

Prediction of Reverse Osmosis Performance of Cellulose Acetate Membrane

C. V. DEVMURARI and M. V. CHANDORIKAR, *Central Salt and Marine Chemicals Research Institute, Bhavnagar-364002, India*

Synopsis

This study illustrates the analytical techniques involved in specifying the membrane and outlines the procedure for predicting the reverse osmosis (RO) performance of these membranes using feed solutions, containing either single solutes or mixed electrolytes having a common ion. The scientific basis for such specification and prediction techniques has been extensively discussed in the literature. In the present work, the governing transport equations for RO systems, involving preferential sorption of water at the membrane-solution interface, are utilized.

INTRODUCTION

A major thrust in the aspect of transport analysis and performance prediction in the field of RO is due to the work of Sourirajan and co-workers, and their results are discussed in great detail in the books^{1,2} of Sourirajan. Their approach is based on preferential sorption and capillary flow mechanism, whereby the solute diffuses through the porous membrane and solvent by a viscous flow mechanism. They have given the transport equations describing the process.

The characterization of the membrane is carried out with an NaCl experiment usually at a concentration of 5000 ppm in the feed unless otherwise stated. The experimental data, such as PWP, PR, and molalities (or ppm) of the feed and the product, are collected at the operating temperature and operating pressure under a specified condition of the flow rate. PWP and PR values are converted to those at 25°C using a density-viscosity correction factor.¹ The quantities, such as the solute transport parameter $(D_{AM}/K\delta)_{\text{NaCl}}$, mass transfer coefficient (k_{NaCl}) , and pure water permeability constant, are determined by Kimura-Sourirajan analysis.

The transport equations used in the Kimura-Sourirajan analysis are as follows: The pure water permeation constant A is given by

$$A = \text{PWP}/(M_B \times S \times 3600 \times P) \quad (1)$$

The solute flux N_A is given by

$$N_A = (D_{AM}/K\delta)(c_2X_{A_2} - c_3X_{A_3}) \quad (2)$$

and the solvent flux N_B is given by the following relations:

$$N_B = A[P - \pi(X_{A_2}) + \pi(X_{A_3})] \quad (3)$$

$$= (D_{AM}/K\delta) \left(\frac{1 - X_{A_3}}{X_{A_3}} \right) (c_2X_{A_3} - c_3X_{A_3}) \quad (4)$$

$$= kc_1(1 - X_{A_3}) \ln \frac{X_{A_2} - X_{A_3}}{X_{A_1} - X_{A_3}} \quad (5)$$

Also,

$$N_B = \frac{PR}{3600 \times M_B \times S} \times (1 - 0.001m_3M_A) \quad (6)$$

For any single solute system, from RO data consisting of PWP, PR, and solute separation f , defined by

$$f = 1 - m_3/m_1 \quad (7)$$

and the literature data of osmotic pressure and molar density at different concentrations, using eqs. (1)–(6), A , $(D_{AM}/K\delta)$, and k could be evaluated. Extensive investigations by Sourirajan and his group on a large number of solute system led them to evolve the following general expressions, applicable for prediction of RO performance from the characterization of membranes with NaCl. The applicable expressions for the prediction procedure are

$$(D_{AM}/K\delta)_{ij} = \ln C^* + n_i(-\Delta\Delta G/RT)_i + n_j(-\Delta\Delta G/RT)_j \quad (8)$$

where

$$\ln C^* = \ln(D_{AM}/K\delta)_{NaCl} - (-\Delta\Delta G/RT)_{NA^+} - (-\Delta\Delta G/RT)_{Cl^-} \quad (9)$$

The term $(-\Delta\Delta G/RT)$ is the so-called free-energy parameter for a given ion.

The mass transfer coefficient k_{ij} for the solute designated as ij is again obtained from the mass transfer coefficient of NaCl determined by Kimura–Sourirajan analysis, by the following correlation:

$$k_{ij} = (D_{ij}/D_{NaCl})^{2/3} \times k_{NaCl} \quad (10)$$

Just as in the characterization procedure, in which we obtain A , $(D_{AM}/K\delta)$, and k from PWP, PR, and f using eqs. (1)–(6), in the prediction procedure, with A , $(D_{AM}/K\delta)_{ij}$, and k_{ij} , PR and f can be calculated with the aid of the above equations, for any operating conditions.

