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 Murthy, Z. V. P. and Gupta, Sharad K.(1998) 'Thin Film Composite Polyamide Membrane Parameters Estimation for Phenol-Water System by Reverse Osmosis', Separation Science and Technology, 33: 16, 2541 — 2557

To link to this Article: DOI: 10.1080/01496399808545318

URL: http://dx.doi.org/10.1080/01496399808545318

SEPARATION SCIENCE AND TECHNOLOGY, 33(16), pp. 2541–2557, 1998

Thin Film Composite Polyamide Membrane Parameters Estimation for Phenol–Water System by Reverse Osmosis

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ABSTRACT

A commercial thin film composite polyamide reverse osmosis membrane is used to separate an aqueous phenol–water binary system. The separation data are analyzed using a combined film theory–solution–diffusion (CFSD) model and a combined film theory–Spiegler–Kedem (CFSK) model. In the present investigation a new phenomenon is observed: there exists a maximum in the rejection when it is plotted against the product flux through the membrane. This behavior is explained for both models. An equation for $J_{v,\min}$, which is the value of the product flux J_v at which the rejection reaches a maximum, is derived from both models. Although the parameters for both models are consistent over the range of operating conditions, the CFSK model is more accurate for the phenol–water system.

INTRODUCTION

Untreated wastewater effluent from certain industrial processes contains various quantities of hazardous chemicals. Phenols in wastewater are the most prevalent form of pollutant in the chemical industry. Phenols, defined as hydroxy derivatives of benzene and its condensed nuclei, may occur in domestic and industrial wastewaters and in natural and potable water supplies. Dis-

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charge of phenol waste may cause serious health problems because it imparts a carboxylic odor to river water and can be toxic to fish and human beings. Major sources of phenol wastes are petroleum refineries, petrochemicals, steel, synthetic resins, pharmaceuticals, paints, plywood, textile processing industries, etc. (1). In general, phenol removal processes in water treatment include superchlorination, chlorine dioxide, ozonization, activated carbon adsorption, ion exchange, etc. After phenol wastes are treated with conventional methods, the treated water has a slight odor and the chlorination produces different wastes (2). A total dose of 1.5 g may be fatal to human beings (3).

Separation methods for phenols which involve membranes are energy saving and can operate at room temperature. Reverse osmosis (RO) separation of organic solutes from aqueous solutions has attracted attention because of its energy-saving nature. Many membranes have been developed and qualified only for seawater desalination, but the best membranes for desalination are not always suitable for the separation of organic solutes. Rejections by membranes are usually very much dependent on the combination of solute and membrane materials.

Most work done on the separation of phenol using reverse osmosis has involved only cellulose acetate membranes (CAMs) (4–13), but a few systems with noncellulosic membranes have been reported (10, 11, 14–18). In most cases CAMs provide some degree of rejection of organic substances; phenol is one of a few notable exceptions. Under conventional RO with CAMs, phenol concentrations in the permeate have been repeatedly found to exceed those in the feed solution. The term "negative rejection" has been coined for this enrichment phenomenon. This negative rejection has been attributed to significant solute–membrane interactions (5, 6, 8, 9).

The selective sorption or desorption of a nonelectrolyte like phenol can be affected by various interactions taking place between the matrix of the membrane and the solute. Some interactions increase the sorption of phenol while others decrease it. It has been established that organic solutes show much larger variations in rejection characteristics for a given membrane than do inorganic solutes (5, 19).

It seems likely that the polymer–solute interactions that produce strong solute sorption by a membrane also impede the translational mobility of the solute molecules. The exact nature of these polymer–solute interactions is unknown (9). In the separation of phenol, the pH of the feed solution plays a very important role.

It is well known that pH variation changes the partition coefficient of a solute, and therefore the separation between immiscible and aqueous layers. Phenol is practically undissociated at $\text{pH} < 7$ and almost completely dissociated at $\text{pH} > 12.3$. The effect of the pH of a solution on the degree of dissociation of phenol is particularly steep in the 9.2 to 11.2 pH range where the degree of dissociation changes from 10 to 91%. At pH 6.3, where phenol is practically undissociated in the feed solution, a negative solute separation of about −5% was obtained with the CAMs tested (7). In the 9.7 to 12.3 pH range, phenol was positively separated with all the CAMs tested (7). The extent of phenol separation increases with an increase in pH of the feed solution, which shows a direct relation in that reverse osmosis separation of phenol increases with an increase in its degree of dissociation in the feed solution. In the case of polyamide membranes the rejection also increased with increasing pH. A new phenol-resistant and rejecting membrane, constructed of polyvinyl alcohol (PVA), resists attack by phenol at concentrations up to 50,000 mg/L, with rejections of 90–95%, while CAMs were rapidly destroyed by an industrial waste containing 2000 mg/L (20). Some of the published data on phenol separation are shown in Table 1.

