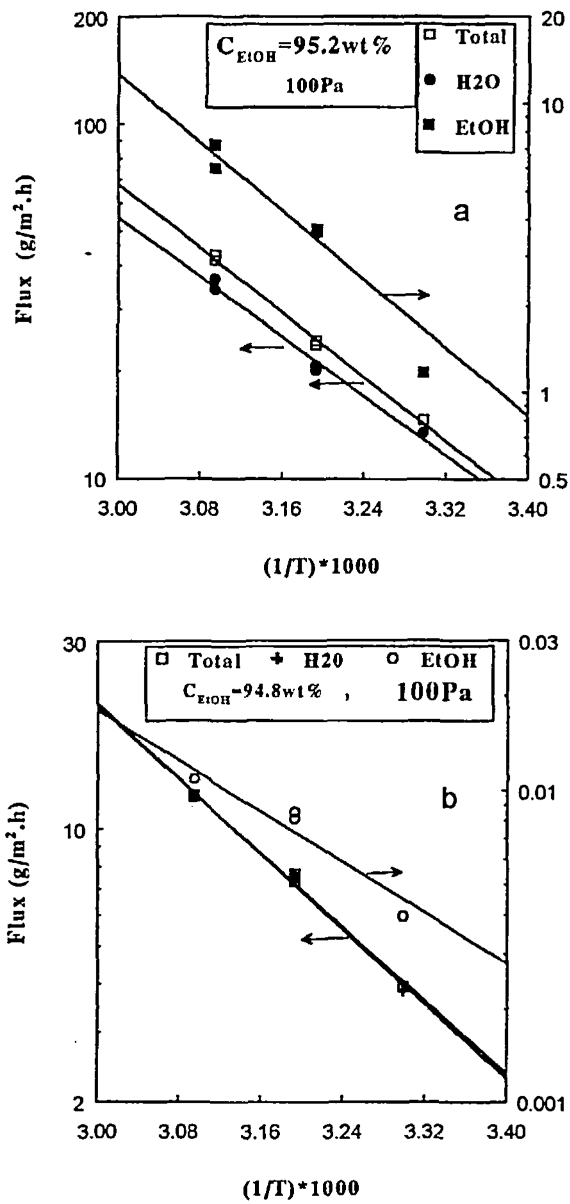


FIG. 11 The partial permeation flux of H_2O and EtOH versus the temperature by the Arrhenius relationship: (a) chitosan membrane (membrane thickness: 57 μm) and (b) H_2SO_4 crosslinking chitosan membrane (membrane thickness: 70 μm). Temperature: 30°C. Permeate pressure: 100 Pa.

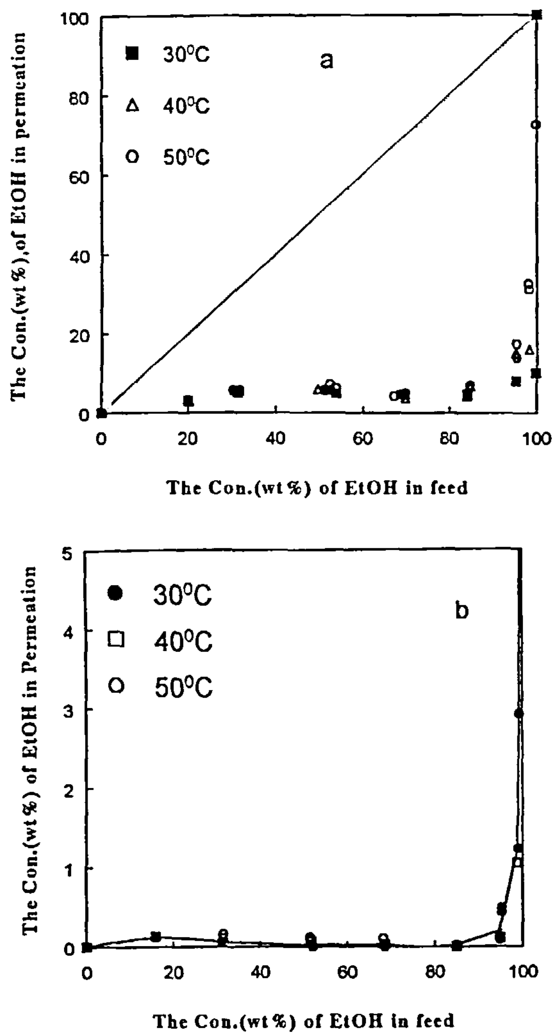


FIG. 12 The concentration of EtOH in the permeate versus the concentration in the feed at various temperatures: (a) chitosan membrane (membrane thickness: 57 μm) and (b) H_2SO_4 crosslinking chitosan membrane (membrane thickness: 70 μm).

Effect of Temperature

The influence of temperature and feed concentration on pervaporation performance for chitosan and H_2SO_4 crosslinking chitosan membranes is shown in Figs. 7 and 8. The permeation fluxes of water and EtOH increased quickly with an increase of temperature. The dependence of the swelling ratio on temperature for chitosan and H_2SO_4 crosslinking chitosan membranes is shown in Figs. 9 and 10. The swelling ratio of water and EtOH scarcely changed with an increase of temperature. The above facts make it clear that the increase of permeation fluxes with an increase of temperature are mainly due to the dependence of the diffusion process on temperature.

Figure 11 showed the influence of temperature on permeation fluxes for 95 wt% EtOH. The permeation fluxes increased quickly with an increase of temperature and show an Arrhenius relationship between permeation fluxes and temperature. The influence of temperature on permselectivity is shown in Fig. 12. An increase of temperature scarcely changed the concentration of EtOH in the permeate for chitosan and H_2SO_4 crosslinking chitosan membranes, which shows the permeation fluxes increased with an increase of temperature but the permselectivity remained almost the same. We can conclude that an increase of temperature promotes an increase of permeation flux, but the permselectivity of pervaporation depends mainly on the thermodynamic swelling process for the chitosan and H_2SO_4 crosslinking chitosan membranes.

CONCLUSIONS

1. The dependence of the EtOH composition in the permeate on the feed concentration shows that strong coupling effects exist in the permeation process. Comparison of the water permeation flux of the H_2SO_4 crosslinking chitosan membrane with the chitosan membrane shows that it changes a little, but the EtOH permeation flux decreases significantly. The permselectivity of the H_2SO_4 crosslinking chitosan membrane was up $\sim 10^4$ and the total flux only changed a little.
2. The permeation fluxes and thermodynamic swelling processes show an analogous relationship versus the concentration in the feed. The thermodynamic swelling distribution relationship directly controls the permselectivity of pervaporation. The high swelling ratio and the high selectivity in the thermodynamic swelling distribution process is the basis of the high flux and high permselectivity of pervaporation.
3. An increase of temperature for the chitosan membrane and H_2SO_4 crosslinking chitosan membrane has a strong influence on the diffusion

process, but the swelling ratio of water and EtOH in membrane scarcely change. An increase of temperature promotes an increase of the permeation flux but has little influence on permselectivity. The permselectivity of pervaporation depends strongly on the thermodynamic swelling process.

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