Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Hanra, M. S. and Ramachandhran, V.(1996) 'Trace Level Separation of Zinc Sulfate and Lead Nitrate from Toxic Effluent Streams by Reverse Osmosis Modular Systems', Separation Science and Technology, 31: 1, 49 — 61
To link to this Article: DOI: 10.1080/01496399608000680
URL: http://dx.doi.org/10.1080/01496399608000680

SEPARATION SCIENCE AND TECHNOLOGY, 31(1), pp. 49–61, 1996

Trace Level Separation of Zinc Sulfate and Lead Nitrate from Toxic Effluent Streams by Reverse Osmosis Modular Systems

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ABSTRACT

Separation of trace toxic metallic constituents from effluent streams by membrane processes has been under investigation in our laboratory. Removal of zinc sulfate and lead nitrate in low concentration, especially in the millimolar range, using cellulose acetate and TFC-polyamide membranes assembled in plate-*n*-frame modules is reported in this paper. Separation data are presented as a function of concentration and pressure in single and mixed solute systems at low feed flow rates. Under the experimental conditions for dilute feed solutions, a decline in solute separation at very low concentrations as well as at high pressures are noticed. The solute and solvent transport across the membranes are analyzed in terms of pure water permeability constant (A) and solute transport parameter using Kimura–Sourirajan's transport equations as applied to very dilute feed systems. Solute separation is predicted for various product permeation velocities and compared with experimental data.

INTRODUCTION

Membranes play a vital role in various separations involving ionic, nonionic constituents in aqueous/nonaqueous systems (1). Separation of trace toxic constituents from effluent streams using membrane techniques is an attractive alternative since they operate isothermally and are rate governed. Moreover, the permeate and concentrate streams are reusable depending on the nature of the industry. RO separation is known to vary with the nature of the membrane, feed system, and operating conditions.

Generation of laboratory-scale data on RO separations and the sensitivity of these data with changes in operational parameters are essential to evolve a design approach for a large-scale RO treatment facility. Application of RO systems for treatment of electroplating and metal-finishing industrial effluents has been considered previously by a number of investigators (2–4). Separation characteristics of various toxic metal pollutants in trace quantities from wastewater using cellulose acetate and polyamide membranes are currently under study in our laboratory (5). This paper deals with our studies with respect to removal of zinc and lead solutes from wastewaters. The main sources of zinc are the galvanizing and alloy industries whereas lead comes from a variety of industries such as storage batteries, type metal for printing, and paint, in addition to auto-emission exhaust. Zinc is known to cause chills, nausea, and vomitting. Lead is known to cause intoxication, colic gestrointestinal disturbance, impaired functioning of the central nervous system, etc. Separation of trace amounts of zinc and lead salts from aqueous solutions as well as in the presence of various concentrations of sodium chloride is reported with respect to their effect and these various factors.

MATERIALS AND METHODS

Plate modules with RO membranes of the thin film composite polyamide type (obtained from De DanskeSukker Fabrikken, Denmark) and of cellulose acetate (locally made) were assembled in series for our experiments. The module system consisted of 4 plates accommodating 6 sheets of polyamide membranes admeasuring 0.25 m^2 area in series with 10 plates accommodating 18 sheets of cellulose acetate membranes of 0.74 m^2 area. The feed is pumped from a feed tank by a reciprocating pump and is passed through the system. The pressure regulating valve connected to the system at the exit of the module is suitably adjusted to set the upstream pressure at the desired values. The permeate and the reject streams are taken back to the feed tank. Samples were periodically drawn and their compositions estimated by conductometry and atomic absorption spectrometry (AAS model GBC-904 AA computerized) and an ion analyzer (Ion 85). The temperature of the feed was maintained at 27.5 ± 0.5°C by suitably cooling the feed.

BASIC TRANSPORT EQUATIONS

The following equations of Kimura–Sourirajan, which come from an analysis of experimental RO data involving single solute systems, are used to characterize the membranes and analyze the RO performance (1).