The details of the philosophy of the development of the free-energy parameter concept and the RO performance prediction scheme may be obtained in the papers by Matsuura et al.³ and Rangarajan et al.⁴

In many practical applications, systems containing more than a single solute are invariably encountered. The prediction of RO performance for simple two-electrolyte mixtures have been reported,⁵ which are amenable to calculations with only large computers. However, the approach of Agrawal and Sourirajan⁶ for the case of common ion systems is simple to use, but requires the performance data with single solutes. For the prediction of RO performance with mixed solutes with common ion, the following equations are used:

$$(m_3)_{A_1} = 55.55 \times \frac{x_1 N_{A_1}}{x_1 N_{B_1} + x_2 N_{B_2}} \quad (11)$$

$$(m_3)_{A_2} = 55.55 \times \frac{x_2 N_{A_2}}{x_1 N_{B_1} + x_2 N_{B_2}} \quad (12)$$

$$(PR)_{mix} = x_1 k_{A_1} N_{A_1} + x_2 k_{A_2} N_{A_2} + k_B (x_1 N_{B_1} + x_2 N_{B_2}) \quad (13)$$

In this paper we illustrate how the free-energy parameter concept could be used for predicting RO performance for different single solutes, thus lending further experimental support to the approach of Sourirajan's group, and also

how the RO performance could be predicted for a mixture of electrolytes with common ion using eqs. (11), (12), and (13) from NaCl data alone.

BRIEF NOTE ON THE PREDICTION SCHEME USED

For all the membranes, characterized by $A (D_{AM}/K\delta)_{NaCl}$, and k_{NaCl} , the following steps are followed for predicting f and PR for any single solute. In the course of the computation, the following two simplifying assumptions are made to facilitate easier calculation: (i) $c = c_1 = c_2 = c_3 = 5.535 \times 10^{-2}$, which is valid up to $\sim 0.5M$, and (ii) $\pi (X_A) = B \times X_A$, which is simply an assumption of linearization of the osmotic pressure vs. mole fraction relationship. The prediction procedure is based on the "search" for X_{A_3} , which satisfies the two simultaneous equations, viz.,

$$N_B = (D_{AM}/K\delta)[(1 - X_{A_3})/X_{A_3}] \cdot c(X_{A_2} - X_{A_3}) \quad (14)$$

and

$$N_B = k(1 - X_{A_3}) \cdot c \cdot \ln[(X_{A_2} - X_{A_3})/(X_{A_1} - X_{A_3})] \quad (15)$$

by an iterative procedure. The steps for predicting RO performance of any solute, ij , are as follows:

Step 1: From $(D_{AM}/K\delta)_{NaCl}$ and the free-energy parameters for ions i and j , $(D_{AM}/K\delta)_{ij}$ is calculated using eqs. (8) and (9).

Step 2: From k_{NaCl} , k_{ij} is calculated using eq. (10).

Step 3: With an initially assumed value of f (usually about 0.1), the X_{A_3} value is computed as follows:

$$(m_3)_A = (1 - f)(m_1)_A$$

$$X_{A_3} = (m_3)_A / [55.55 + (m_3)_A]$$

Step 4: Now calculate $(X_{A_2} - X_{A_3})$ using the relation

$$X_{A_2} - X_{A_3} = \frac{AP}{AB + \{[(1 - X_{A_3})/X_{A_3}] \cdot (D_{AM}/K\delta)_{ij} \cdot c\}}$$

Step 5: Substitute the value of $(X_{A_2} - X_{A_3})$ in the following equation to get $(N_B)_1$:

$$(N_B)_1 + (D_{AM}/K\delta)_{ij} \times [(1 - X_{A_3})/X_{A_3}] \times c \times (X_{A_2} - X_{A_3})$$

Step 6: Now calculate $(N_B)_2$ using the equation relating k_{ij} and N_B for the solute ij as follows:

$$(N_B)_1 = (D_{AM}/K\delta)_{ij} \times [(1 - X_{A_3})/X_{A_3}] \times c \times (X_{A_2} - X_{A_3})$$

Note that there is one unique value of f which will result in values of $(N_B)_1$ and $(N_B)_2$, which does not differ markedly in order to satisfy all the transport equations described earlier.

Step 7: Increment the value of f until $(N_B)_2/(N_B)_1$ is nearly equal to 1. In the numerical computation, $(N_B)_2/(N_B)_1 - 1$ is set equal to a very small number chosen in such a way to meet the required accuracy, and to terminate the calculation using a digital computer.

Step 8: Once a satisfactory value of f is obtained, it is easy to calculate the corresponding PR value. Thus, by following the eight steps, f and PR for any

single solute can be calculated (or predicted) for any given operating conditions from only NaCl data.

In the case of electrolyte mixture with solutes A_1 and A_2 , similar predictions of f and PR and therefore N_{A_1} , N_{A_2} , N_{B_1} , and N_{B_2} can be made, and the performance of the mixture predicted, using eq. (11)–(13).