TABLE 1
Some Phenol Separation Data Reported in the Literature

Type of membrane	Feed pH	Operating pressure (atm)	Percent separation	Ref.
Asymmetric CAM			−34	12
Asymmetric CAM		50	−2.6 to −10.6	4
Asymmetric CAM			−10.8 to −22.9	5
Asymmetric CAM	11.2	34	+76 to +85	7
Asymmetric CAM	6.3	34	−5	7
Asymmetric CAM	4.4	34	+9	9
Asymmetric CAM	11.2	34	+88	9
Asymmetric CAM	4.4	68	+12	9
Asymmetric CAM	11.2	68	+83	9
Asymmetric CAM		41	−14	10
Asymmetric CAM			−34	12
Asymmetric CAM		30–100	−10 to −30	13
Composite/polyamide		27	+44.67	10
Composite/polyamide	4.5	20	+80.6[a]	15
Composite/polyamide	5.8	20	+83.0[a]	15
Composite/polyamide	7.35	20	+89.8[a]	15
Composite/polyamide	11.4	20	+98.8[a]	15
Composite/polyamide	4.9	68	+93.0	16
Composite/polyamide	12.0	68	>+99.0	16
Composite/polyamide	5.2	56	+99.0	17
Dynamic			+10	14
Dynamic	6.6–9.6		+86–100	18

[a] True rejection.

The objective of the present work is to obtain separation data on phenol using a commercial composite polyamide membrane and to estimate membrane transport parameters using different membrane transport models.

THEORY

The following two methods were used to analyze the separation data obtained on the laboratory experimental setup.

Graphical Method

The film theory is combined with the solution-diffusion model (21, 22), and after some rearrangement the following equation is obtained (23):

$$\ln[(1 - R_o)*J_v/R_o] = \ln(D_{AM}K/\delta) + J_v/k \tag{1}$$

where observed rejection $= R_o \equiv (C_{A1} - C_{A3})/C_{A1}$ (2)

true rejection $= R \equiv (C_{A2} - C_{A3})/C_{A2}$ (3)

J_v = permeate volume flux

$D_{AM}K/\delta$ = solute transport parameter

k = mass transfer coefficient

By using R_o and J_v data, taken at different pressures but at a constant feed rate and a constant feed concentration for each set, a plot of $\ln[(1 - R_o)*J_v/R_o)]$ vs J_v will yield a straight line with a slope equal to $1/k$. $D_{AM}K/\delta$ can be obtained from the intercept which is equal to $\ln(D_{AM}K/\delta)$.

Combined Film Theory–Spiegler–Kedem (CFSK) Model

The nonlinear membrane transport model of Spiegler–Kedem (24–27) is combined with the film theory to get a single working equation to estimate the membrane transport parameters and mass transfer coefficient (28).

The final equation of the CFSK model (28) is

$$R_o/(1 - R_o) = a_1[1 - \exp(-J_v a_2)][\exp(-J_v/k)] \tag{4}$$

where $a_1 = \sigma/(1 - \sigma)$ (5)

$a_2 = (1 - \sigma)/P_M$ (6)

Here σ is the reflection coefficient which represents the rejection capability of a membrane, i.e., $\sigma = 0$ means no rejection and $\sigma = 1$ means 100% rejection, P_M is the overall permeability coefficient, and L_p is the hydraulic permeability coefficient of the membrane. By using a nonlinear parameter estimation method by supplying the data of R_o vs J_v, taken at different pressures but at a constant feed rate and a constant feed concentration for each set, one can estimate the membrane parameters σ and P_M, and the mass transfer coefficient, k, simultaneously. In the present case the nonlinear parameter estimation method used is the Box–Kanemasu method (29). Equation (4) shows that a maximum in the observed rejection is possible for certain values of J_v. If we differentiate Eq. (4) with respect to J_v and set this derivative to zero, we obtain the following equation:

$$J_{v,\min} = k\left[\frac{\ln(1 + \mathrm{Pe}^*)}{\mathrm{Pe}^*}\right] \tag{7}$$

where

$$\mathrm{Pe}^* = \frac{(1 - \sigma)k}{P_M} \tag{8}$$

Here $J_{v,\min}$ is the value of J_v where a minimum of $(1 - R_o)/R_o$ occurs, i.e., $R_{o,\max}$. Equation (7) predicts that the maximum in observed rejection occurs at $J_{v,\min}$ values. In a similar way, differentiation of Eq. (1) with respect to J_v and setting this derivative to zero gives

$$J_{v,\min} = k \tag{9}$$

This means that if we use the combined film theory–solution–diffusion model to explain the maximum rejection phenomena with respect to $J_{v,\min}$, the maximum rejection occurs when J_v is equal to the mass transfer coefficient and is independent of the membrane parameters.