Pure Water Permeability (PWP) Constant *A*

This gives an idea of the overall porosity of a membrane available for fluid transport:

$$A = \frac{\text{PWP}}{(M_B)(S)(3600)(P)} \tag{1}$$

The solvent water flux through membrane pores is

$$N_B = A[P - \pi(X_{A2}) + \pi(X_{A3})] \tag{2}$$

Solute Transport Parameter ($D_{AM}/K\delta$)

This incorporates solute diffusivity in the membrane phase (D_{AM}), the partition coefficient of solute between membrane phase and the interfacial fluid (K), and the membrane thickness (δ). It is treated as a single quantity and signifies the equilibrium and kinetic aspects of solute sorption and mobility through membranes.

$$D_{AM}/K\delta = \frac{N_B}{C\left[\dfrac{(1 - X_{A3})}{X_{A3}}\right](X_{A2} - X_{A3})} \tag{3}$$

Solute separation (f):

$$f = \frac{X_{A1} - X_{A3}}{X_{A1}} \tag{4}$$

Product rate through the membranes (PR):

$$\text{PR} = (N_B)(M_B)(S)(3600)\left[1 + \frac{m_1(1 - f)M_A}{1000}\right] \tag{5}$$

Mass transfer coefficient on the high pressure side of the membranes (k):

$$k = \frac{N_B}{C(1 - X_{A3})\ln\left(\dfrac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right)} \tag{6}$$

Assumptions:

1. The molar density of the bulk feed, interface water, and permeate are treated as a constant, i.e., $C_1 = C_2 = C_3 = C$.
2. The osmotic pressure of the solution is proportional to the mole fraction of the solute.

RESULTS AND DISCUSSIONS

Analysis of RO Performance

The RO performance data obtained for sodium chloride, zinc sulfate, and lead nitrate at low concentrations for both the membrane systems are given in Table 1. The separation data with a change in feed concentration in the millimolar region for the three solutes are given in Table 2. Separation of sodium chloride at low concentration by polyamide membranes is comparatively higher than that of cellulose acetate membranes. The TFC polyamide membranes also offer higher product flux compared to cellulose acetate membranes. A comparison of the separation data for zinc sulfate and lead nitrate with sodium chloride indicates that the rejections of these nitrate salts at trace level are higher. The higher separation obtained is consistant with what is generally observed for multivalent electrolytes. The comparative separation behaviors of both zinc sulfate and lead nitrate indicate that higher rejection of sulfate ions over nitrate ions is balanced by better rejection of lead ions over zinc ions.

Data on the effect of concentration with respect to sodium chloride indicate that RO separation declines at the trace level as well as at high feed concentrations. The decline in solute separation in the case of zinc and lead salts can be seen clearly in Table 2. Such a decline in RO separation at low concentrations was previously reported from our laboratory (6, 7).

The pure water permeability and product rate data for cellulose acetate and polyamide membranes in the case of 0.77 mM zinc sulfate feed are given in Fig. 1. Pure water permeability and product rate are higher for TFC polyamide membranes, and the rate of increase of pure water permeability and product rate values with pressure are also found to be higher

TABLE 1
Separation Data for Various Contaminants at Trace Level[a]

		Cellulose acetate		TFC polyamide	
Solute	Concentration (mM)	PR × 10^3 (g/h)	f (%)	PR × 10^3 (g/h)	f (%)
NaCl	0.34	16.33	80.37	6.77	87.4
$ZnSO_4$	0.20	16.02	94.59	6.62	97.66
$Pb(NO_3)_2$	0.16	16.27	94.39	6.47	97.23

[a] Pressure: 20 kg/cm^2. Pure water permeability: CA = 10.6 × 10^3 g/h at 17 atm; TFC-PA = 6.75 × 10^3 g/h at 12 atm.

TABLE 2
Separation Data for Sodium, Zinc, and Lead Salts as a Function of Feed Concentration[a]

Solute	Feed concentration (mM)	Solute separation (%)	
		Cellulose acetate	TFC polyamide
NaCl	0.34	80.37	87.4
	0.85	81.6	89.2
	1.7	83.2	91.4
	8.5	86.7	93.5
	42.6	84.3	89.1
$ZnSO_4$	0.038	93.2	96.54
	0.103	94.31	97.18
	0.211	93.46	96.03
$Pb(NO_3)_2$	0.17	93.09	95.09
	0.53	94.72	96.72
	0.77	94.12	96.35

[a] Pressure = 20 kg/cm^2.

