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Reverse Osmosis Transport of Alkali Halides and Nickel Salts through Cellulose Triacetate Membranes. Performance Prediction from NaCl Experiments*

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Abstract

The separation of alkali metal halides, nickel chloride, and nickel sulfate was determined for cellulose triacetate reverse osmosis (CTA RO) membranes. From transport analysis, the relative free energy parameters for transport of these salts through CTA membranes were determined. From these relative free energy parameters of salts, the solute separation by CTA membranes could be predicted from RO experiment with NaCl solution. The transport analysis and an illustration of how the concept is useful are presented in this paper.

INTRODUCTION

To design reverse osmosis (RO) systems for specific applications, one needs to analyze the effect of operating conditions and the nature of the feed solution on the performance. Reverse osmosis transport of ions has been analyzed from the standpoint of thermodynamics of ions in solution and in the membrane. The analyses based on the enthalpy of hydration by Fang and Chian (*1*), the concept of partial molal free energy of hydration by Johnston (*2*), and the free energy parameter by Sourirajan et al. (*3–7*) are well documented in the literature. The concept of a free energy parameter developed by Matsuura et al. (*3*) can be successfully extended to the case of a mixture of inorganic ions (*7*) as well as to a system as complex as seawater (*8*). A general approach to prediction of RO performance with a feed system containing several ions was illustrated by Rangarajan et al.

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(*9*). For the application of the concept to a membrane system which uses a cellulose triacetate membrane, it is necessary to determine the free energy parameters (FEP) for different ions in cellulose triacetate (CTA) membranes. However, the procedure used, while similar to that of Matsuura et al. (*3*), necessitated a negative value for the correction factor for ionic radii in a CTA membrane. In order to circumvent the situation, it was decided to generate a relative free energy parameter (RFEP) with respect to sodium chloride, and it was found that such an approach yielded a reliable prediction scheme for RO performance with different electrolytes. Such RFEPs were determined for a few ions of special interest in industrial wastes, and these are reported in this paper.

EXPERIMENTAL

Cellulose triacetate membranes were made from casting solutions containing CTA, dioxane–acetone mixed solvent (with a dioxane–acetone ratio of 1.38), maleic anhydride, and methanol in the ratio 9.5:76.5:5:9. Membranes were cast on glass plates to a thickness of 130–150 μm and gelled in a water bath kept at a temperature of 0–2°C after different evaporation periods to obtain membranes with different NaCl separations (rejections). In RO experiments with different feed solutions, the membranes made as described above were used without any annealing treatment. The operating pressure and feed flow rate employed were 600 psig (40.8 kg/cm^2, 4133 kPa) and 730 mL/min, respectively. The test membrane area was 15.38 cm^2. With different feeds, the membrane-permeated solution was collected for a definite time in order to evaluate the product rate (PR) in liters per square meter per day (lmd) and to determine the concentration of solute in the permeate. The feeds used were 1) KF, 2) KCl, 3) KBr, 4) RbCl, 5) CsCl, 6) KI, 7) $NiCl_2$, and 8) $NiSO_4$. The concentration of all alkali halides were determined by conductivity using conductivity vs concentration calibration curves. Nickel was determined by atomic absorption spectrophotometry. The separation of salts was calculated from their concentration, C, in the feed and the permeate by using the relation given below. The subscripts F and P represent the feed and permeate, respectively.

$$\%\ \text{Separation (or rejection)},\ f = \frac{C_F - C_P}{C_F} \times 100$$

The product rates determined at the temperature of the experiments are converted to 25°C with the density–viscosity correction factor. The pure water permeability (PWP) was determined for all membranes before runs with salt solutions.