EXPERIMENTAL PROCEDURE

A systematic experimental study was carried out for phenol separation using the commercial thin film composite polyamide membrane Perma-TFC (Permionics, Baroda, India). This membrane has three layers. The first layer is a 500 to 2000 Å polymer layer that does the actual separation. The second layer is made of polysulfone of 50 μm thickness. The third layer, used for tear resistance and strength, is made of polyester with a thickness of about 150 μm. The Perma-TFC membranes are capable of withstanding pH values in the 2 to 12 range, pressures up to 50 atm, and temperatures up to 50°C. The separation experiments were performed on a reverse osmosis experimental setup constructed in our laboratory. The experimental setup and the detailed method of experimentation were mentioned elsewhere (23, 28). A wide range of operating parameters was covered in order to see the effects of phenol concentration in the feed (13–540 ppm), feed flow rate (300–900 mL/min), and operating pressure (5–35 atm) without changing the pH of the feed solution. The experiments were performed at around 25°C. The solutions were prepared with distilled water. All the chemicals used were reagent grade. The feed and product samples of phenol were analyzed by a UV-1201 Spectrophotometer (Shimadzee Corporation, Kyoto, Japan) according to standard methods (30).

RESULTS AND DISCUSSION

The effect of applied pressure on pure water permeability [PWP] for the Perma-TFC membrane is shown in Fig. 1, which shows a linear relationship.

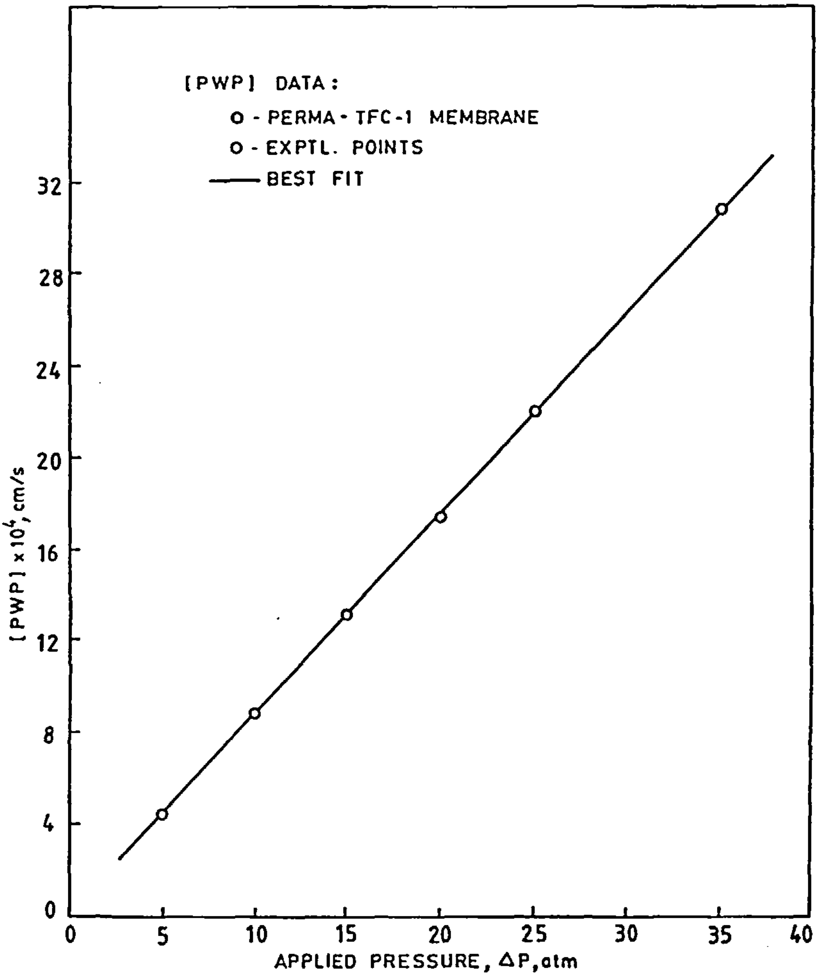

FIG. 1 The effect of applied pressure on [PWP] using the Perma-TFC-1 membrane.