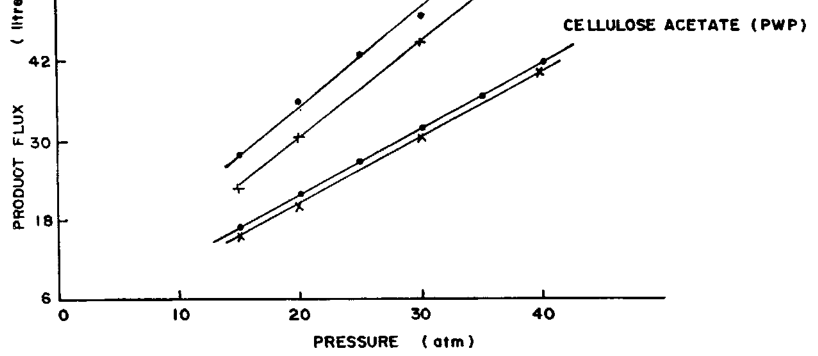

FIG. 1 Pure water permeability and product rate as a function of pressure.

for polyamide membranes. This highlights the advantage of using TFC-PA membranes for high-pressure applications. The effect of pressure on separation of trace levels of zinc sulfate and lead nitrate for both membrane systems are given in Figs. 2 and 3. It can be seen that solute separation increases as the pressure increases and declines at higher pressures. This trend is noticeable for both membrane systems and for both solutes.

Transport Parameters

The *A*, $D_{AM}/K\delta$, and *k* values for zinc sulfate and lead nitrate solute systems are computed from the experimental data. The *A* values are nearly independent of applied pressure for both CA and PA membranes, as can be seen in Fig. 4. The *A* values for PA membranes are found to be higher compared to CA membranes. The effect of feed concentration on $D_{AM}/K\delta$ values for CA and PA membrane systems with respect to zinc sulfate is given in Fig. 5. The $D_{AM}/K\delta$ values show a strong dependence on feed concentration for both CA and PA membranes. The $D_{AM}/K\delta$ values go through a minimum with an increase in feed concentration at the trace level for both membrane systems, reflecting the solute separation behavior observed previously. The mass transfer coefficients on the high-pressure

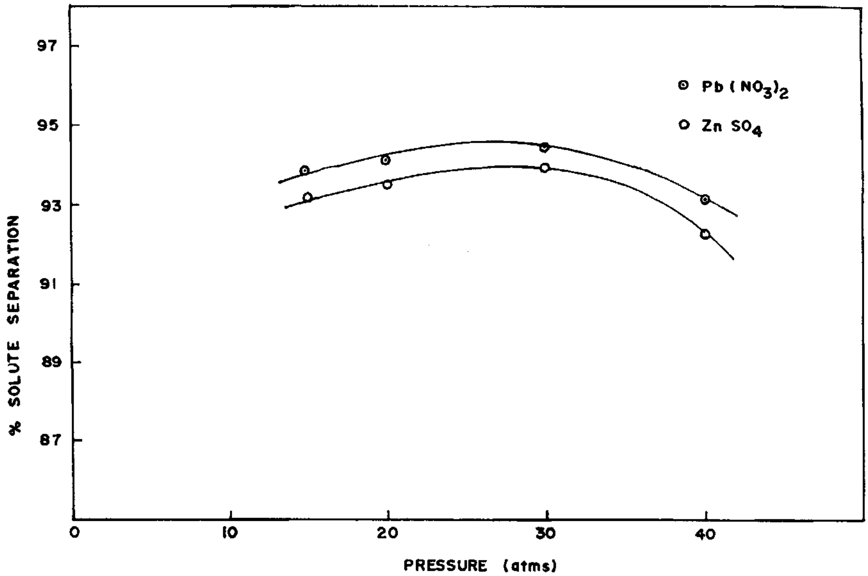

FIG. 2 Effect of pressure on solute separation: cellulose acetate membrane.

