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Studies on Syntheses and Permeabilities of Special Polymer Membranes

42. Separation of Binary Organic Solvent Mixtures Through Nylon 12 Membranes

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Summary

The permeation and separation characteristics of methanol/n-pentanol systems and n-propanol/n-heptane systems through nylon 12 membranes were studied by changing the feed composition of the binary organic mixtures. These characteristics were discussed from the viewpoints of physical and chemical nature of the permeating molecules and the membrane.

Introduction

Nylon 12 has very good resistance agasist hydrolysis in aqueous solution and to various organic solvents. From its advantages, nylon 12 membranes are expected to be suitable for the separation of systems for both, aqueous organic solvent solutions and binary organic liquid mixtures. In the previous papers, we reported the permeation characteristics in concentration of aqueous polymer solutions[1] and the permeabilities[2] of alcohol and hydrocarbons using nylon 12 membranes. In the present paper the permeation and separation characteristics for binary organic solvent mixtures are studied. Factors affecting these characteristics are discussed.

Experimental

Materials Nylon 12(N-12)(nylon powder 500/PWI from Toray Co. Ltd.) was used as membrane substance.

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Pure commercial N-methyl 2-pyrrolidone (NMP) is used as solvent for the casting solutions. Paraformaldehyde (PF) used as hydroxymethylation reagent of (N-12) and triethyl amine(TEA) used as catalyst were commercial reagents. Methanol(MeOH), n-propanol(n-PrOH), n-pentanol(n-PeOH), and n-heptane(n-Hep) used as feed were commercial sources.

Preparation of membranes N-12 powder (4 g) immersed in NMP (96 g) was stirred in a stream of nitrogen gas for 30 min at 110°C. PF(5 g) and TEA(0.02 ml) were added to the above heterogeneous solution contained N-12 powder and simultaneously nitrogen gas was stopped. When this mixture was stirred for 60 min for 115°C, N-12 powder was dissolved. This dissolution of N-12 was due to the fact that N-12 molecules were hydroxymethylated by formaldehyde generated with the decomposition of PF, as well as the dissolution of cellulose[3]. This N-12 solution was filtrated with gauze consisted of multiple layer to remove undecomposed PF. The membranes were made by pouring this clear filtrate onto a rimmed glass plate in the oven set at 70°C, setting to evaporate the solvent for 2h, and immersing the glass plate together with the membrane into water(25°C). It was confirmed by the method of phosphoric acid decomposition[4] that the hydroxymethylated N-12 membranes were converted into the N-12 membranes by hydrolyzing during this water treatment. The thickness of dry membranes used were 25 μm.

Apparatus and measurements The apparatus and the experimental procedure have been reported[5]. The compositions of feed and membrane-permeated liquid were determined by gas chromatograph (GC-4CPTF) of Shimadzu Co. Ltd.

Results and discussion

The effect of feed composition on the permeation and separation characteristics, and swelling degree of the membrane for MeOH/n-PeOH mixtures is shown in Figure 1. Experimental data in Figure 1 show the existence of equisorptic composition, which is obviously functions of the chemical nature of membrane material and that of the feed solution. The swelling degree of membrane in this composition has a maximum value and consequently the permeation rate is maximum.

The permeation process through the polymer membrane is mainly divided into two steps, namely the dissolution of molecules into the polymer membrane and the diffusion of these molecules through it[7]. Therefore, the separation is dependent on defferences in either the solubility or the diffusivity. The solubility difference is due primarily to the difference in physicochemical nature of the permeating molecules. On the other hand, the diffusivity difference is determined mainly by the size and shape of these molecules, by the degree of aggregation among the diffusing species within the membrane, and by the interaction between the polymer membrane substance and the diffusing species. The permeation characteristics in higher MeOH content in the feed may be influenced by the solubility difference. The molecular size, molecular shape, and solubility parameter of pure organic solvents are summarized in Table 1. In general, solvent with the solubility parameter δ close to that of the polymer membrane substance sorbs to a greater extent than solvent which has a value of δ which is far from that of the polymer membrane substance. On this basis n-PeOH would be expected to permeate N-12 membrane faster than MeOH. Also, in these systems the fact that the aggregation of MeOH molecules is greater is related to the separation characteristic.