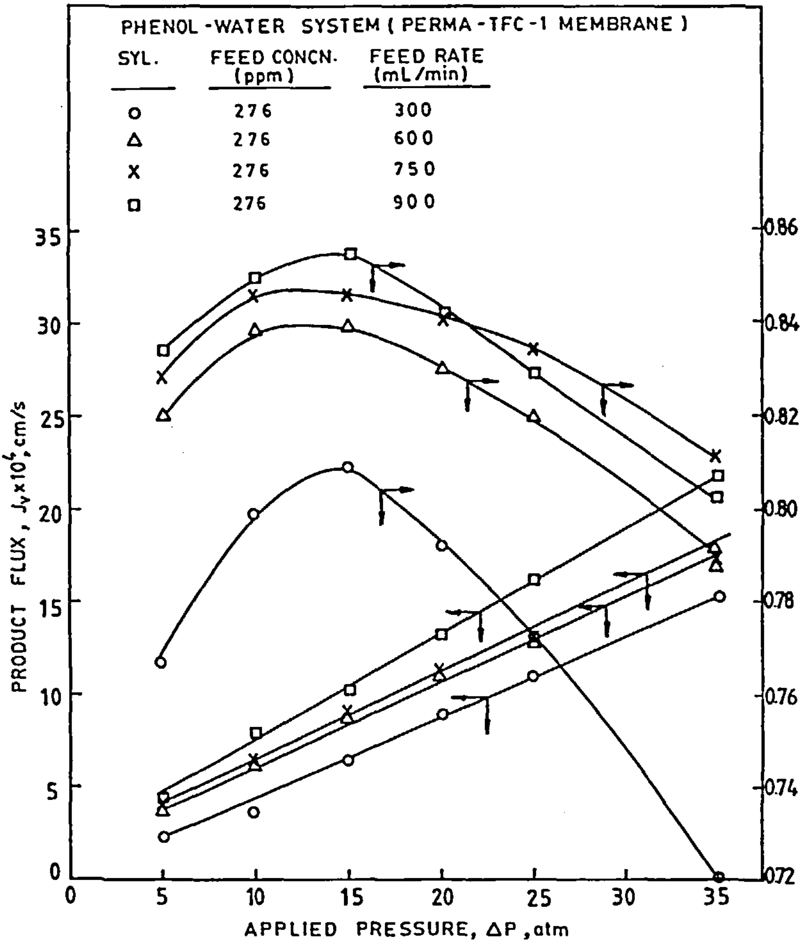

FIG. 2 Effect of varying the applied pressure on the product flux and observed rejection (276 ppm phenol feed).

The slope of the plot is the [PWP] constant or hydraulic permeability constant. Some of the separation data are presented in Figs. 2 and 3, where the observed rejection (R_o) and the product flux (J_v) are plotted against applied pressure for different feed flow rates and feed concentrations. The observed rejection of phenol first increases with increasing pressure up to 15 atm and then decreases gradually, which is in contrast to the general trend. The maximum separation obtained is around 85% at 15 atm.