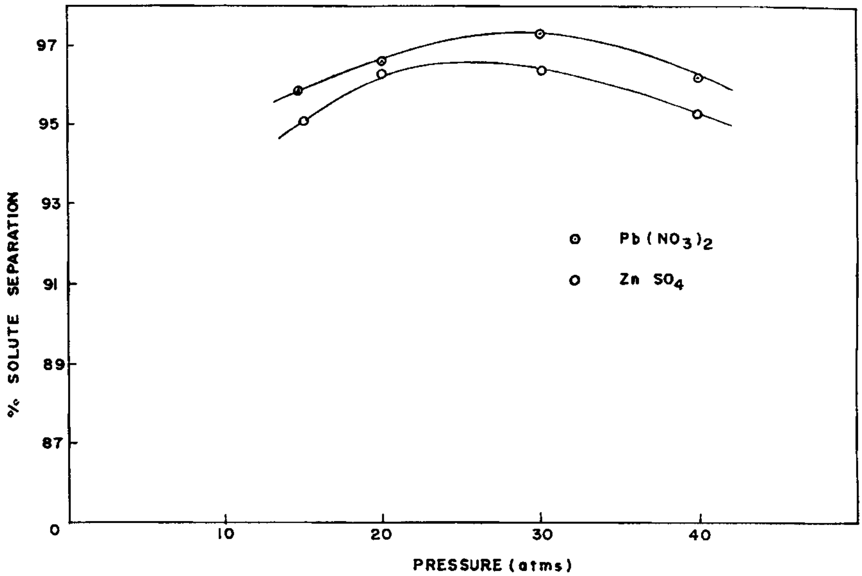

FIG. 3 Effect of pressure on solute separation: polyamide membrane.

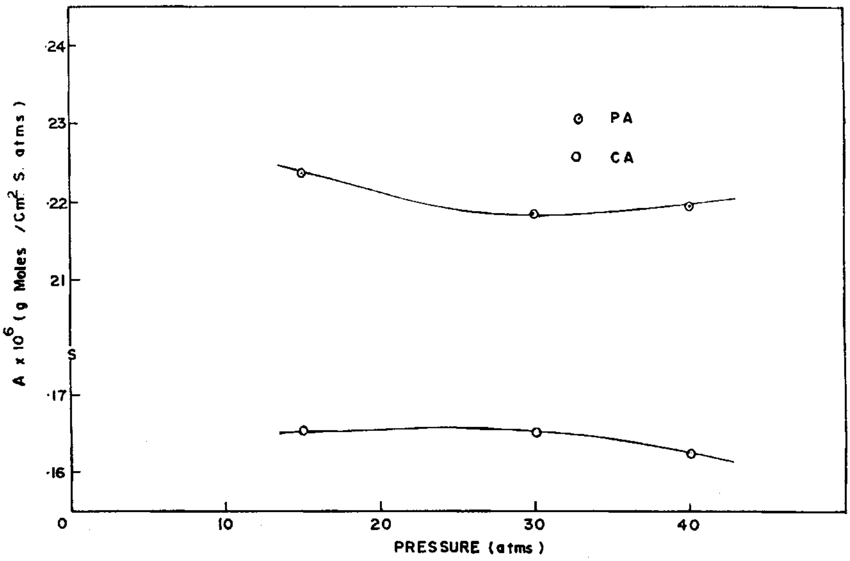

FIG. 4 Effect of pressure on pure water permeability constant A.

