Separation performances of a nanofiltration membrane for chlorides, nitrates and sulfates aqueous solutions

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ABSTRACT

Permeation experiments of a commercial nanofiltration membrane (nominated as ESNA 1) were carried out with aqueous solutions of various single salts, that is, five chlorides (NH_4Cl, $NaCl$, KCl, $MgCl_2$ and $CaCl_2$), three nitrates ($NaNO_3$, $Mg(NO_3)_2$ and $Ca(NO_3)_2$) and three sulfates (($NH_4)_2SO_4$, Na_2SO_4 and $MgSO_4$). The experimental results showed that (1) the permeate volume flux of the ESNA 1 membrane increased and decreased with the growth of the applied pressure and the feed concentration of salts, respectively. The real rejection of ESNA 1 membrane to most single salts increased with the growth of the permeate volume flux. (2) The reflection coefficients of ESNA 1 membrane to chlorides, nitrates and sulfates are 0.97, 0.96 and 0.99, respectively. The solute permeability of most salts except for magnesium and calcium salts increased with the growth of feed concentration. (3) The sequence of the rejections of ESNA 1 membrane to anions is $R(SO_4^{2-})$ > $R(Cl^-)$ > $R(NO_3^-)$ at the same feed concentration. While the sequence of the rejections to cations is cataloged into two cases: $R(Na^+)$ > $R(K^+)$ > $R(Mg^{2+})$ > $R(Ca^{2+})$ at the concentration of 10 mol/m^3 and $R(Mg^{2+})$ > $R(Ca^{2+})$ > $R(Na^+)$ > $R(K^+)$ at the concentration of 100 mol/m^3. The separation capability of a NF membrane is usually affected by the electrostatic effect and the steric-hindrance effect. In this case, the electrostatic effect is the major factor at low concentration and the steric-hindrance effect is the major factor at high concentration. Both the specific sorption and the hydration also reasonably influenced the separation performance of NF membrane to salts.

INTRODUCTION

Nanofiltration(NF) membranes have been largely developed for the past decade. NF membranes have two interesting features[1-3]: one is the intermediate molecular weight cut-offs(MWCO) between reverse osmosis(RO) membranes and ultrafiltration(UF) membranes, which ranges from 200 to 2000 Dalton; the other is salt rejection caused by the charge effect due to their materials. According to these two features, NF membranes have individually effect for production of high quality drinking water, which can be used for the removal of inorganic pollutants (such as hardness, nitrate, arsenic, fluorides and heavy metals) and organic pollutants (such as pesticides, trihalomethanes, hormone and natural organic matter)[4-6]. Furthermore, a great advantage of NF compared with RO is the applied pressure that can be much smaller while keeping relatively high permeate volume flux [7].

The knowledge of separation performance to inorganic salts by a NF membrane is always important in the development of NF processes for the removal of salts in water. Nowadays, the electrostatic and the steric-hindrance effects between the membrane and the external solutions are considered as the major factors that can be applied to explain the separation mechanism of the NF membrane process. The Electrostatic and Steric-hindrance (ES) model[8] and the Donnan-Steric Pore Model (DSPM)[9] are very successful in describing neutral molecules and univalent electrolytes. However, the quality of agreement with experimental data is less good in studies of multivalent cations such as Mg^{2+} and Ca^{2+}. This result is explained by the specific adsorption of cations which can reverse the sign of the NF membrane charge [10-13]. Recently, one new effect, dielectric exclusion, is introduced into the existing model. The inclusion of dielectric exclusion can

also account for the previous phenomenon [14-16].

In this work the separation capability of NF membrane is investigated. First, permeation experiments have been carried out with five chlorides, three nitrates and three sulfates under various conditions of the applied pressure and concentration. Next, the effects of the type and the feed concentration (c_b) of salts as well as the applied pressure (ΔP) on the separation performances of NF membrane (such as the permeate volume flux (J_v) and the real rejection (R_{real})) were investigated. Then, the reflection coefficient (σ) and solute permeability (P) of NF membrane were calculated by the Spiegler-Kedem equation from experimental data. Finally, the rejection sequences are discussed taking into consideration the separation mechanisms known.