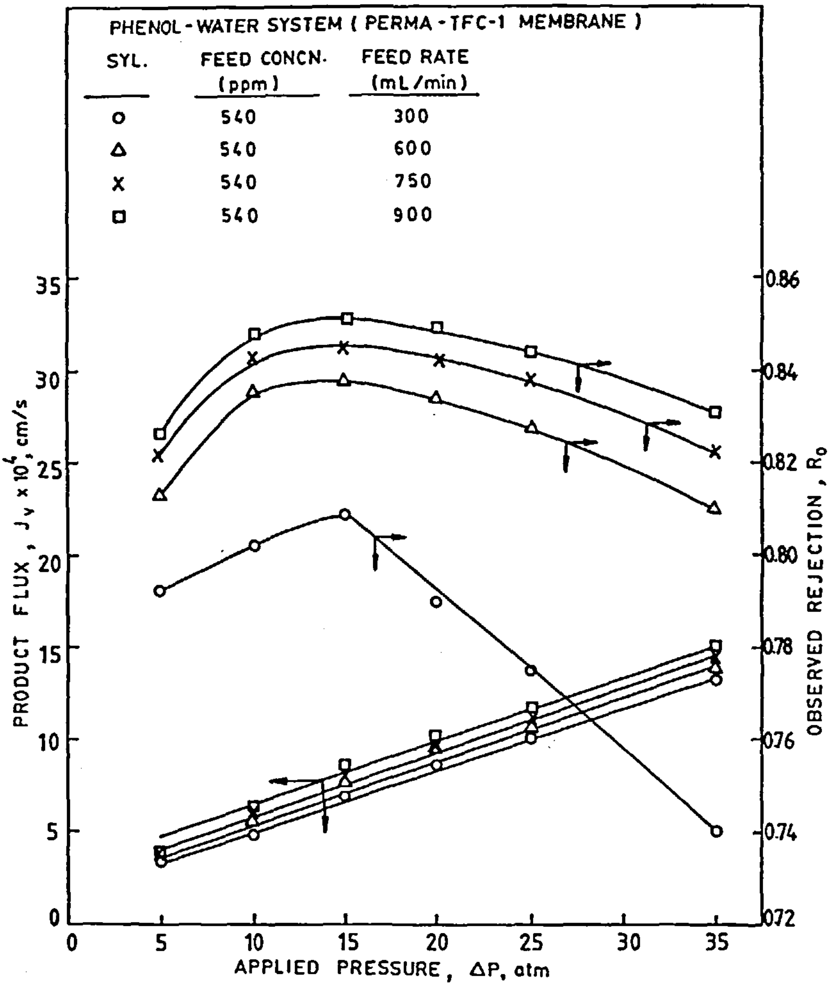

FIG. 3 Effect of varying the applied pressure on the product flux and observed rejection (540 ppm phenol feed).

The data were analyzed using a newly proposed graphical method which is a form of a combined film theory–solution–diffusion (CFSD) model (23) and a combined film theory–Spiegler–Kedem (CFSK) model (28). The advantages of using a graphical method over the widely used Kimura–Sourirajan analysis (KSA) (31, 32) are specified in previous work (23). Plots of the graphical method, $\ln[(1 - R_o)J_v/R_o]$ versus J_v, are shown in Fig. 4. The straight lines show that the graphical method may be used for the phenol–water system. The total results from the graphical method are shown in Table 2. Using the values of k and $(D_{AM}K/\delta)$, the observed rejections were calculated and are compared with the experimental values (Figs. 2 and 3). The variations in the R_o values are within ± 10%. The membrane parameters estimated from the CFSK model are shown in Table 3. The root-mean-square

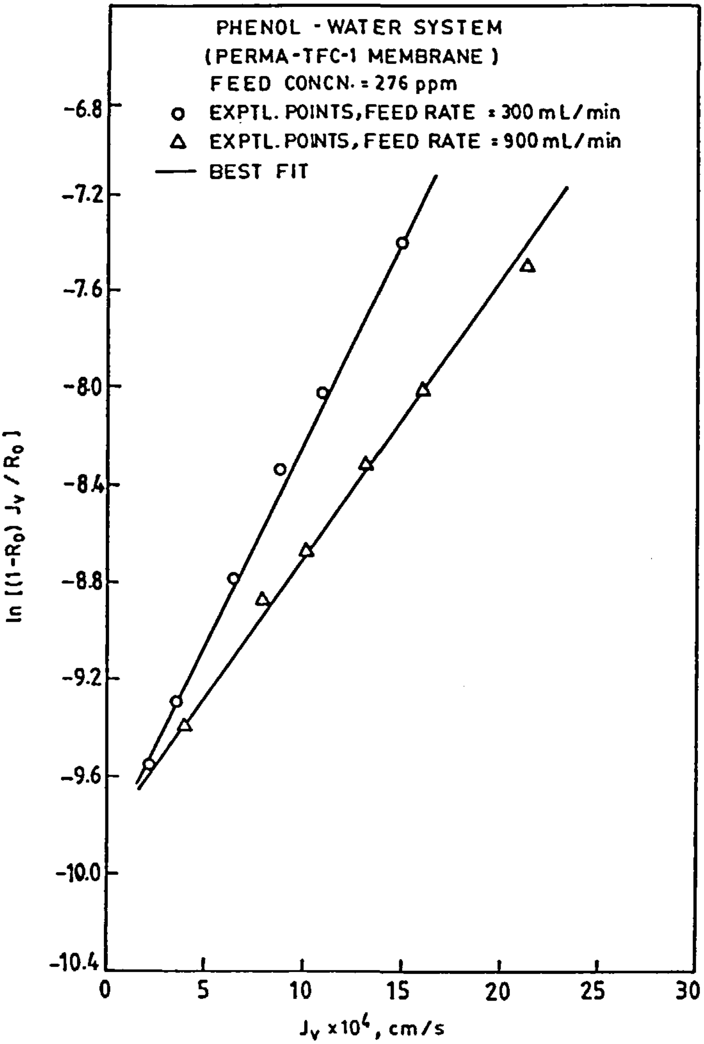

FIG. 4 Plot of $\ln[(1 - R_o)J_v/R_o]$ versus J_v for the phenol–water system of 276 ppm feed concentration, with feed flow rates of 300 and 900 mL/min using the Perma-TFC-1 membrane.

