Ion Separation by Porous Silica-Zirconia Nanofiltration Membranes

Toshinori Tsuru, Hirohiko Takezoe, and Masashi Asaeda
Dept. of Chemical Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

Recently developed nanofiltration (NF) membranes have attracted a great deal of attention since they have molecular weight cutoffs (MWCO) in the range of 200 to 1,000, which is intermediate between conventional reverse osmosis and ultrafiltration membranes. An important and useful feature of nanofiltration membranes is that many NFs are positively or negatively charged, thus allowing the separation of ions according to valence type, based on the electrical interaction between the membrane surface charge and ions (Tsuru et al., 1991a,b; Wang et al., 1995a,b, 1997; Rios et al., 1996). Figure 1 shows the proposed strategy for separating metal ions and acid from mixtures using a positively charged nanofiltration membrane. It should be noted that the driving force for the separation is pressure difference across the membrane. Multivalent coions such as metal ions are more strongly repelled by the membrane charge than are monovalent ones such as hydrogen ions. As a result, metal ions are rejected to a greater extent than hydrogen ions, and consequently, the simultaneous concentration of metal ions in the feed and the recovery of acid in a permeate would be feasible. Although dialysis has been conventionally employed to recover hydrogen ions, it cannot be expected to simultaneously concentrate metal ion in the feed and acid in the permeate because the driving force for the separation is the concentration difference of ions across a membrane.

At present, commercially available NF membranes are typically composed of polymeric materials such as poly(amide) (Petersen, 1993). Their chemical stability is not sufficient for use in acidic or caustic solutions, and as a result, they can only be used over a limited pH (typically pH 3–10). The development of NFs made of inorganic materials, which have excellent resistance to high temperature, pH, and organic solvents, is anticipated, however, few studies have focused on the development of inorganic nanofiltration membranes (Tsuru et al., 1996; Larbot et al., 1994). Moreover, most polymeric NF membranes are negatively charged (Petersen, 1993; Tsuru et al., 1994). It should be noted that inorganic materials such as ceramics can exist in either a positively or negatively charged state in an aqueous solution, depending on the pH, often referred to as the "zeta potential." Therefore, ceramic NF membranes would be expected to separate ions in much the same manner as charged membranes (Alami-Younssi et al., 1994; Rios et al., 1996).

In the present study, porous silica-zirconia NF membranes were fabricated and used for permeation experiments of single electrolyte solutions, and in addition, were studied in terms of their potential for use in the separation of mixtures of metal and hydrogen ions.

Experimental Studies

Preparation of colloidal sols and NF membranes

Silica-zirconia colloidal sols were prepared using a two-step procedure, involving hydrolysis and condensation, as described previously (Tsuru et al., 1996). Colloidal diameters, which were measured by laser light scattering (ELS-800, Otsuka Electric Co., Japan), were controlled from several nm to 50 nm by adjustment of the sol concentration during the second step of the procedure. NF membranes were prepared by coating sols on cylindrical porous α-alumina microfiltration membranes (outer diameter 1 cm; 9 cm long) and firing the coated membranes at 570°C.

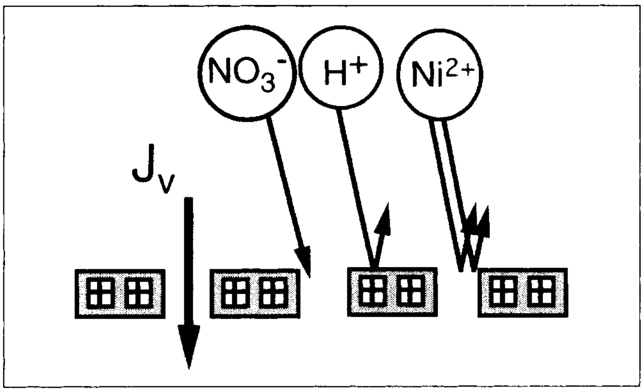

Figure 1. Concept of ion separation by a positively charged membrane.

Correspondence concerning this article should be addressed to T. Tsuru.

Nanofiltration experiments

The following solutions were prepared and used as model electrolytes: sodium chloride as a mono-valent (1-1) electrolyte, sodium sulfate as a mono-divalent (1-2) one, and nickel nitrate as a mono-divalent (2-1) one. All were individually nanofiltrated, and their concentrations were adjusted from 1 to 1,000 mol·m^{-3}. The pressure applied ranged from 0.25 to 1.0 MPa. Electrolyte concentrations of single solutions were determined using an electric conductivity meter. For experiments involving the separation of mixed solutions of metal ions and hydrogen ions, nickel nitrate for which the feed concentration was adjusted from 10–100 mol·m^{-3} was separated from the acidic solutions (pH 1.0–6.0) at an applied pressure of 1.0 MPa. Nickel ion was determined with an inductively coupled plasma mass spectrometer, and the acid concentration was measured by titration.