RESULTS AND DISCUSSION

From PWP, PR, and *f* for all the seven CTA membranes listed in Tables 1 and 3, A, $D_{AM}/K\delta$, and k were determined by using the Kimura–Sourirajan analysis by solving the following simultaneous transport equations (*10*). $D_{AM}/K\delta$ and k obtained from NaCl experiments carry the subscript NaCl.

$$\text{Pure water permeability constant, } A = \frac{\text{PWP}}{M_B \times S \times P \times 3600} \tag{1}$$

$$\text{Solvent flux, } N_B = \frac{\text{PR}}{3600 \times 18 \times S} \times (1\text{–}10^{-3}\text{m}_3 M_A) \tag{2}$$

$$= A[P - \pi(X_{A2}) + \pi(X_{A3})] \tag{3}$$

$$= \left(\frac{D_{AM}}{K\delta}\right)\left(\frac{1 - X_{A3}}{X_{A3}}\right)(c_2 X_{A2} - c_3 X_{A3}) \tag{4}$$

$$\text{Solute flux, } N_A = \left(\frac{D_{AM}}{K\delta}\right)(c_2 X_{A2} - c_3 X_{A3}) \tag{5}$$

A and $(D_{AM}/K\delta)_{NaCl}$ determined for the CTA membranes by using NaCl data are presented in Table 1.

TABLE 1

Characterization of CTA Membranes by Kimura–Sourirajan Analysis with NaCl Data

Membrane area = 15.38×10^{-4} m^2
Feed flow rate = 7.3×10^{-4} m^3/min
Operating pressure = 32.75 atm (3318 kPa)

Membrane	NaCl separation (%)	$A \times 10^6$ (kg·mol/m^2·S·kPa)	$-\ln\left(\frac{D_{AM}}{K\delta}\right)_{NaCl}$
1	63.6	1.66	12.16
2	68.8	1.70	12.40
3	89.8	1.31	14.48
4	38.2	2.72	11.23
5	38.9	2.44	12.04
6	91.9	1.35	14.86
7	93.3	1.21	15.01

Matsuura et al. (*3*) derived the following expression relating $D_{\mathrm{AM}}/K\delta$ and the free energy parameter FEP as follows:

$$\ln\,(D_{\mathrm{AM}}/K\delta)_{\mathrm{NaCl}} = \ln\,C^{*}_{\mathrm{NaCl}} + \left(\frac{-\Delta\Delta G}{RT}\right)_{i} \tag{6}$$

where the summation is carried out for Na^{+} and Cl^{-} ions and $-\Delta\Delta G/RT$ for different ions was estimated from experiments with several alkali metal halides and other salts. From a set of several equations, as in Reference *6*, ionic FEP could be determined by using the Born equation. For the reason pointed out earlier, we determined RFEP for the salts as a whole for CTA membranes using the relation

$$\ln\left(\frac{D_{\mathrm{AM}}}{K\delta}\right)_{ij} = \ln\left(\frac{D_{\mathrm{AM}}}{K\delta}\right)_{\mathrm{NaCl}} - \left(\frac{-\Delta\Delta G}{RT}\right)_{\mathrm{Na}^{+}} - \left(\frac{-\Delta\Delta G}{RT}\right)_{\mathrm{Cl}^{-}} + \left(\frac{-\Delta\Delta G}{RT}\right)_{i} + \left(\frac{-\Delta\Delta G}{RT}\right)_{j} \tag{7}$$

where

$$(\mathrm{RFEP})_{ij} = (\mathrm{FEP})_{ij} - (\mathrm{FEP})_{\mathrm{NaCl}} \tag{8}$$

$$\ln\left(\frac{D_{\mathrm{AM}}}{K\delta}\right)_{ij} = \ln\left(\frac{D_{\mathrm{AM}}}{K\delta}\right)_{\mathrm{NaCl}} + (\mathrm{RFEP})_{ij} \tag{9}$$

TABLE 2
Relative Free Energy Parameter for Alkali Metal Halides and Some Nickel Salts with Respect to Sodium Chloride

Solute	RFEP
KF	0.32
KCl	−1.14
KBr	−1.30
RbCl	−1.92
CsCl	−2.97
KI	−1.50
$\mathrm{NiCl_2}$	−3.25
$\mathrm{NiSO_4}$	−3.89

As the concentrations of all salt solutions used for RO experiments were dilute (~1000 ppm), PWP and PR for these experiments do not differ appreciably. $(D_{AM}/K\delta)_{ij}$ for different salts could be calculated from experimental data of PR and f as per the procedure given by Sourirajan and Matsuura (*11*) for dilute solutions. Through the use of Eq. (9), RFEP for different salts in CTA membranes were calculated and are presented in Table 2. The RFEP values obtained were the average for three or four membranes, and a prediction of performance was carried out for the remaining membranes. The prediction of RO performance was carried out as follows: First, from ln $(D_{AM}/K\delta)_{NaCl}$ for the given membrane,