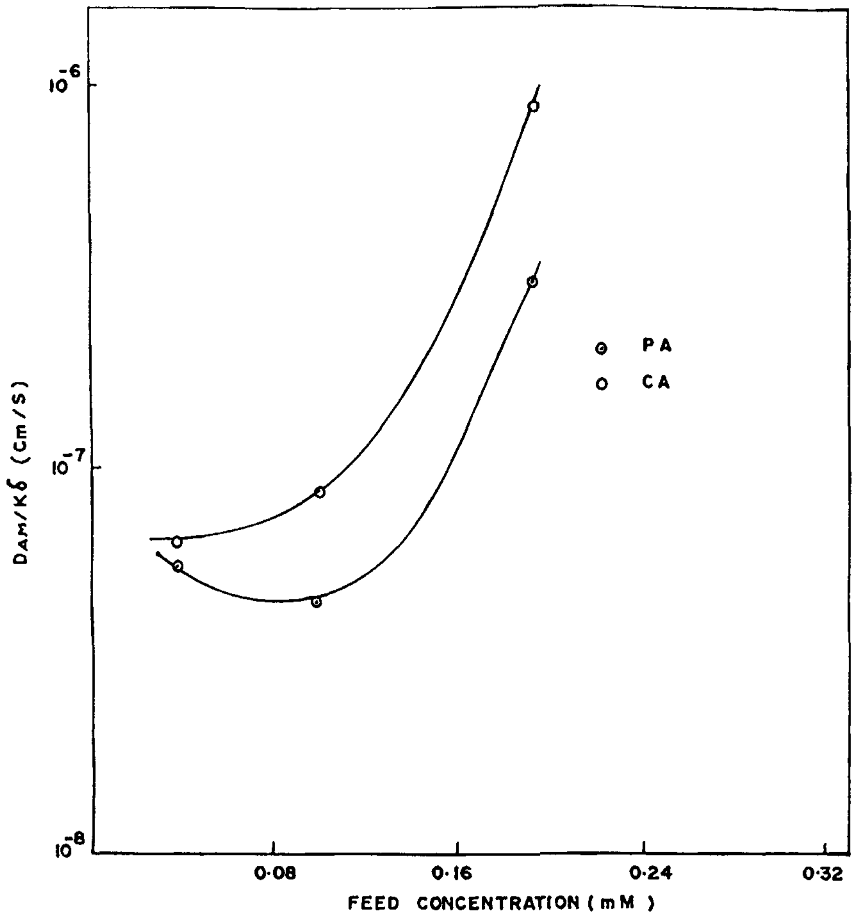

FIG. 5 Effect of feed concentration on ($D_{AM}/K\delta$) with respect to $ZnSO_4$.

side of the membrane for sodium chloride, zinc sulfate, and lead nitrate solutes are given in Table 3. The mass transfer coefficient values are two orders of magnitude higher compared to the solute transport parameters. The mass transfer coefficient values, however, are lower by an order of magnitude as compared to reported values which are in the range of 10^{-3} cm/s. This could be due to the lower feed velocity prevalent in the module. The noticeable increase in *k* values in TFC polyamide membranes could also be due to the higher feed velocity compared to cellulose acetate membranes systems because the modules are connected in series.

TABLE 3
Mass Transfer Coefficient Values for Different Solute and Membrane Systems

Solute	Feed concentration (mM)	Applied pressure (atm)	$k \times 10^4$ (cm/s)	
			Cellulose acetate	TFC polyamide
$ZnSO_4$	0.038	40	1.787	2.467
	0.103	40	1.911	2.708
$Pb(NO_3)_2$	0.17	20	2.23	2.74
	0.77	30	2.22	2.79

Mixed Systems

The separation behavior of zinc and lead ions through CA and PA membrane systems in the presence of a high concentration of sodium chloride were studied since these trace elements are present along with other macroconstituents in actual effluent systems. The RO separation data for zinc sulfate in the presence of sodium chloride of various concentrations are given in Table 4. The results indicate that although the rejection of sodium chloride is not affected, the rejection of zinc sulfate in the presence of sodium chloride is greatly improved. Similar trends have been observed for CA and PA membrane systems although the separation observed for the PA membrane system is higher. Similar observations have been reported for the cases of chromium, uranium, nickel, and copper solutes

TABLE 4
Separation Data for Trace Level Separation of Zinc in Mixed Systems

No.	Feed concentration		Pressure (atm)	Solute separation (%)			
				TFC-PA		CA	
	NaCl (mM)	$ZnSO_4$ (mM)		NaCl	$ZnSO_4$	NaCl	$ZnSO_4$
1	7.9	0.16	30	87.0	98.4	80.6	97.0
2	13.5	0.16	30	89.8	98.03	81.2	97.7
3	27.8	0.16	30	91.2	98.00	82.7	97.8
4	65.7	0.16	30	94.4	98.00	87.6	96.4
5	7.9	0.16	40	90.6	97.6	81.4	96.3
6	13.5	0.16	40	94.2	98.7	82.7	97.6
7	27.8	0.16	40	95.4	97.8	83.4	96.8
8	65.7	0.16	40	94.7	97.0	86.9	96.3

(8, 9). This indicates that the separation of trace toxic constituents is expected to improve in actual effluent streams because they are often loaded with other major constituents.