Measurement of zeta potential

Zeta potentials of silica-zirconia sols at various pH values were determined by electrophoresis (ELS 800, Otsuka Electric Co., Japan). After fabrication of a membrane, the streaming potential was measured as a function of applied pressure and the Helmholtz-Smoluchowski equation was used to calculate the uncorrected zeta potential as described by Nyström et al. (1994). The pH was adjusted using potassium hydroxide and hydrochloric acid.

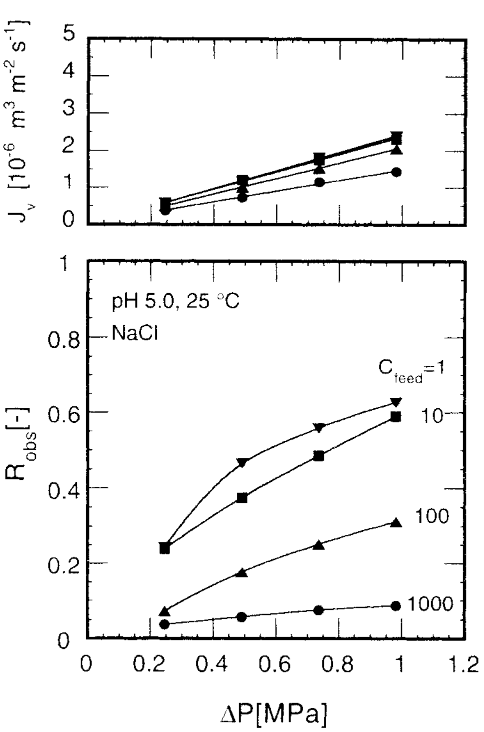

Figure 3. Rejection of sodium chloride and permeate volume flux at pH 5.0 as a function of applied pressure.

Results and Disussion

Zeta potentials of silica-zirconia composites are shown in Figure 2. The iso-electric point (pI) was estimated to be approximately pH 4 by streaming potential measurements as well as by electrophoresis measurements. The pI of silica-zirconia is intermediate between that of silica and zirconia which have been reported to be approximately pH 2 and 7, respectively.

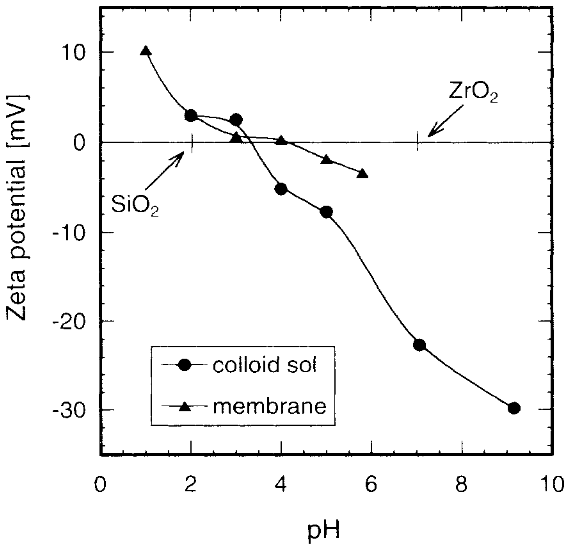

Figure 2. Zeta potential of silica-zirconia colloids and the NF membranes as a function of pH.

Figures 3 and 4 show rejection and volume flux as a function of applied pressure for, respectively, sodium chloride and sodium sulfate at pH 5 at which conditions the silica-zirconia membrane is negatively charged. Rejection increased with applied pressure and appears to reach a constant level, which is similar to polymeric NF membranes. In addition, rejection was strongly dependent upon feed concentration with a higher rejection observed at lower feed concentrations. This is characteristic of charged membranes (Tsuru et al., 1991a,b). The permeate volume flux was nearly linear with respect to the applied pressure at low feed concentration, but decreased with feed concentration, especially for sodium sulfate, which is probably due to osmotic pressure.