TABLE 3
Comparison of Predicted and Experimental Separation of Alkali Halides and Nickel Salts in CTA Membranes

Membrane	Feed solution	Separation (%)	
		Predicted	Experimental
1	KCl	78.5	81.0
	KBr	81.2	77.5
	CsCl	95.6	98.0
2	KF	88.8	87.4
	KI	97.5	98.0
	RbCl	98.6	98.6
3	CsCl	99.2	99.2
	KCl	95.5	95.8
	RbCl	97.9	98.9
	$NiSO_4$	99.5	99.8
4	KCl	59.7	61.0
	KBr	63.7	64.8
	RbCl	76.6	78.0
5	CsCl	95.4	91.6
	KI	73.6	69.4
6	KF	90.9	91.3
	KCl	97.8	94.7
	KBr	98.2	98.5
7	RbCl	99.1	99.3
	CsCl	99.9	99.9
	KI	98.2	93.4
	$NiCl_2$	99.2	99.7
	$NiSO_4$	99.8	99.9

ln $(D_{\mathrm{AM}}/K\delta)_{ij}$ was calculated by using Eq. (9). From $(D_{\mathrm{AM}}/K\delta)_{ij}$ and PR, f was calculated using Relation (11):

$$f_{ij} = \frac{V_s}{V_s\left[1 + \frac{(D_{\mathrm{AM}}/K\delta)_{ij}}{k_{ij}}\right] + (D_{\mathrm{AM}}/K\delta)_{ij}} \qquad (10)$$

where

$$V_s = \frac{(\mathrm{PR})}{3600ScM_{\mathrm{B}}} \qquad (11)$$

and the mass transfer coefficient, k_{ij}, is given by (12)

$$k_{ij} = k_{\mathrm{NaCl}}(D_{ij}/D_{\mathrm{NaCl}})^{2/3} \qquad (12)$$

The solute separation thus predicted by using Eqs. (10), (11), and (12) employing experimental data with NaCl, viz., $(D_{\mathrm{AM}}/K\delta)_{\mathrm{NaCl}}$ and RFEP, are presented in Table 3 along with experimental values of separation. The agreement is quite good.

CONCLUSIONS

A quantity called the "relative free energy parameter" has been introduced; it is similar to the free energy parameter concept developed by Sourirajan et al. It can be successfully applied for the prediction of RO separation of alkali halides, nickel chloride, and nickel sulfate through cellulose triacetate membranes.

NOMENCLATURE

A	pure water permeation constant [kg·mol/(m^2·s·kPa)]
C	concentration of solute
C^*	parameter defined by Eq. (6) representing porosity of membrane
D_{NaCl}, D_{ij}	diffusion coefficient of NaCl and salt ij, respectively (m^2/s)
$(D_{\mathrm{AM}}/K\delta)_{\mathrm{NaCl}}$, $(D_{\mathrm{AM}}/K\delta)_{ij}$	solute transport parameter of NaCl and solute ij, respectively (m^2/s)
FEP	free energy parameter
K	equilibrium constant for distribution of solute between membrane and solution

M_A, M_B	molecular weight of solute and solvent (water) (kg)
N_A, N_B	flux of solute and solvent through membrane, respectively [kg·mol/(m^2·s)] and [kg·mol/(m^2·s)]
P	pressure applied across the membrane (kPa)
PR	product rate [kg/hr]
PWP	pure water permeation rate [kg/hr]
R	gas constant
RFEP	relative free energy parameter
S	membrane area (m^2)
T	temperature
X	mole fraction of solute
c	molar density of solution (kg·mol/m^3)
f	solute separation
k_{NaCl}, k_{ij}	mass transfer coefficient of NaCl and solute ij, respectively (m/s)
V_s	permeation velocity of product solution (m/s)
δ	effective thickness of membrane (m)
$\pi(X_{A2})$, $\pi(X_{A3})$	osmotic pressure of concentrated boundary layer and permeate solution (kPa)
$\Delta\Delta G/RT$	free eneregy parameter

Subscripts

1, 2, 3	represent the feed, concentrated boundary, and permeate solutions
A1, A2, A3	represent the concentrations of solute A in the feed, concentrated boundary, and permeate solutions
B	represents solvent B

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