Predictability of RO Performance in Dilute Aqueous Feed Solutions

In the case of treatment of dilute aqueous feed solutions by reverse osmosis where the solute flux is faster than the solvent flux, the solvent mole fraction is nearly equal to 1, and the operating pressure of the feed is sufficiently high compared to the osmotic pressures of the feed, the following equations can be written:

$$f = \frac{(\mathrm{ppm})_{\mathrm{feed}} - (\mathrm{ppm})_{\mathrm{product}}}{(\mathrm{ppm})_{\mathrm{feed}}} \tag{7}$$

so that

$$(\mathrm{ppm})_{\mathrm{product}} = (\mathrm{ppm})_{\mathrm{feed}}(1 - f) \tag{8}$$

$$N_{\mathrm{A}} = \frac{\mathrm{PR}(\mathrm{ppm})_{\mathrm{feed}}(1 - f)}{(3600)(S)(M_{\mathrm{A}} \times 10^6)} \tag{9}$$

$$N_{\mathrm{B}} = \frac{\mathrm{PR}}{(3600)(S)(M_{\mathrm{B}})} \tag{10}$$

Equations (3) and (6) may be written

$$N_{\mathrm{A}} = C\left(\frac{D_{\mathrm{AM}}}{K\delta}\right)(X_{\mathrm{A2}} - X_{\mathrm{A3}}) \tag{11}$$

$$N_{\mathrm{B}} = Ck \ln\left(\frac{X_{\mathrm{A2}} - X_{\mathrm{A3}}}{X_{\mathrm{A1}} - X_{\mathrm{A3}}}\right) \tag{12}$$

Combining Eqs. (10) and (12):

$$\frac{\mathrm{PR}}{(3600)(S)(M_{\mathrm{B}})} = Ck \ln\left(\frac{X_{\mathrm{A2}} - X_{\mathrm{A3}}}{X_{\mathrm{A1}} - X_{\mathrm{A3}}}\right) \tag{13}$$

Therefore

$$(X_{\mathrm{A2}} - X_{\mathrm{A3}}) = (X_{\mathrm{A1}} - X_{\mathrm{A3}}) \exp\left[\frac{\mathrm{PR}}{(3600)(S)(M_{\mathrm{B}})Ck}\right] \tag{14}$$

$$C(X_{\mathrm{A2}} - X_{\mathrm{A3}}) = C(X_{\mathrm{A1}} - X_{\mathrm{A3}}) \exp\left(\frac{\mathrm{PR}}{(3600)(S)(M_{\mathrm{B}})Ck}\right) \tag{15}$$

$$= [(\mathrm{ppm})_{\mathrm{feed}} - (\mathrm{ppm})_{\mathrm{product}}] \frac{\rho}{10^6 M_\mathrm{A}} \times \exp\left(\frac{\mathrm{PR}}{(3600)(S)(M_\mathrm{B})Ck}\right) \tag{16}$$

$$= (\mathrm{ppm})_{\mathrm{feed}} \frac{f}{10^6} \frac{\rho}{M_\mathrm{A}} \exp\left(\frac{\mathrm{PR}}{(3600)(S)(M_\mathrm{B})Ck}\right) \tag{17}$$

where ρ is the density in g/cm^3 of solution.

