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Application of Pitzer's electrolyte solution theory to frictional model of charged nanofiltration membrane[1]

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Abstract

Using Pitzer's electrolyte solution theory to calculate volumetric properties of electrolyte solution, the apparent frictional coefficients, f_{ij}^* of the friction model for the aqueous NaCl-weak polyacid membrane system were calculated and compared with those of $NaNO_3$-similar membrane system. These values of apparent frictional coefficients between membrane and water, f_{mw}^* were very close to one another, and the frictional coefficients between membrane and solute, f_{ms}^*, and between water and solute, f_{ws}^*, were significantly different in both systems. This difference can be explained by ionic hydration. © 1998 Elsevier Science B.V.

Keywords: Electrolyte nanofiltration; Friction model; Ion-exchange membrane; Ionic hydration; Pitzer's theory

1. Introduction

The physical interpretation of the membrane process has been provided by 'friction models' introduced by Spiegler [1] for ion-exchange membrane, and applied to formed-in-place Zr(IV) hydrous oxide-polyacrylate membranes (FIP–ZPA membrane) by Szaniawska and Spencer [2]. The aims of this paper were three-fold: (1) to obtain the frictional coefficients of a friction model from the nanofiltration data for the NaCl solution-weak polyacid membrane system measured by Szaniawska and Spencer [3], (2) introduce Pitzer's electrolyte solution theory into the membrane processes, and (3) compare the values of the frictional coefficient for the NaCl solution with those of the $NaNO_3$ solution obtained by us [3] for the FIP–ZPA membrane.

2. Procedure

According to the friction model, the driving forces for any species in the steady state are balanced by the frictional forces exerted on it by other components including the membrane. These frictional forces, F_{ij}, are proportional to the mean relative velocities of the components i and j

$$F_{ij} = f_{ij}(u_i - u_j) \tag{1}$$

where f_{ij} is the frictional coefficient between components i and j, and u_i and u_j the mean linear velocities of the respective components. When one of the species is the membrane, its velocity is normally set equal to zero. Thus, the membrane will be the reference component.

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The total force acting on water and salt is written by using general equations

$$F_{\mathrm{w}} = (\bar{c}_{\mathrm{s}}/\bar{c}_{\mathrm{w}})f_{\mathrm{sw}}(u_{\mathrm{w}} - u_{\mathrm{s}}) + f_{\mathrm{wm}}(u_{\mathrm{w}} - u_{\mathrm{m}}) \tag{2}$$

$$F_{\mathrm{s}} = f_{\mathrm{sw}}(u_{\mathrm{s}} - u_{\mathrm{w}}) + f_{\mathrm{sm}}(u_{\mathrm{s}} - u_{\mathrm{m}}) \tag{3}$$

where $\bar{c}_{\mathrm{s}}$ and $\bar{c}_{\mathrm{w}}$ are the concentration of solute and water in membrane, subscripts m, s and w mean membrane, solute and water, respectively.

The practical transport coefficients L_{p}, σ and ω obtained from irreversible thermodynamical analysis can be used to evaluate the frictional coefficients. The following equations were used to show the relation between practical transport coefficients and frictional coefficients from the friction model for the membrane process [5].

$$f_{\mathrm{sw}} = (1 - \sigma - \omega\bar{V}_{\mathrm{s}}/L_{\mathrm{p}}) \oint_{\mathrm{w}} /\omega d \tag{4}$$

$$f_{\mathrm{sm}} = (\sigma + \omega\bar{V}_{\mathrm{s}}/L_{\mathrm{p}}) \oint_{\mathrm{w}} /\omega d \tag{5}$$

$$f_{\mathrm{wm}} = (\oint_{\mathrm{w}} \bar{V}_{\mathrm{w}}/d)[(1/L_{\mathrm{p}}) - (1 - \sigma)(\sigma + \omega\bar{V}_{\mathrm{s}}/L_{\mathrm{p}})(\bar{c}_{\mathrm{s}}/\omega)] \tag{6}$$

where L_{p} denotes the hydrodynamic permeability coefficient, σ the reflection coefficient, ω the solute permeability coefficient, $\bar{V}_{\mathrm{s}}$ and V_{w} the partial molal volume of solute and water, respectively, $\oint_{\mathrm{w}}$ the water content of the membrane, d the membrane thickness. But it is difficult to measure the values of $\oint_{\mathrm{w}}$ and d, so that the apparent frictional coefficients, f_{ij}^{*}, have been introduced according to the expressions

$$f_{\mathrm{sw}}^{*} = df_{\mathrm{sw}}/\oint_{\mathrm{w}} \tag{7}$$

$$f_{\mathrm{sw}}^{*} = df_{\mathrm{sm}}/\oint_{\mathrm{w}} \tag{8}$$

$$f_{\mathrm{wm}}^{*} = df_{\mathrm{wm}}/\oint_{\mathrm{w}} \tag{9}$$

In Eqs. (4)–(6), the partial molal volumes of solute and water, $\bar{V}_{\mathrm{s}}$ and $\bar{V}_{\mathrm{w}}$, can be calculated by Pitzer's electrolyte solution theory.