TABLE 2
Results from Graphical Method for Phenol Separation Data

Set	Feed concentration (ppm)	Feed rate (mL/min)	$k \times 10^4$ cm/s	$(D_{AM}k/\delta) \times 10^5$ cm/s
1	13	300	7	7
		600	8	6
		750	9	6
		900	10	6
2	70	300	7	6
		600	8	6
		750	9	6
		900	9	6
3	276	300	6	5
		600	8	5
		750	8	5
		900	9	6
4	540	300	6	5
		600	7	5
		750	8	5
		900	8	5

TABLE 3
Results from Combined Film Theory–Spiegler–Kedem Model for Phenol Separation Data

Set	Feed concentration (ppm)	Feed rate (mL/min)	σ	$P_M \times 10^5$ cm/s	$k \times 10^4$ cm/s	RMSE $\times 10^3$
1	13	300	0.89	5	14	25
		600	0.90	4	21	10
		750	0.90	4	24	11
		900	0.90	4	26	7
2	70	300	0.90	4	13	9
		600	0.90	4	20	3
		750	0.90	4	24	3
		900	0.90	4	26	4
3	276	300	0.89	4	13	1
		600	0.90	4	19	1
		750	0.90	4	24	0
		900	0.90	4	25	3
4	540	300	0.90	4	11	5
		600	0.90	4	18	0
		750	0.90	4	22	0
		900	0.90	4	25	0

error (RMSE) of the nonlinear regression, reported in Table 3, is found to be less than 3%. The solute transport parameter from both models is nearly constant over the operating conditions, but P_M from the CFSK model is more consistent than the $(D_{AM}K/\delta)$ of the graphical method. The variation in mass transfer coefficient with the feed rate is more reasonable in the CFSK model than the k from the graphical method. This difference may be attributed to the presence of a reflection coefficient, as observed in the case of the sodium chloride–water system [28].

The new finding is that for phenol with the thin film composite polyamide membrane, there is a maximum in the observed rejection, as outlined in the Theory Section. This behavior of observed rejection, however, is not reported in the literature for reverse osmosis membranes. However, this behavior has been observed for ultrafiltration membranes (33–35). Some plots of $[(1 - R_o)/R_o]$ versus J_v are shown in Fig. 5, from which we can see that there exists a maximum in rejection at a particular J_v, which is called $J_{v,\mathrm{min}}$ here. One of the reasons why this behavior was not reported for reverse osmosis membranes earlier may be that their maximum observed rejection for a number of other systems occurs at very large values of J_v, which may be beyond the working range of the experimental setup. For example, the data obtained on sodium chloride–water and sodium sulfate–water systems using CAMs showed that $J_{v,\mathrm{min}}$ is higher than the working range of the setup (see Table 4), as is predicted by the theory explained above and shown in Figs. 6 and 7.

Although both models can represent the experimental data available, the CFSK model predicts the rejection more accurately (maximum error ± 3%) than the CFSD model (maximum error ± 10%) in the present phenol–water system. The $R_{o,\mathrm{max}}$ (or $J_{v,\mathrm{min}}$) predicted from both models is different, but there is no experimental verification as to which is more accurate.

CONCLUSIONS

The rejection data of phenol using a commercial thin film composite polyamide membrane are analyzed with the help of the combined film theory–solution–diffusion (CFSD) model (graphical method) and the combined film theory–Spiegler–Kedem (CFSK) model. The observed rejection of phenol showed a maximum when plotted against the product flux. This may be the first time this kind of behavior has been observed for reverse osmosis membranes. An explanation for this is provided by both models and the equations for predicting the volume flux for which the maximum observed rejection occurs is derived. Although both models can represent the experimental data available, the CFSK model predicts the rejection more accurately (maximum error ± 3%) than the CFSD model (maximum error ± 10%) in the present