EXPERIMENTAL

The membranes were prepared by the procedure described elsewhere.⁷ The membranes were characterized by runs with 0.5% (wt/vol) NaCl solution as feed. The data collected were PWP and PR by carrying out experiments with pure water and NaCl solution, respectively, as feed, and these were corrected to 25°C, as prescribed by Sourirajan.¹ The solute concentration in feed and product was determined by the conductance measurement, using a concentration-vs.-conductance calibration chart. After the NaCl experiment, subsequently, different feed solutions were used to collect PR and separation data, the system being washed each time thoroughly with distilled water. The analytical procedure used for the determination of the ion concentration in feed and product for different solutions was as follows: Conductance: NaCl, KCl, KH_2PO_4 , Na_2SO_4 , and K_2SO_4 . Sulfate analysis: cross checks were obtained by sulfate analysis with conductance in case of sulfate ion. EDTA titration: Mg^{2+} , Cu^{2+} , Ni^{2+} . Flame photometry: Na, K. In the case of mixtures, the individual ion separations were determined by the combination of the above methods.

RESULTS

The different membranes used in the entire course of this investigation were characterized by experiments with NaCl and the characteristics were determined by Kimura–Sourirajan analysis (Table I: all the calculations were made with a DCM Microcomputer 1121). Table II presents calculated and experimental RO performance with single solute systems. Table III compares the experimental and calculated RO performance with mixed solutes. Some of the physicochemical properties that are necessary were obtained from the literature. These are presented in Table IV.

DISCUSSION

It can be seen (Table II) that, in general, the predicted and the experimental values of the solute separation and of the product rate for all the single solute aqueous systems studied, using different membranes (Table I), agree fairly well from the practical point of view. The product rates determined experimentally are subject to an error of about $\pm 5\%$ due to the pressure fluctuations and of about $\pm 2\%$ due to the temperature fluctuations. Thus, allowing a possible additive error of about $\pm 10\%$ in the product rate, the agreement between the predicted and the experimental values is fairly satisfactory. Due to the membrane-fouling effect, because of the precipitation of iron hydroxide to some extent on the membrane-active surface, there is observed a significant difference between the

TABLE I
 Characterization of CA Membranes Used in Study of Single-Solute Systems

Membrane no.	PWP at 25°C (g/h)	PR at 25°C (g/h)	Feed (ppm)	Separation (%)	Operating pressure (psig)	$A \times 10^6$ g·mol H ₂ O/cm ² ·s·atm	$(D_{AM}/K\delta) \times 10^5$ (cm·s)	$k_{NaCl} \times 10^4$ (cm·s)
1	45.53	34.32	7750	95.6	570	1.1378	2.0347	17.77
2	41.34	33.00	7750	97.5	560	1.0999	1.1875	22.54
3	47.84	39.74	7500	93.3	640	1.1137	3.8585	23.86
4	38.92	33.50	6000	93.0	580	0.9980	3.6473	25.88
5	32.40	28.00	6000	93.0	580	0.8323	3.1260	24.18
6	44.72	39.50	5394	92.0	620	1.0746	4.9277	29.52
7	37.97	33.53	5394	92.0	620	0.9125	4.1755	24.87
8	34.20	26.50	11700	87.5	620	0.8219	5.7911	26.67

TABLE II
Comparison of Predicted and Experimental RO Performance with Single-Solute Systems

Solute no.	System	Feed molality ($\times 10^2$)	Pressure (psig)	Membrane no.	Membrane performance			
					Separation (%)		Product flux (gfd) ^a	
					Predicted	Exptl	Predicted	Exptl
1	KCl	7.0	560	2	97.5	95.0	16.9	15.8
		20.0	580	4	91.6	91.9	12.2	13.6
		20.0	580	5	91.6	91.9	10.2	11.6
2	KH ₂ PO ₄	4.3	640	3	98.6	98.8	21.3	19.0
3	Na ₂ SO ₄	3.5	570	1	99.7	99.3	16.4	12.2
4	K ₂ SO ₄	2.9	570	1	99.4	99.5	17.2	14.1
		20.0	580	4	99.4	97.5	11.1	13.6
5	MgCl ₂	5.3	570	1	98.9	98.4	13.6	15.3
		20.0	620	6	97.1	97.0	10.9	12.6
		20.0	620	7	97.1	97.0	9.3	10.5
6	CaCl ₂	2.9	560	2	99.4	98.8	16.9	15.5
		20.0	620	6	96.8	96.7	11.1	14.3
		20.0	620	7	96.8	96.7	9.4	11.9
7	MgSO ₄	4.7	570	1	99.9	99.8	16.5	14.6
8	CuSO ₄	20.0	620	6	99.9	98.0	17.2	14.6
		20.0	620	7	99.9	98.0	14.5	12.6
9	NiSO ₄	3.3	560	2	99.9	99.3	20.3	18.7
10	FeCl ₃	3.4	640	3	99.9	98.7	20.4	11.6

^a gal/ft² day.

predicted and the experimental product rate values, while working with the FeCl₃-H₂O system.