According to the thermodynamic relationship, the total volume of solution V, is given by the pressure derivative of the total Gibbs energy of the solution at a constant temperature,

$$V = (\partial G/\partial P)_T \tag{10}$$

where G is the Gibbs energy of solution. The definition of the excess Gibbs energy G^{EX} is

$$G = n_{\mathrm{w}}G_{\mathrm{w}}^{0} + n_{\mathrm{s}}G_{\mathrm{s}}^{0} + G^{\mathrm{EX}} + n_{\mathrm{s}}\nu RT(\ln m - 1) \tag{11}$$

where m denotes the molality. The pressure derivative of G becomes

$$V = n_{\mathrm{w}}\bar{V}_{\mathrm{w}}^{0} + n_{\mathrm{s}}\bar{V}_{\mathrm{s}}^{0} + (\partial G^{\mathrm{EX}}/\partial P)_T \tag{12}$$

where $\bar{V}_{\mathrm{w}}^{0}$ and $\bar{V}_{\mathrm{s}}^{0}$ are partial molar volumes of water and the solute at infinite dilution, respectively. The apparent molar volume φ_{v} is defined as

$$\varphi_{\mathrm{v}} = \bar{V}_{\mathrm{s}}^{0} + (1/n_{\mathrm{s}})(\partial G^{\mathrm{EX}}/\partial P)_T \tag{13}$$

where n_{w} and n_{s} are mole numbers of water and solute, respectively. According to Pitzer's theory [6,7], G^{EX} may be expressed as

$$\begin{aligned}1000G^{\mathrm{EX}}/(n_{\mathrm{w}}M_{\mathrm{w}}RT) &= -A_{\varphi}(4I/1.2) \\ &\times \exp(1 + 1.2I^{1/2}) + 2m^2\nu_{\mathrm{m}}\nu_{\mathrm{x}}\{\beta_{\mathrm{MX}}^{(0)} \\ &+ (2\beta_{\mathrm{MX}}^{(1)}/4I)[1 - (1 - 2I^{1/2})\exp(-2I^{1/2})]\} \\ &+ m^3(\nu_{\mathrm{X}}\nu_{\mathrm{M}})^{3/2}C_{\mathrm{MX}}^{\varphi}\end{aligned} \tag{14}$$

where M_{w} represents the molar mass of water, $\beta_{\mathrm{MX}}^{(0)}$, $\beta_{\mathrm{MX}}^{(1)}$ and $C_{\mathrm{MX}}^{\varphi}$ Pitzer's parameters, ν_{M} and ν_{X} mole numbers of positive and negative ions produced by dissociation of 1 mol MX electrolyte, respectively, and $\nu_{\mathrm{M}}+\nu_{\mathrm{X}}=\nu$, $I = (1/2)\sum mZ_{\mathrm{i}}^2$ the ionic strength of solution, A_{φ} the Debye–Hückel coefficient for the osmotic function as defined by

$$A_{\varphi} = (1/3)(2\times3.14N_0\rho/1000)^{1/2}[e^2/(DkT)]^{3/2}$$

where N_0 is the Avogadro constant, k the Boltzman constant, e the electron charge, ρ and D the density and dielectric constant of pure water, respectively. The substitution of Eq. (14) into Eq. (13) yields

$$\varphi_{\mathrm{v}} = \bar{V}_{\mathrm{s}}^{0} + \nu|Z_{\mathrm{M}}Z_{\mathrm{X}}|A_{\mathrm{v}}h(I) + 2\nu_{\mathrm{M}}\nu_{\mathrm{X}}RT[mB_{\mathrm{MX}}^{\mathrm{v}} + m^2(\nu_{\mathrm{M}}Z_{\mathrm{M}})C_{\mathrm{MX}}^{\mathrm{v}}] \tag{15}$$

where Z_{M} and Z_{X} are charge numbers of positive and negative ions, respectively. Some quantities in Eq. (15) were defined by the following equations