Using Eq. (17) and noting that

$$\rho = CM_\mathrm{B} \tag{18}$$

Eq. (11) becomes

$$N_\mathrm{A} = \left(\frac{D_\mathrm{AM}}{K\delta}\right) (\mathrm{ppm})_{\mathrm{feed}} \frac{f}{10^6} \frac{\rho}{M_\mathrm{A}} \exp\left[\frac{\mathrm{PR}}{(3600)Sk\rho}\right] \tag{19}$$

Establishing the identity of Eqs. (9) and (19), the parameter $D_\mathrm{AM}/K\delta$ may be expressed as

$$D_\mathrm{AM}/K\delta = \frac{\mathrm{PR}}{(3600)S\rho} \frac{1-f}{f} \left[\exp\left(\frac{\mathrm{PR}}{(3600)Sk\rho}\right)\right]^{-1} \tag{20}$$

Equation (20) may also be written

$$f = \left[1 + \frac{(D_\mathrm{AM}/K\delta)(3600)S\rho}{\mathrm{PR}} \exp\left(\frac{\mathrm{PR}}{(3600)Sk\rho}\right)\right]^{-1} \tag{21}$$

Let V_s be the permeation velocity (cm/s) of product solution which can be expressed as

$$V_\mathrm{s} = \mathrm{PR}/(3600)S\rho \tag{22}$$

Equation (21) can then be written

$$\frac{1}{f} = 1 + \frac{(D_\mathrm{AM}/K\delta)\exp(V_\mathrm{s}/k)}{V_\mathrm{s}} \tag{23}$$

Equation (23) predicts that solute separation is related to the parameter V_s/k with the assumption that $D_\mathrm{AM}/K\delta$ remains constant. When V_s/k is sufficiently small, then

$$\exp\frac{V_\mathrm{s}}{k} \simeq 1 + \frac{V_\mathrm{s}}{k} \tag{24}$$

and Eq. (23) becomes

$$f = \frac{V_s}{V_s\left[1 + \frac{D_{AM}/K\delta)}{k}\right] + (D_{AM}/K\delta)} \tag{25}$$

When $D_{AM}/K\delta$ and k remain constant in the range of operating pressures involved, and PR $\propto P$, Eq. (25) assumes a form similar to the Langmuir absorption equation:

$$f = \frac{K_2P}{K_3P + 1} \tag{26}$$

where K_2 and K_3 are constants. This indicates that for dilute feed solution systems, when V_s/k is far less than unity, solute separation tend to increase with an increase in operating pressure. When the solute mass transfer coefficient on the high-pressure side of the membrane is higher than the permeation velocity of the product solution across the membrane, solute separation increases with an increase in pressure. But at higher values of V_s/k ($V_s/k > 1$), Eq. (23) predicts that solute separation declines with an increase in pressure. At higher values of V_s/k, the permeation velocity of product solution far exceeds the solute mass transfer coefficient on the higher pressure side. This leads to a progressive build up of concentration polarization at higher pressure, resulting in a drop in solute separation. This has been confirmed experimentally for zinc sulfate–water–cellulose acetate and zinc sulfate–water–polyamide membrane systems. The predicted solute separation data for various permeation velocities of product

TABLE 5
Predictability of RO Performance

Feed	Membrane	Feed concentration (mM)	Pressure (atm)	V_s/k	% Solute separation	
					Obsd	Calcd
$ZnSO_4$	TFC-polyamide	0.037	15	2.416	98.66	99.79
		0.037	30	4.783	97.54	98.91
		0.037	40	6.445	95.77	95.79
$ZnSO_4$	Cellulose acetate	0.037	15	1.91	97.08	98.66
		0.037	30	3.868	95.46	95.47
		0.037	40	4.567	94.72	92.51

solution obtained using Eq. (23) are given in Table 5, and they have been compared with experimental data. The agreement is satisfactory.

NOMENCLATURE

PWP	pure water permeability in g/h across a membrane of specified area and pressure
PR	product rate in g/h
S	membrane area in cm^2
P	pressure in atmospheres
M_A, M_B	molecular weight of solute and solvent
N_A, N_B	solute and solvent fluxes in $g \cdot mol/cm^2 \cdot s$
X_{A1}, X_{A2}, X_{A3}	mole fraction of solute in bulk feed, boundary layer, and product solution
C_1, C_2, C_3	molar density of feed, boundary layer, and product solution in $g \cdot mol/cm^3$
f	solute separation in %
M_1	molarity of the feed
k	mass transfer coefficient on the high pressure side, cm/s

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Received by editor April 17, 1995