Permeation of Organic Solutions through Inorganic Porous Membranes

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Introduction

Inorganic membranes have been expected to be applied for separation not only in aqueous solutions but also in non-aqueous solutions because of its excellent resistance to various solvents (1-3). In the present study, silica-zirconia nanofiltration (NF) membranes of various pore diameters (1~3 nm) were fabricated by the sol-gel method, and employed for nanofiltration experiments of pure solvents and organic aqueous solutions.

Experimental

Silica-zirconia colloidal sols having various diameters were prepared by hydrolysis and condensation of tetraethoxysilane (TEOS) and zirconium tetra-n-butoxide using hydrochloric acid as an acid catalyst. The molar ratio of Si/ Zr of the composite oxide was adjusted to 0.9/ 0.1. The NF membranes were prepared by coating the sols on cylindrical α-alumina microfiltration membranes (average diameter 1 μm, outer diameter 1 cm, length 9 cm) and firing at 500 °C. This coating-firing process was carried out for sol solutions from larger diameter to smaller diameter, and pore sizes of porous membranes were controlled by appropriate choice of colloidal diameters at the final coating step (1). Nanofiltration experiments were carried out for pure solvents (water, methanol, ethanol, 1-propanol, acetone) and the aqueous mixtures.

Result and Discussion

Permeate flux of pure solvents through silica-zirconia nanofiltration membranes at a steady state shows a linear relation with the applied pressure, which indicates that the pressure difference is the only driving force of the permeation. Solvent permeability, L_p [$m^3 m^{-2} s^{-1} Pa^{-1}$], through porous membranes (pore radius r_p, surface porosity A_k) is formulated as the following equation, based on the viscous flow (Hagen-Poiseuille flow) mechanism.

$$L_p = \frac{r_p^2}{8\mu} \frac{A_k}{\Delta x}$$

The transport mechanism of pure solutions for membranes having pore diameters as large as 70 nm obeyed the viscous flow mechanism, since $L_p\mu$, defined as volumetric permeability, L_p, multiplied by the solvent viscosity, μ, showed constant values irrespective of permeation temperature and the types of

solvents. On the other hand, the permeation mechanism through porous membranes of 1 ~ 3 nm in diameter deviated from the viscous mechanism. $L_p\mu$ was larger for smaller molecules, i.e., H_2O > MeOH > EtOH >1-PrOH, and $L_p\mu$ increased with temperature. This tendency was clearly observed for membranes of smaller pore size (2). It should also be added that permeate flux showed reproducible data for the repeated experiments, and it was confirmed that silica-zirconia membranes were stable in water and alcohols in temperature range from 20 to 60 °C.

A similar tendency was observed for organic aqueous solutions, as shown in Fig.1 and 2. For α-alumina membranes of 160 nm in diameter, the $L_p\mu$ for the mixtures of water and ethanol was almost constant irrespective of its composition, while L_p was not constant. On the other hand, when ethanol and acetone aqueous solutions were filtrated through a membrane having pore size of 1.5 nm, $L_p\mu$ showed a steep decrease by adding a small amount of organic molecules (ethanol and acetone), and then seems to approach constant values. Organic molecules were suggested to adsorb on the membrane surface covered with silanol functional groups, and result in a decrease of effective pore size for permeation. Decrease in $L_p\mu$ in a low concentration range was more clearly observed for water-ethanol mixtures than for water-acetone mixtures, probably because of larger affinity with silanol functional groups. Therefore, the permeation of solvent through nanofiltration membranes was found to be affected by the size difference between pore and permeating molecules as well as the affinity between the membrane surface and the permeating molecules.

References

1)T. Tsuru et al., J. Membrane Sci., 149 (1998) 127-135; 2) T. Tsuru et al., J. Colloid & Interface Sci., 228 (2000) 292-2961; 3) T. Tsuru et al., J. Membrane Sci., accepted.
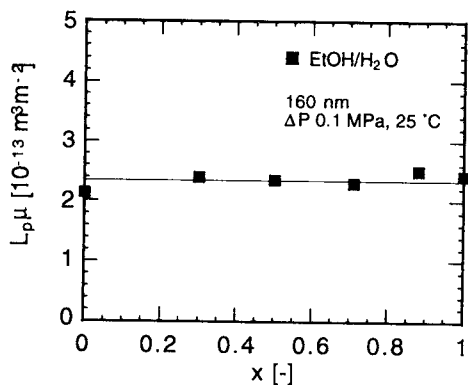

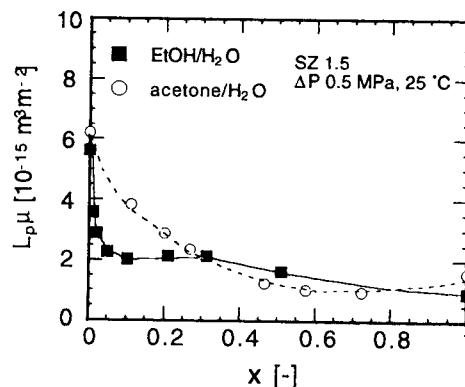Fig. 1 $L_p\mu$ as a function of mole fraction of ethanol in feed (d_p~160 nm)

Fig. 2 $L_p\mu$ as a function of mole fraction of organic component (d_p~1.5 nm)