THEORETICAL

Transport phenomena of UF, NF and RO membranes in pressure-driven processes can be described by irreversible thermodynamics model. The model assumes that the membrane is a black box, the relation of the volume flux (J_v) and the solute flux (J_s) through a membrane was originally given by Kedem and Katchalsky [17] in the following equations.

$$J_v = L_P \left(\Delta P - \sigma \cdot \Delta \pi \right) \tag{1}$$

$$J_s = P \cdot \left(c_m - c_p \right) + \left(1 - \sigma \right) \cdot J_v \bar{c} \tag{2}$$

where σ, P and L_P are the membrane parameters called reflection coefficient, solute permeability and pure water permeability, respectively. When high concentration difference between the retentate and the permeate exists, Spiegler and Kedem [18] expressed Eq. (2) in a differential form as follows:

$$J_s = -P' \left(\frac{dc}{dx} \right) + \left(1 - \sigma \right) J_v c \tag{3}$$

P' is the local solute permeability defined as $P' = P \cdot \Delta x$. Integrating Eq. (3) across the membrane thickness yields the rejection, R, as follows:

$$R = 1 - \frac{c_p}{c_m} = \frac{\sigma \left(1 - F \right)}{\left(1 - \sigma F \right)} \tag{4}$$

where $F = \exp\left(-\frac{1-\sigma}{P} J_v \right)$

Eq. (4) is the well-known Spiegler-Kedem equation. One can see that σ corresponds to the maximum rejection at infinite volume flux from Eq. (4). σ and P can be determined directly from experimental data of R as a function of J_v by a best-fit method.

For the cases of high concentration difference between the retentate and the permeate, $\sigma \approx 1$, Eq. (1) can be expressed in a simplified form as follows:

$$J_v \approx L_P \left(\Delta P - \Delta \pi \right) = L_P P_0 \tag{5}$$

where P_0 corresponds to the effective pressure to cause volumetric flux and $\Delta \pi$ is the osmotic pressure difference across the membrane which is approximately proportional to the salt concentration difference of the retentate and the permeate in the following equation[3].

$$\Delta\pi = RT\left(v_1 + v_2\right)\left(c_m - c_p\right) \qquad (6)$$

where R is gas constant, T is temperature, v_1 and v_2 are respectively stoichiometric coefficient of cations and anions, c_m and c_p are respectively the salt concentration of the membrane surface and the permeate.

On account of the effect of concentration polarization, the solute concentration of the membrane surface is higher than one of the feed solution. Therefore, according to Eq. (4) the real rejection (R_{real}) is more than the observed rejection (R_{obs}) which is the experimentally measured rejection. The concentration polarization equation[19] can be used to calculate R_{real} and c_m, that is expressed as:

$$\frac{c_m - c_p}{c_b - c_p} = \frac{R_{real}/(1-R_{real})}{R_{obs}/(1-R_{obs})} = \exp\left(J_v/k\right) \qquad (7)$$

where k is the mass transfer coefficient. The k value is generally represented as a function of the cross flow velocity, the diffusion coefficient of the solute and the hydraulic diameter of the flow channel etc., which can be calculated by using the semi-empirical equation.

EXPERIMENTAL

Membrane and solutes The NF membrane used in this study, labeled ESNA 1, is manufactured by Nitto Denko Corporation. The effective pore radius which can be estimated through the permeation experiments of neutral solutes with different Stokes radii [3] is about 0.3 nm. It is flat-sheet type and membrane area is 0.00353 m^2. Inorganic salts used in the experiment were NH$_4$Cl, NaCl, KCl, MgCl$_2$, CaCl$_2$, NaNO$_3$, Mg(NO$_3$)$_2$, Ca(NO$_3$)$_2$, (NH$_4$)$_2$SO$_4$, Na$_2$SO$_4$ and MgSO$_4$. The concentrations of solutes ranged from about 500 to 10000 mg/L and were measured with an electrical conductivity meter (model DDS-307) which was made by Shanghai LEICI Analysis Instruments Factory.

Permeation experiments The experimental set-up was described in the proceeding paper [20], which was from Nitto Denko Corporation. Both the retentate and the permeate were recycled back to the feed tank in order to keep a constant feed concentration of salts. The feed cross-flow rate(Q) and the applied pressure were adjusted through changing by-pass and outlet valve. Experimental conditions were as follows: temperature, 25 °C; pressure, 0.3~2.0 MPa; feed cross-flow rate, 5.7 L/min. After each experiment when salt nature is changed, the membrane was rinsed with deionized water until the conductivity of water was under 10 μS/cm and the initial membrane permeability was reached.