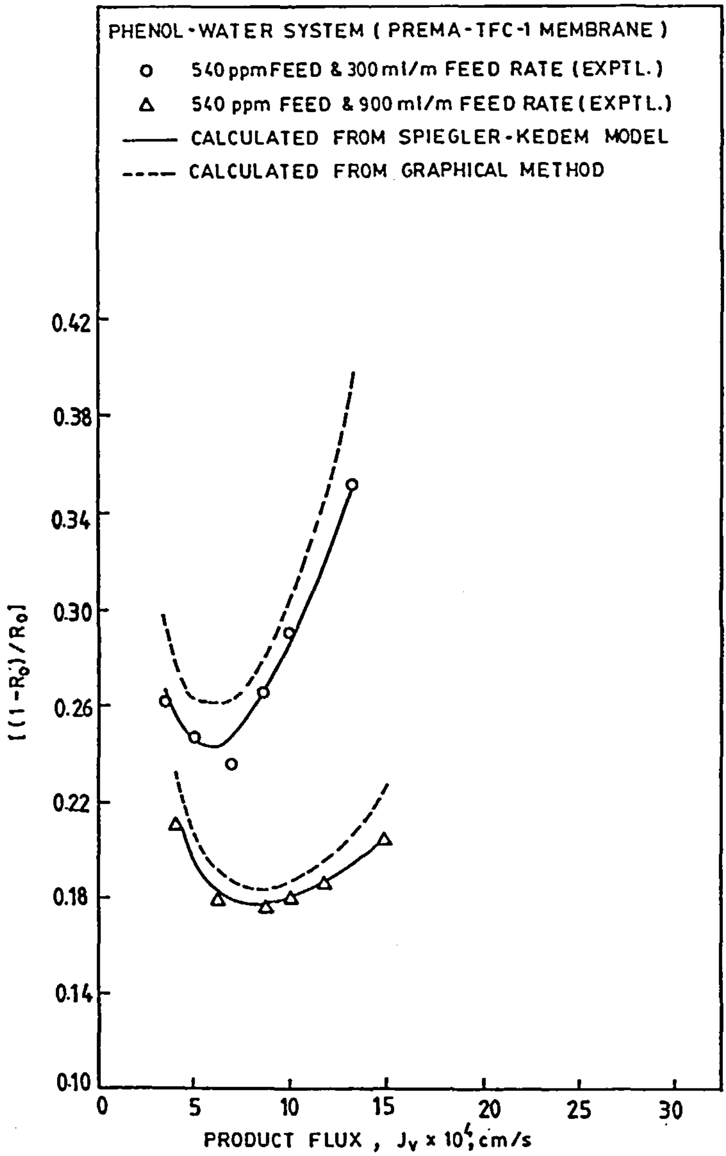

FIG. 5 Plot of $[(1 - R_o)/R_o]$ versus J_v for the phenol-water system using the Perma-TFC-1 membrane (540 ppm phenol feed).

TABLE 4
Values of $J_{v,min}$ for Sodium Chloride–Water and Sodium Sulfate–Water Systems

Feed concentration (ppm)	Feed rate (mL/min)	ΔP (atm)	R_o	$J_v \times 10^4$ cm/s, experimental	$J_{v,min} \times 10^4$ cm/s, predicted from CFSK model	$J_{v,min} \times 10^4$ cm/s, predicted from CFSD model
		Sodium Chloride–Water System				
6000	900	100	0.92	13	23	15
		Sodium Sulfate–Water System				
6000	900	100	0.97	17	22	16

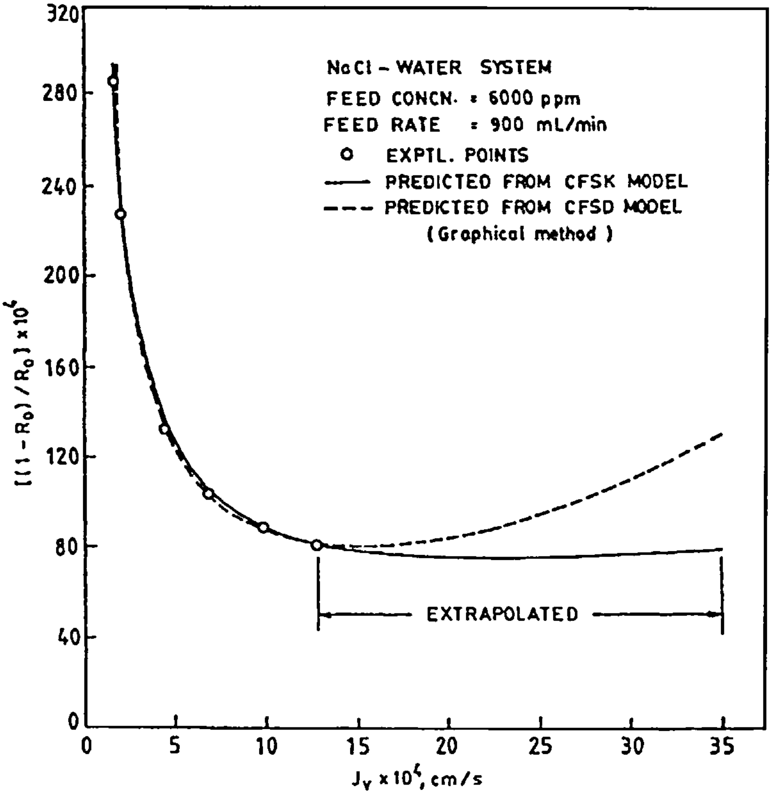

FIG. 6 Plot of $[(1 - R_o)/R_o]$ versus J_v for the NaCl–water system (6000 ppm feed concentration and 900 mL/min feed rate).