$$h(I) = \ln(1 + 1.2I^{1/2})/2.4 \tag{16}$$

$$B^{\mathrm{v}}_{\mathrm{MX}}(I) = (\partial B_{\mathrm{MX}}/\partial P)_{T,I} \tag{17}$$

$$C^{\mathrm{v}}_{\mathrm{MX}} = (\partial C_{\mathrm{MX}}/\partial P)_T \tag{18}$$

$$B_{\mathrm{MX}}(I) = \beta^{(0)}_{\mathrm{MX}} + 2\beta^{(1)}_{\mathrm{MX}}[1 - (1 + 2I^{1/2}) \times \exp(-2I^{1/2})/4I \tag{19}$$

$$C_{\mathrm{MX}} = C^{\varphi}_{\mathrm{MX}}/2|Z_{\mathrm{M}}Z_{\mathrm{X}}|^{1/2} \tag{20}$$

$$A_{\mathrm{v}} = 2A_{\varphi}RT[3(\partial \ln D/\partial P)_T + (\partial \ln V_{\mathrm{w}}/\partial P)_T] \tag{21}$$

Rogers and Pitzer [7] pointed out that in preliminary isothermal, isobaric calculations, the pressure dependence of $\beta^{(1)}_{\mathrm{MX}}$ could be approximated to be zero with an reasonable accuracy. Therefore,

$$(\partial\beta^{(1)}_{\mathrm{MX}}/\partial P)_T = 0$$

this means

$$B^{\mathrm{v}}_{\mathrm{MX}} = (\partial\beta^{(0)}_{\mathrm{MX}}/\partial P)_T \tag{22}$$

In order to calculate the $B^{\mathrm{v}}_{\mathrm{MX}}$ and $C^{\mathrm{v}}_{\mathrm{MX}}$ for NaCl aqueous solution following empirical equations were obtained by Rogers and Pitzer [7]

$$\begin{aligned} B^{\mathrm{v}}_{\mathrm{MX}} = {} & U_1 + U_2/2(T - 277) + U_3T + U_4T^2 \\ & + U_5/(680 - T) + (p - p_0) \\ & \times [U_6 + U_7/(T - 277) + U_8T + U_9T^2 \\ & + U_{10}/(680 - T)] + (p - p^0)^2 \\ & \times [U_{11} + U_{12}/(T - 277) + U_{13}T \\ & + U_{14}T^2 + U_{15}/(680 - T)] \end{aligned} \tag{23}$$

$$\begin{aligned} C^{\mathrm{v}}_{\mathrm{MX}} = {} & U_{15} + U_{16}/(T - 227) + U_{17}T + U_{18}T^2 \\ & + U_{19}/(680 - T) \end{aligned} \tag{24}$$

where U_i's are empirical constants, their values for NaCl aqueous solution obtained from volumetric experimental data [7] are listed in Table 1. In Eqs. (23) and (24), T is the temperature in Kelvin, P the pressure in bar (0.1 MPa), P^0= 0.101325 MPa.

The expressions of partial molar volume are

$$\overline{V}_{\mathrm{s}} = \varphi_{\mathrm{v}} + (m^{1/2}/2)(\partial\varphi_{\mathrm{v}}/\partial\sqrt{m}) \tag{25}$$

$$\overline{V}_{\mathrm{w}} = V^0_{\mathrm{w}} - (M_{\mathrm{w}}/2000)m^{3/2}(\partial\varphi_{\mathrm{v}}/\partial\sqrt{m}) \tag{26}$$

Table 1
The values of U_i for NaCl aqueous solution [7]

i	U_i
1	−2.1451068E-5
2	2.2324909E-3
3	−6.4950599E-8
4	2.4503020E-10
5	0
6	1.0033371E-7
7	−1.2784026E06
8	−4.6468063E-10
9	5.7054131E-3
10	0
11	0
12	1.3581172E-10
13	0
14	0
15	−6.815243E-6
16	2.5382945E-4
17	6.2480692E-8
18	−1.0731284E-10
19	0