RESULTS AND DISCUSSION

The permeate volume flux and the real rejection Figure 1 shows the permeate volume flux of ESNA 1 membrane for NaCl as functions of the applied pressure and the effective pressure for different feed concentrations of salts. As shown in Fig. 1 (a), the permeate volume flux of ESNA 1 membrane as a function of the applied pressure can be plotted as a linear line with a wide range of salt feed concentrations. And the permeate volume flux decreased with increasing feed concentration of salts at the same applied pressure. According to Eqs. (5)~(7), the effective pressure can be obtained. Figure 1 (b) shows the dependency of the permeate volume flux of ESNA 1 membrane on the effective pressure and the pure water permeation flux (J_w). One can consider that the permeate volume flux is close to the pure water permeation flux of ESNA 1 membrane at the same effective pressure, irrespective of the feed concentration of inorganic salts.

Figure 2 shows the real rejections of NaCl, NaNO₃ and Na₂SO₄ as functions of permeate volume flux for various concentrations. With the help of the Spiegler-Kedem equation (4), the membrane parameters (σ and P) are fitted and the fitted curves are also demonstrated in Fig. 2.

Figure 2 illustrates that the real rejection of ESNA 1 membrane to most single salts increased with the growth of the permeate volume flux. The increase of the rejection with the water flux is a general phenomenon. Physically that occurs because the growth of the applied pressure causes a higher water flux whereas the anions and cations are electrically and sterically hindered, therefore, the permeation of the salt does not change that much.

Fig. 1 The permeate volume flux of ESNA 1 membrane to NaCl as functions of the applied pressure (a) and the effective pressure (b) at different feed concentrations.
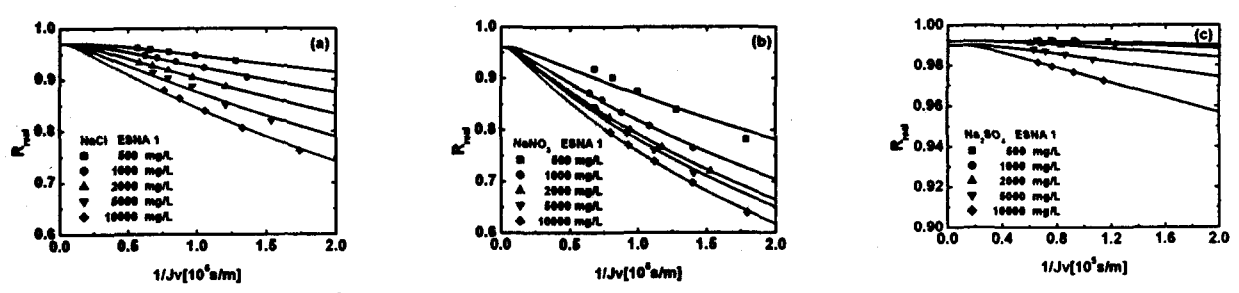

Fig. 2 The real rejection of ESNA 1 membrane to NaCl (a), NaNO₃ (b) and Na₂SO₄ (c) as functions of the permeate volume flux at different feed concentrations of salt.
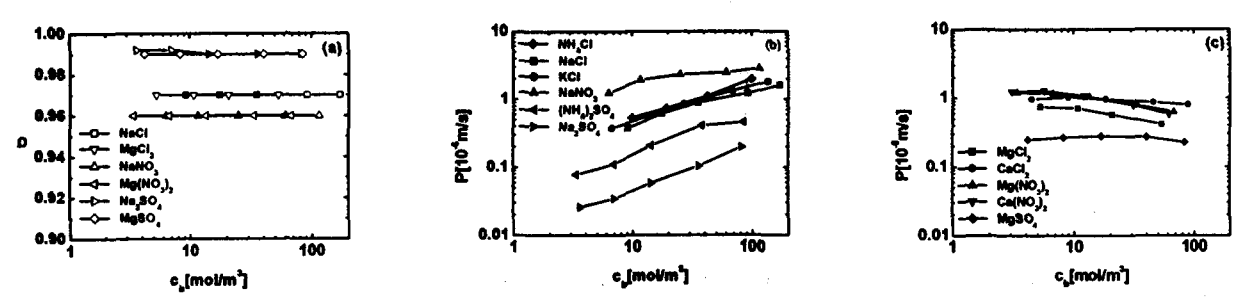

Fig. 3 The reflection coefficients (a) and the solute permeability (b and c) of ESNA 1 membrane to inorganic salts as functions of the feed concentration.