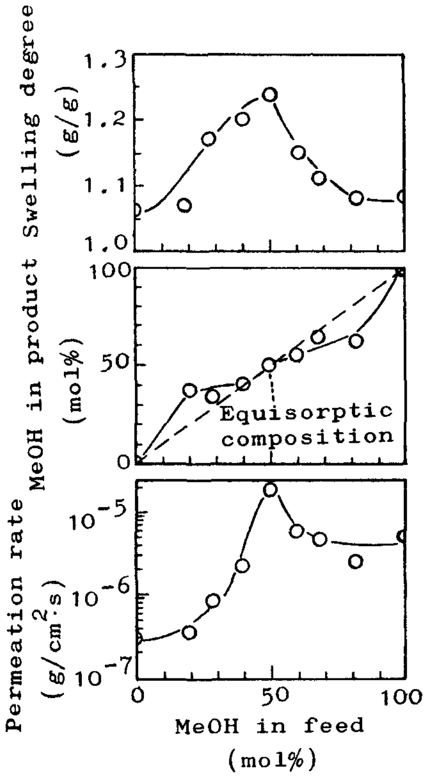

Figure 1

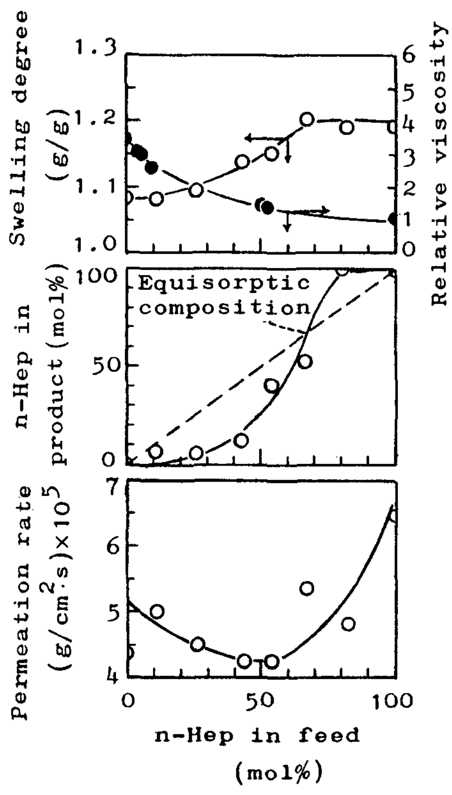

Figure 2

Figure 1 Effect of feed mixture composition of MeOH and PeOH on permeation and separation characteristics. Operating conditions: 40 °C, 5 kg/cm^2.

Figure 2 Effect of feed mixture composition of n-PrOH and n-Hep on permeation and separation characteristics. Operating conditions: 40 °C, 5kg/cm^2.

The permeation rate is attributable to the swelling degree. The permeation characteristics in lower MeOH content are mainly governed by the molecular size. That is, since the aggregation of n-PeOH molecules is higher, MeOH having smaller molecular size permeates predominantely.

Figure 2 shows the permeation characteristics and swelling degree of the membrane for n-PrOH/n-Hep mixtures. In this system, there is the equisorptic composition at the n-Hep content of 70 mol% in the feed. This is caused by the fact that the swelling degree of membrane is maximum in this composition. Below 70 mol % of n-Hep in the feed, the permeation characteristics are attributed to the solubility difference. Since the solubility parameter of n-PrOH closes to that of N-12, n-PrOH is dissolved predominantely into N-12 membrane. Therefore, the separation for n-Hep becomes greater. Smaller permeation rates in this range of feed compositions depend on smaller swelling degree of the membrane and higher viscosity of the permeated liquid as shown in Figure 2. When the n-Hep content in the feed is over 70 mol%, the permeability of n-Hep increases significantly.

Table 1. Physicochemical nature of permeating molecules

Permeant	Molecular volume, $\overline{V}$ (Å^3)	Molecular length, $\overline{L}$ (Å)	$\overline{V}/\overline{L}$ (Å^2)	Solubility parameter $(cal/cm^3)^{\frac{1}{2}}$ δ
MeOH	67.2	2.9	23.2	14.3
n-PrOH	124	5.4	23.0	12.0
N-PeOH	180	7.8	23.0	10.6
n-Hep	237	9.9	24.0	7.4
N-12*				11.1

*This solubility parameter is for m-cresol which is the best solvent for nylon 12.

The permeation rate is governed by the swelling degree and viscosity of the permeated liquid. In the spite of these facts, however, the separation for n-PrOH is high. This result probably is due to the diffusivity difference based on the molecular size of permeating species.

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