In Table III, a comparison of the predicted and the experimental RO performance, using feed systems containing mixed electrolytes having common ions, is given. It is again observed that the agreement between these two performance values is fairly good.

The foregoing observations thus lead to the following two inferences: (i) the application of the free-energy parameter concept, developed by the Sourirajan group, has been demonstrated to have wide applicability; (ii) the combination of the above approach, principally used for the single solute, with the approach of Agrawal and Sourirajan⁶ results in the capability of predicting for the binary electrolyte mixture with a common ion from only NaCl data for the given membrane.

TABLE III
Comparison of Predicted and Experimental RO Performance with Some Mixed Electrolyte Systems with Common Ions^a

Ion	Separation (%)		Product flux (gfd) ^b	
	Predicted	Exptl	Predicted	Exptl
System 1: 0.2M MgCl ₂ + 0.2M KCl				
K ⁺	95.6	94.5		
Mg ²⁺	98.6	98.0	12.0	11.6
Cl ⁻	97.6	96.4		
System 2: 0.2M K ₂ SO ₄ + 0.2M CuSO ₄				
K ⁺	99.5	97.9		
Cu ²⁺	99.9	99.1	11.9	13.6
SO ₄ ²⁻	99.7	99.5		

^a Operating pressure = 620 psig; membrane no. 8; membrane area = 15.2 cm².

^b gal/ft² day.

TABLE IV
Physicochemical Data Necessary for Prediction Calculations

System	Diffusion coefficient [(cm ² /s) × 10 ⁵]	B _i (atm/mol fraction)
KCl ¹	1.9948	2480.2
Na ₂ SO ₄ ²	1.2300	2668.6
K ₂ SO ₄ ^a	1.4090	2764.9
MgCl ₂ ¹	1.2502	4610.5
CaCl ₂ ¹	1.3355	4329.8
MgSO ₄ ²	0.8490	1453.8
NiSO ₄ ³	0.8510	1352.6

^a Calculated using equivalent conductance at infinite dilution.

CONCLUSION

This investigation illustrates the analytical techniques involved in specifying the membrane and outlines the procedure for predicting the performance of these membranes, using feed solutions containing either single solutes or mixed electrolytes having a common ion. The scientific basis for such specification and prediction techniques have been extensively discussed in the literature. In the present work, the governing transport equations for RO systems, involving preferential sorption of water at the membrane-solution interface, are utilized.

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APPENDIX: NOMENCLATURE

<i>A</i>	pure water permeability constant (g·mol H ₂ O/cm ² ·s·atm)
<i>B</i>	proportionality constant
<i>C</i>	molar density (mol/cm ³)
$(D_{AM}/K\delta)$	solute transport parameter (cm·s)
$(D_{AM}/K\delta)_{ij}$	solute transport parameter for solute <i>ij</i> (cm·s)
D_{ij}, D_{NaCl}	diffusion coefficient of solute <i>ij</i> and NaCl, respectively (cm ² ·s)
<i>f</i>	solute separation defined by eq. (7).
<i>k</i>	mass transfer coefficient (cm·s)
M_A, M_B	Mol wt of solute and water, respectively
m_1, m_3	molalities of feed and product phases, respectively
N_A	solute flux (mol/cm ² ·s)
N_B	solvent flux (mol/cm ² ·s)
N_{A_1}	flux of solute A ₁ through membrane for feed system (A ₁ -H ₂ O) (g·mol/cm ² ·s)
N_{A_2}	flux of solute A ₂ through membrane for feed system (A ₂ -H ₂ O) (g·mol/cm ² ·s)
N_{B_1}	flux of solvent through membrane for feed system (A ₁ -H ₂ O) (g·mol/cm ² ·s)
<i>P</i>	pressure (atm)
PR	product rate (g/h)
PWP	pure water permeability (g/h)
<i>R</i>	gas constant
<i>S</i>	membrane area (cm ²)
<i>T</i>	absolute temperature
$X_{A_1}, X_{A_2},$ X_{A_3}	mole fractions of solute A, in feed, concentrated boundary layer, and product, respectively (the subscripts 1, 2, and 3 refer to the indicated phases)
$\pi(X_A)$	osmotic pressure at a given mole fraction of solute (atm)
$(-\Delta\Delta G/RT)_i$	free energy parameter of ion <i>i</i>

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