The reflection coefficient and the solute permeability Figure 3 shows the dependency of the reflection coefficient and the solute permeability of ESNA 1 membrane on the feed concentration. As shown in Fig. 3 (a), the reflection coefficients of ESNA 1 membrane for chlorides, nitrates and sulfates are respectively 0.97, 0.96 and 0.99. The reason for this phenomenon may be that the ESNA 1 membrane is negative charged membrane and has high enough surface charge density to keeping the electrostatic effect constant. In Fig. 3 (b) and (c), the solute permeability for most

inorganic salts except for magnesium and calcium salts increase with the growth of feed concentration. The reason for the increase of the solute permeability with increasing feed concentration of inorganic salts is that the effective area of the membrane pore becomes larger due to the thickness of electrical double layer being thinner. However, because the Stokes radii which is calculated from the Stokes-Einstein equation($r_s = kT/6\pi\mu D_s$) of Mg^{2+} and Ca^{2+} are larger than those of NH_4^+, Na^+, K^+, Cl^-, NO_3^- and SO_4^{2-}, the change of the effective area of the membrane pore can hardly effect the solute permeability for magnesium and calcium salts.

The rejection sequence Figure 4 shows the real rejection of ESNA 1 membrane to NH_4Cl, NaCl, KCl, $MgCl_2$, $CaCl_2$, $NaNO_3$, $Mg(NO_3)_2$, Na_2SO_4 and $MgSO_4$ as functions of the permeate volume flux at the same feed concentrations. The curves in Fig. 4 are plotted by the Spiegler-Kedem equation (4), and the membrane parameters (σ and P) were obtained through interpolation according to Fig. 3. From Fig. 4 (a), the rejection sequence of ESNA 1 membrane on anions can be written as follows: $R(SO_4^{2-}) > R(Cl^-) > R(NO_3^-)$. The same rejection sequence of ESNA 1 membrane on anions can be obtained from Fig. 4 (b). Fig. 4 (c) and (d) show that the rejection sequence of ESNA 1 membrane on cations can be written as follows: $R(Na^+) > R(K^+) > R(Mg^{2+}) > R(Ca^{2+})$ at 10 mol/m^3 concentration and $R(Mg^{2+}) > R(Ca^{2+}) > R(Na^+) > R(K^+)$ at 100 mol/m^3 concentration.
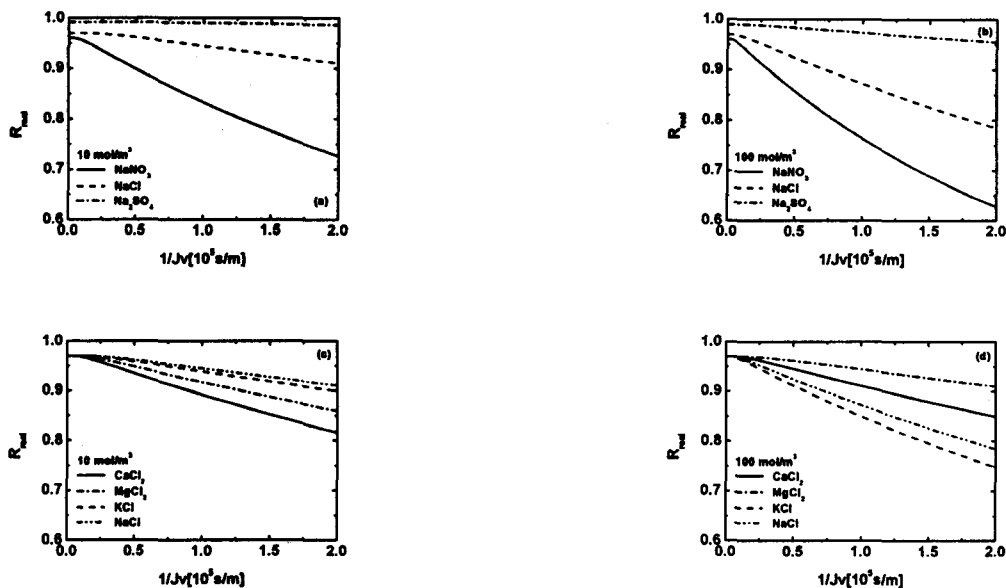

Fig. 4 The real rejection of ESNA 1 membrane to inorganic salts as functions of the permeate volume flux at the same feed concentrations.

For the different valence ions, the anionic rejection sequence and the cationic rejection sequence at 10 mol/m^3 concentration can be explained by the Donnan exclusion theory which suggests that for single salt solution, a higher valence co-ion caused a higher ion rejection whereas a higher valence counter-ion leads to a lower rejection of the salt. For the same valence ions, the rejection sequence could be affected by the difference in ion diffusion coefficients (D), i.e. an ion is the more retained as it has the smaller diffusion coefficient. Indeed, the order of ion diffusion coefficients is $D(Na^+) < D(K^+)$, $D(Mg^{2+}) < D(Ca^{2+})$, which is inversely reflected in the rejection sequence.