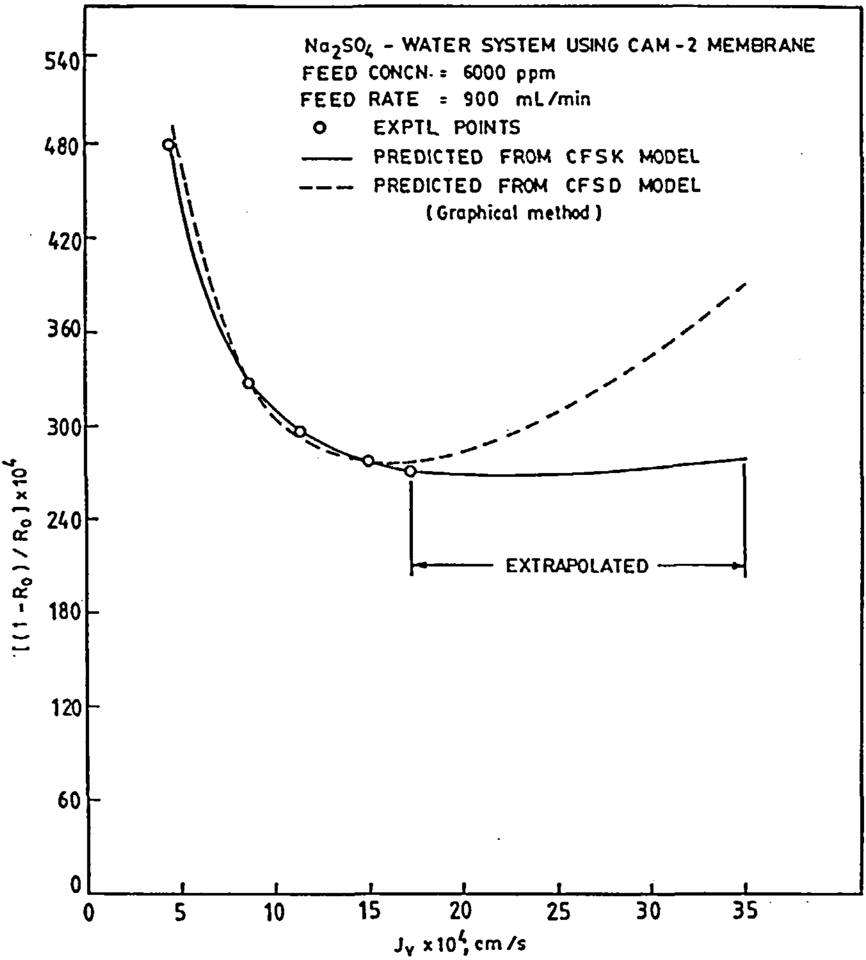

FIG. 7 Plot of $[(1 - R_o)/R_o]$ versus J_v for the Na_2SO_4–water system (6000 ppm feed concentration and 900 mL/min feed rate).

phenol–water system. The $R_{o,max}$ (or $J_{v,min}$) predicted from both models is different, but there is no experimental verification as to which is more accurate. This analysis may be used to characterize reverse osmosis and nanofiltration membranes.

NOTATIONS

a_1	$\sigma/(1 - \sigma)$
a_2	$(1 - \sigma)/P_M$
A	proportionality constant in Eq. (1) ($kmol/m^2 \cdot kPa$)
C_{ij}	molar concentration of Component i in Phase j ($kmol/m^3$)
$D_{AM}K/\delta$	solute transport parameter (m/s)
D_{ij}	diffusivity of Component i in Component j (m^2/s)
J_v	permeate volume flux ($m^3/m^2 \cdot s$)
$J_{v,min}$	value of J_v where a minimum of $(1 - R_o)/R_o$ occurs ($m^3/m^2 \cdot s$)
K	solute partition coefficient
k	mass transfer coefficient (m/s)
L_P	hydraulic permeability coefficient ($m/s \cdot kPa$)
N_i	molar flux of Component i ($kmol/m^2 \cdot s$)
ΔP	pressure difference across the membrane (kPa)
Pe^*	Peclet number defined by Eq. (8)
P_M	overall permeability coefficient (m/s)
Q	feed flow rate (mL/min)
R	true rejection
R_o	observed rejection

Greek Symbols

δ	effective thickness of a membrane (m)
$\Delta\pi$	osmotic pressure difference across the membrane (kPa)
σ	reflection coefficient

Subscripts

A	solute
B	solvent
M	membrane
1	feed solution
2	boundary layer solution
3	permeate solution

ACKNOWLEDGMENTS

The authors acknowledge Mr. V. Y. Jose, General Manager, and Mr. Mayur Joshi, Deputy Manager (Technical), Permionics, Baroda, India, for providing the Perma-TFC membranes. This work was supported in part by Grant RP 00986 from the Department of Science and Technology, India.

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Received by editor August 22, 1997
Revision received February 1998