Making the derivative of Eq. (15) with respect to $\sqrt{m}$, and substituting it into Eqs. (25) and (26) they become

$$\begin{aligned} \overline{V}_{\mathrm{s}} = {} & \overline{V}^0_{\mathrm{s}} + (Av/1.2)[\ln(1 + 1.2I^{1/2}) \\ & + I^{1/2}/2(1 + 1.2I^{1/2})] \\ & + 2RT[2mB^{\mathrm{v}}_{\mathrm{MX}} + 3m^2C^{\mathrm{v}}_{\mathrm{MX}}] \end{aligned} \tag{27}$$

$$\begin{aligned} \overline{V}_{\mathrm{w}} = {} & \overline{V}^0_{\mathrm{w}} - M_{\mathrm{w}}m^{3/2}Av/[2000(1 + 1.2I^{1/2})] \\ & - 4RTm^2M_{\mathrm{w}}B^{\mathrm{v}}_{\mathrm{MX}}/2000 \\ & - 8RTm^3M_{\mathrm{w}}C^{\mathrm{v}}_{\mathrm{MX}}/2000 \end{aligned} \tag{28}$$

where the value of Av has been obtained by Bradley and Pitzer [8] over a wide region of temperature and pressure.

3. Results and discussion

Szaniawska and Spencer [3] investigated the nanofiltration of 0.02–1.0 mol/dm^3 sodium chloride solutions at 313.15 K over the pressure range of 1.5–5.5 MPa at pH 4.0, 6.0 and 8.0 with a dynamically formed Zr(IV) hydrous oxide-PAA membrane and obtained the practical transport coefficients, L_{p}, σ and ω for this system in term of the linear and nonlinear relationships of the thermodynamics of irrever-

Table 2

Apparent frictional coefficients f_{ij}/(m^2 s MP mol^{-1}) for an FIP–ZPA membrane in aqueous solution of NaCl at 40°C calculate from practical transport coefficients obtained by the nonlinear analysis procedure

pH	c/(mol dm^{-3})	f^*_{wm}	f^*_{sw}	f^*_{sm}	S	σ
8.0	0.02	3.1 (5.0)	83 (43)	630 (624)	0.12	0.88
	0.1	3.0 (4.8)	130 (54)	260 (158)	0.34	0.66
	0.5	3.2 (4.3)	100 (8.2)	50 (22)	0.69	0.30
	1.0	5.3 (4.3)	260 (4.6)	98 (15)	0.75	0.25
6.0	0.02	2.0	230	320	0.42	0.58
	0.1	2.0	300	260	0.54	0.46
	0.5	2.3	100	30	0.79	0.20
	1.0	3.8	250	65	0.81	0.19
4.0	0.02	1.4 (3.4)	200 (197)	130 (238)	0.61	0.39
	0.1	1.6 (2.8)	220 (13)	140 (30)	0.62	0.38
	0.5	1.7 (28)	96 (16)	22 (8.9)	0.83	0.17
	1.0	2.8 (2.8)	200 (2.7)	42 (7.2)	0.84	0.16

Note: In order to compare with $f^*_{\mathrm{sw}}, f^*_{\mathrm{wm}}$ and f^*_{sm} obtained by us from the nanofiltration of $NaNO_3$ with a dynamically formed Zr (IV) hydrous oxide-PAA membrane are listed in brackets in this table.

sible processes. In this paper their experimental data, L_p, σ and ω, were converted into apparent frictional coefficients, $f^*_{\mathrm{sw}}, f^*_{\mathrm{wm}}$ and f^*_{sm} using Eqs. (7)–(9) and the results are listed in Table 2. This conversion is based on the assumption that three types of interactions are encountered in the membrane: interaction between solute and water in the membrane described by f^*_{sw}; interaction between water and the membrane described by f^*_{wm} and; the interaction between solute with the membrane represented by f^*_{sm}. In order to compare the values with similar experimental data, the values of f^*_{sw}, f^*_{wm} and f^*_{sm} obtained by us from the nanofiltration of aqueous $NaNO_3$ with a dynamically formed Zr(IV) hydrous oxide-PAA membrane are also listed in brackets in Table 2 [4].

