Zwitterionic Nanofiltration Membranes

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Introduction

The most popular NF membrane developed so far are composite in nature, with a selective layer on top of the microporous substrate. There are many methods for the preparation of composite membranes for NF including plasma-initiated polymerization, photo-initiated polymerization, and interfacial polymerization. Interfacial polymerization, however, is still a key method to produce commercial NF membrane such as the NF series membranes produced by Filmtec Corporation (USA), the NTR series membrane produced by Nitto Denko Company (Japan), and the UTC series produced by Toray Industries (Japan) and so forth. The interfacial polymerized NF membrane is generally synthesized by condensating water soluble diamines and water insoluble trimesoyl chloride in water-organics interface \cite{1-2}. The membranes are mostly negatively charged. Therefore, studies on positively charged NF membrane are scarce. In this study, we try to manipulate the membrane charge by substituting ethylenediamine (EDA) by diethylenetriamine (DETA) or polyethylenimine (PEI). The resulting membranes are either neutral or positive charged. The molecular weight cut-off and the permeation fluxes of these membranes are determined. The membrane rejection, between sodium and magnesium salts, between chloride and sulfate salts, are compared. The effects of positive or negative charges on NF membranes can therefore be elucidated.

Experiment

The NF membranes were prepared by interfacial polymerization with different amine solution and trimesoyl chloride (TMC) solution. The amine solutions were EDA, DETA, and PEI respectively. At first, the PAN/PVP support membranes were immersed in any kind of 1v/v% amine/H\textsubscript{2}O solution for 3 hours. The wet membranes containing amine solution were fixed by a steel model and then cleaned with delicate task wipers to remove the residual drops of NaOH solution on the PAN/PVP membrane surface. The cleaning membranes were immersed in 1v/v% TMC/toluene solution for different time of interfacial polymerization, and then washed with pure toluene solution to remove the residual TMC solution. The membranes were immersed in 75\% ethanol/H\textsubscript{2}O solution to remove the residual toluene, and then washed with deionized water to remove the residual ethanol. Finally, the composite amine/TMC NF membranes were stored in water.

The NF membranes storing in water phase were cut to a suitable size and set on a filtration equipment (The scheme of molecular/Pro stirred cell, spectrum). We chose MgSO\textsubscript{4} solution, NaCl solution, PEG200 solution, PEG1000 solution, PEG3400 solution, and PEG8000 solution to determine salt rejection and molecular weight cut off (MWCO). All feed solutions were 1000ppm. The operation pressure and filtration area were 4 atm and 11.95 cm\textsuperscript{2}. The salt permeate solutions were analyzed by a conductivity instrument (Shodex CD-5). The nature molecular permeate solutions were analyzed by RI detector (GL Sciences 504R). The rejection, R, was calculated using \[ R = \frac{(C_f - C_p)}{C_0} \] where \( C_f \) and \( C_p \) are the concentration of permeate and feed, respectively.

Results and discussions

Surface zeta potential measurements

The zeta potential of membrane surface was measured by a self-assembled flow chamber. The membranes were thoroughly washed by the solution containing 1000 ppm KCl. The pH of the solution was adjusted by a small amount of HCl or NaOH. Figure 1 showed the zeta potentials of membranes at various different pHs. It was found that the PEI/TMC membrane had a positive zeta potential at pH = 6–6.5. The estimated isoelectric point was 6.7. At a pH higher than 6.7, negative zeta potential was obtained. The zeta potential of EDA membrane was negatively charged at pH 6-6.5. The estimated isoelectric point was 4.8. The positive zeta potential was only observed at very low pH. The DETA membrane had an estimated pl value of 5.8, that was, the membrane was almost neutral at pH 6.0-6.5. The zeta potential curves showed zwitterionic behavior of DETA and PEI membranes. We could change the membrane charges from positive to negative by varying the pHs of filtered solutions.

Performance of the three membranes
The performance of these three nanofiltration membranes was tested by 1000 ppm of (a) MgSO$_4$, (b) MgCl$_2$, (c) Na$_2$SO$_4$, and (d) NaCl aqueous solution. Figure 3. and 4. compared the membrane rejection against sulfate salt with that against chloride salts. It was found from figure 4 that the DEA and DETA membranes rejected more sodium sulfate than sodium chloride. The similar observation was also found in Figure 3, which compared the rejections of magnesium sulfate and magnesium chloride. Apparently, the DEA and DETA membranes had higher rejections against sulfate salts than chloride salts. It was obviously due to the larger size and stronger negativity of sulfate ions. The PEI membranes had similar rejections against sulfate salts and chloride salts. The rejections against Na$_2$SO$_4$ and NaCl were similar. The MgSO$_4$ and MgCl$_2$ rejections were also similar. These results suggested that the salt rejection by the PEI membrane was mainly contributed by its positive charges, which rejected cations by charge repulsion.

Figure 3 and 4 compared the membrane rejection against magnesium salts with that against sodium salts. It was found that all the three membranes had a higher rejection toward magnesium than sodium salts. The higher magnesium salts rejection from the PEI membranes might be due to the positive charges on membranes, which rejected more divalent magnesium than monovalent sodium ions. The higher magnesium salts rejection from the DEA and DETA membranes may be due to their smaller pore sizes (Figure 2), which hindered the migration of magnesium ion through membranes.

Figure 1  Zeta potential of membranes at various pH values

Figure 2  The MWCO of three types NF membrane

Figure 3  Permeation properties of three type NF membrane and DK commercial membrane (MgSO$_4$, MgCl$_2$)

Figure 4  Permeation properties of three type NF membrane and DK commercial membrane (Na$_2$SO$_4$, NaCl)

Reference