Figure 5 shows the rejection of sodium chloride, sodium sulfate, nickel nitrate and nitric acid as a function of feed concentration. The pH of the NaCl and the Na_2SO_4 solution was maintained at pH 5.0. The pH for the $Ni(NO_3)_2$ solutions having feed concentrations of 1 and 10 mol·m^{-3} was also kept at pH 5. For the case of the feed concentration at 100 and 1,000 mol·m^{-3}, the pH of the feed solutions were pH 4.1 and pH 2.7, respectively. With respect to rejection at pH 5.0, the rejection of sodium sulfate is higher than that for sodium chloride and nickel nitrate. The order of rejection is Na_2SO_4 (1-2 type) > NaCl (1-1) > $Ni(NO_3)_2$ (2-1), which is characteristic of negatively charged NF membranes. This is due to the fact that divalent anions are more strongly repelled by the negatively charged membranes, while divalent cations are more strongly attracted than are monovalent cations. Rejection of all the electrolytes tested decreased to

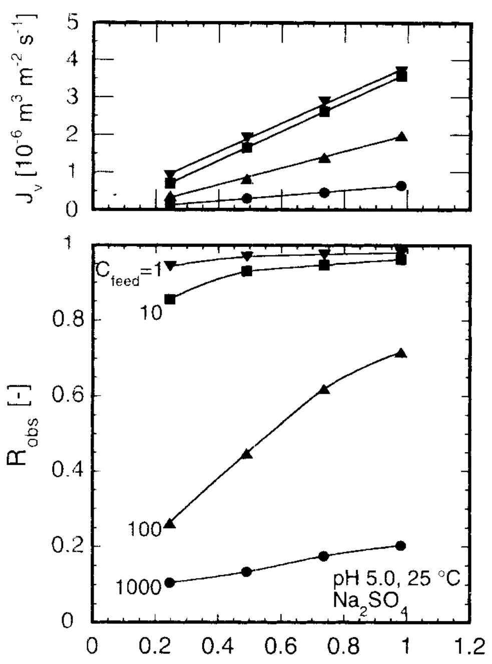

Figure 4. Rejection of sodium sulfate and permeate volume flux at pH 5.0 as a function of applied pressure.

nearly zero at a feed concentration of 1,000 mol·m^{-3}, suggesting that size effects (molecular sieving) do not significantly contribute to rejection. This is also confirmed by the fact that the molecular weight cutoff determined at 90% rejection using various neutral organic solutes (Tsuru et al., 1996) was approximately 200; the pore diameter seems to be regarded as large enough for ion permeation. It should be noted that nitric acid showed an extremely low rejection, which is probably due to the higher mobility of hydrogen ion in aqueous solution.

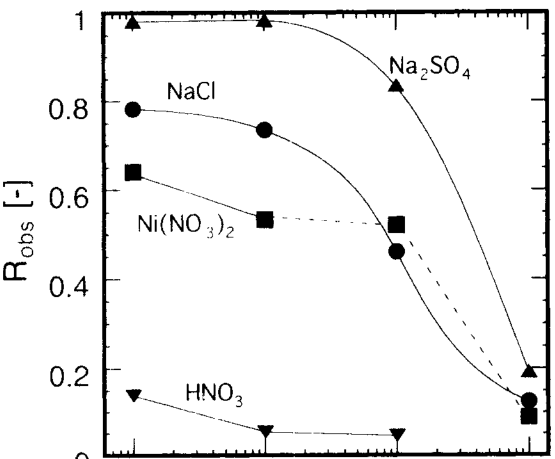

Figure 5. Rejection in single electrolyte solutions at an applied pressure of 1.0 MPa.

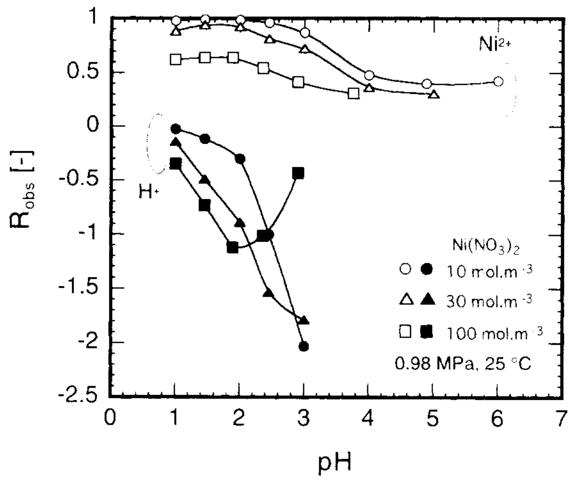

Figure 6. Rejection of nickel nitrate and nitric acid as a function of pH of feed solution.

Feed concentration of nickel nitrate was kept at 10, 30 and 100 mol·m^{-3}.