The comparisons shows that values of $f^*_{\mathrm{wm},cl}$ for the NaCl experiments are very close to $f^*_{\mathrm{wm,NO}}$ for the $NaNO_3$ experiments, where subscript Cl and NO denote NaCl and $NaNO_3$ aqueous solution, respectively. This means that the properties of the membranes used in these experiments are very similar, that is, they are all FIP–ZPA membranes. But the values of $f^*_{\mathrm{ms},cl}$ and $f^*_{\mathrm{sw},cl}$ for the NaCl experiments are significantly different from $f^*_{\mathrm{ms,NO}}$ and $f^*_{\mathrm{sw,NO}}$ for the $NaNO_3$ ones. The values of $f^*_{\mathrm{ms},cl}$ and $f^*_{\mathrm{sw},cl}$ are larger than those of the $NaNO_3$ experiments at the same concentration except dilute solution 0.02 mol/dm^3. This is because of the difference of hydration between NO_3^- and Cl^-. Hydrated ion has a definite geometric structure. When the hydrated ion is pressured through the pore of the membrane, the hydrated ion's geometric structure has been crushed out of shape, that is the water molecules around the ion have been partially dehydrated. The stronger the hydrated structure, the more difficult to be crushed out of shape under the same condition. The hydration of Cl^- is stronger than NO_3^-; hydration number 7.9 for NaCl and 1.8 for $NaNO_3$ [9]. Since the hydration of NO_3^- is weaker than Cl^-, NO_3^- is easier to go through the membrane and the values of $f^*_{\mathrm{sm,NO}}$ and $f^*_{\mathrm{sw,NO}}$ for the NO_3^- experiments are smaller than those of $f^*_{\mathrm{ms},cl}$ and $f^*_{\mathrm{sw},cl}$ for the NaCl experiments.

A relationship between the reflection coefficient at osmotic pressure π=0, i.e. $(\sigma)_{\pi=0}$, and the product of an exclusion or distribution term, K, and a kinetic or transport term, S, a function of frictional coefficient ratios, were also reported by Spiegler and Kedem [10].

$$\sigma = 1 - KS \tag{29}$$

where

$$K = (\bar{c}_{\mathrm{s}}/c_{\mathrm{s}})/(\bar{c}_{\mathrm{w}}/c_{\mathrm{w}}) \tag{30}$$

and

$$S = [1 + (f^*_{\mathrm{wm}}/f^*_{\mathrm{sw}})(\bar{V}_{\mathrm{s}}/\bar{V}_{\mathrm{w}})/[1 + f^*_{\mathrm{sm}}/f^*_{\mathrm{sw}}] \tag{31}$$

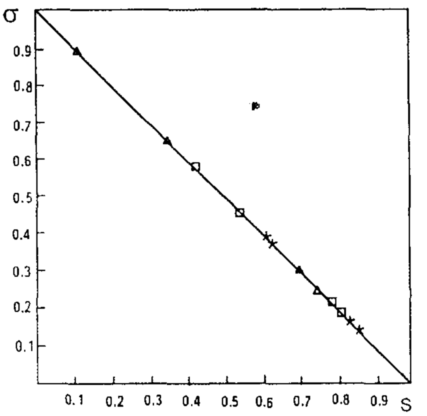

Fig. 1. σ versus S. △ – pH=8.0; □ – pH=6.0; ★ – pH=4.0.

Eqs. (8), (9) and (31) are correct expressions for f^*_{sm}, f^*_{sw} and S for a membrane modeled by water-filled capillaries. In this model the value of K is unity. As a test of the model, the experimental values of σ obtained at pH=4.0, 6.0 and 8.0 in literature [3] were plotted against the values of S calculated from f^*_{ij} in Table 2 by Eq. (31). Fig. 1 shows a good linear dependence of σ on S with a intercept of 1.001, a slope ca. −1.00 and correlation coefficient of 0.9999. The estimated value of K=1.00 supports the assumption that the membrane can be modeled as water-filled capillaries. The constant value of K which is unity within experimental error, over the range of pH and concentration implies that the kinetic term, S, determines the values of σ.

4. Symbols

A_φ	Debye–Hückel coefficient of osmotic function
B_{MX}	as defined by Eq. (19)
$B^{\mathrm{v}}_{\mathrm{MX}}$	as defined by Eq. (17)
c	concentration, mol/dm^3
$C^{\mathrm{v}}_{\mathrm{MX}}$	as defined by Eq. (18)
e	electron charge
f_{ij}	friction coefficient
f^*_{ij}	apparent friction coefficient as defined by Eqs. (7)–(9)
F_{ij}	frictional force
G^{EX}	excess Gibbs free energy of the solution
h(I)	function defined by Eq. (16)
K	as defined by Eq. (29)
I	ionic strength
L_{P}	hydrodynamic permeability coefficient m/(sMPa)
m	molality, mol/kg
P	pressure, MPa
S	as defined by Eq. (30)
u_i	mean linear velocity of species i
$\overline{V}$	partial mole volume, m^3
Z_{i}	charge numbers of positive and negative ion
$\beta^{(i)}_{\mathrm{MX}}$	Pitzer's parameters of electrolyte MX
ν_{i}	molar numbers of ion, i, in a mole electrolyte
π	osmotic pressure, MPa
σ	reflection coefficient
φ_{v}	apparent molar volume
ω	solute permeability coefficient, mol/(m^2 sMPa)

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