However, $R(Cl^-) > R(NO_3^-)$ can not be explained by this theory because the diffusion coefficient of nitrate ion is smaller than one of chloride ion. One assumption was reported in order to explain this phenomenon [5], which is that the nitrate ion having a larger molar volume

corresponding larger surface area would have lower surface charge density round the molecule comparing to the smaller molar volume of chloride ion, so the electrostatic effect between the nitrate ion and the membrane was weaker and the observed rejection to nitrate ions was lower.

One hypothesis was reported in order to explain the cationic rejection sequence at 100 mol/m^3 concentration, which is that the NF membrane appeared to be positively charged in presence of Mg^{2+} and Ca^{2+} by the means of adsorption at high salt feed concentration, so this phenomenon can be explained by the Donnan exclusion theory. Nevertheless the anionic rejection sequence at 100 mol/m^3 concentration can not be explained according to the hypothesis. Wang et al.[12] suggested that the steric-hindrance effect is the major factor at high salt feed concentration which influenced the separation capability of NF membrane. According to the Electrostatic and Steric-hindrance (ES) model, the steric-hindrance effect is increasing with the ratio of solute radius(r_s) to pore radius(r_p), where r_s is Stokes radius of solute. The order of ionic Stokes radii is $r_s(Mg^{2+}) > r_s(Ca^{2+}) > r_s(Na^+) > r_s(K^+)$, so the rejection sequence at 100 mol/m^3 concentration is $R(Mg^{2+}) > R(Ca^{2+}) > R(Na^+) > R(K^+)$. However, $R(Cl^-) > R(NO_3^-)$ can not be explained by the ES model, because $r_s(Cl^-)$ is a little smaller than $r_s(NO_3^-)$. One supposition is that the hydration between the nitrate ion and water results in the lower observed rejection of NF membrane to nitrate ions.

ACKNOWLEDGEMENTS

REFERENCES

[1] R. Rautenbach, A. Groschl, *Desalination*, **77** (1990) 73.

[2] P. Schirg, F. Widmer, *Desalination*, **89** (1992) 89.

[3] X.L. Wang, T. Tsuru, M. Togoh, *et al.*, *J. Chem. Eng. Jpn.*, **28** (1995) 186.

[4] B. Van der Bruggen, K. Everaert, D. Wilms *et al.*, *J. Membr. Sci.*, 193 (2001) 239.

[5] M. Thanuttamavong, K. Yamamoto, J.I. Oh, *et al.*, *Desalination*, **145** (2002) 257.

[6] A.I. Schäfer, L.D. Nghiem, T.D. Waite, *Environ. Sci. Technol.*, 37 (2003) 182.

[7] H. Nicoll, *Filtr. Separat.*, **38** (2001) 22.

[8] X.L. Wang, T. Tsuru, S. Nakao, *et al.*, *J. Membr. Sci.*, **135** (1997) 19.

[9] W.R. Bowen, A.W. Mohammad, N. Hilal, *J. Membr. Sci.*, **126** (1997) 91.

[10] J.M.M. Peeters, J.P. Boom, M.H.V. Mulder *et al.*, *J. Membr. Sci.*, **145** (1998) 199.

[11] J. Schaep, C. Vandecasteele, A.W. Mohammad, *et al.*, *Sep. Sci. Technol.*, **34** (15) (1999) 3009.

[12] X.L. Wang, W.N. Wang, D.X. Wang, *Desalination*, **145** (2002) 115.

[13] C. Labbez, P. Fievet, A. Szymczyk, *et al.*, *Sep. Pur. Technol.*, **30** (2003) 47.

[14] A.E. Yaroshchuk, *Sep. Pur. Technol.*, **22-23** (2001) 143.

[15] W.R. Bowen, J.S. Welfoot, *Chem. Eng. Sci.*, **57** (2002) 1121.

[16] S. Bandini, D. Vezzani, *Chem. Eng. Sci.*, **58** (2003) 3303.

[17] O. Kedem, A. Katchalsky, *Trans. Faraday Soc.*, **59** (1963) 1918.

[18] K.S. Spiegler, O. Kedem, *Desalination*, **1** (1966) 311.

[19] S. Kimura, S. Sourirajan, *AIChE J.*, **13** (1967) 497.

[20] X.L. Wang, A.L. Ying, W.N. Wang, *J. Membr. Sci.*, **196** (2002) 59.