Figure 6 shows the rejection of nickel nitrate and nitric acid from the mixture over a pH range of 1.0 to 6.0. At pH values lower than the pI, where silica-zirconia is positively charged, nickel ion, which is more strongly repelled than hydrogen ion, shows a high rejection; at a $Ni(NO_3)_2$ feed concentration of 10 mol·m^{-3}, nickel ion was almost completely rejected between pH 1 and pH 3. It should be noted that very few polymeric NF membranes commercially available are positively charged and most polymeric NFs cannot be used at a pH lower than 3 (Tsuru et al., 1994). In addition, hydrogen ion shows a negative rejection, that is, nitric acid was concentrated in the permeate. This is due to the fact that the permeation of hydrogen ion is enhanced so as to maintain electroneutrality with the permeation of nitric ion (counterion to the membrane charge) as shown in Figure 1. As a result, nickel nitrate was rejected in the feed and consequently concentrated, while nitric acid was concentrated in the permeate. These data clearly show that the simultaneous concentration of metal ion and the recovery of acid is possible using positively charged nanofiltration membranes. Our previous theoretically study predicted these phenomena (Tsuru et al., 1991b). In addition, at pH values higher than the pI where silica-zirconia is negatively charged, the rejection of nickel nitrate decreased.

Literature Cited

Alami-Younssi, S., A. Larbot, M. Persin, J. Sarrazin, and L. Cot, "Gamma Alumina Nanofiltration Membrane: Application to the Rejection of Metallic Cations," *J. Memb. Sci.*, **91**, 87 (1994).

Larbot, A., A. Alami-Younssi, M. Persin, J. Sarrazin, and L. Cot, "Preparation of a γ-Alumina Nanofiltration Membrane," *J. Memb. Sci.*, **97**, 167 (1994).

Nyström, M., A. Pihlajamäki, and N. Ehsani, "Characterization of Ultrafiltration Membranes by Simultaneous Streaming Potential and Flux Measurements," *J. Memb. Sci.*, **87**, 245 (1994).

Petersen, R. J., "Composite Reverse Osmosis and Nanofiltration Membranes," *J. Memb. Sci.*, **83**, 81 (1993).

Rios, G. M., R. Joulie, S. J. Sarrade, and M. Carlès, "Investigation of Ion Separation by Microporous Nanofiltration Membranes," *AIChE J.*, **42**, 2521 (1996).

Tsuru, T., M. Urairi, S. Nakao, and S. Kimura, "Reverse Osmosis of Single and Mixed Electrolytes with Charged Membranes: Experiment and Analysis," *J. Chem. Eng. Japan*, **24**, 518 (1991a).

Tsuru, T., S. Nakao, and S. Kimura, "Calculation of Ion Rejection by Extended Nernst-Planck Equation with Charged Reverse Osmosis Membranes for Single and Mixed Electrolyte Solutions," *J. Chem. Eng. Japan*, **24**, 511 (1991b).

Tsuru, T., T. Shutou, S. Nakao, and S. Kimura, "Peptide and Amino Acid Separation by Nanofiltration Membranes," *Sep. Sci. Technol.*, **29**, 971 (1994).

Tsuru, T., S. Wada, S. Izumi, and M. Asaeda, "Porous Silica-Zirconia Membranes for Nanofiltration," Proceedings of International Congress on Membranes and Membrane Processes, Yokohama, Japan, p. 444 (1996).

Wang, X. L., T. Tsuru, M. Togoh, S. Nakao, and S. Kimura, "Evaluation of Pore Structure and Electrical Properties of Nanofiltration Membranes," *J. Chem. Eng. Japan*, **28**, 186 (1995a).

Wang, X. L., T. Tsuru, S. Nakao, and S. Kimura, "Electrolyte Transport through Nanofiltration Membranes by Space Charge Model and the Comparison with Teorell-Meyer-Sievers Model," *J. Memb. Sci.*, **103**, 117 (1995b).

Wang, X. L., T. Tsuru, S. Nakao, and S. Kimura, "The Electrostatic and Steric-Hindrance Model for the Transport of Charged Solutes through Nanofiltration Membranes," *J. Memb. Sci.*, **135**, 19 (1997).

Manuscript received Oct. 7, 1997, and revision received Dec. 18, 1997.

Correction

In the article titled "*In-Situ* CIR-FTIR Study of the Diffusion of Supercritical Hydrocarbons in Zeolite L," by M. G. Süer, Z. Dardas, Y. Lu, W. R. Moser, and Y. H. Ma (Vol. 43, p. 1717), Eqs. 2 and 5 should read:

$$C = 0 \qquad 0 \le r \le a \qquad t = 0 \tag{2}$$

$$C = -\frac{2D}{\pi a}\sum_{n=1}^{\infty}(-1)^n \exp\left(-\frac{D\pi^2 n^2 t}{a^2}\right) n\pi \sin\left(\frac{n\pi r}{a}\right)\int_0^t \exp\left(-\frac{Dn^2\pi^2}{a^2}t\right)\phi(t)dt \tag{5}$$