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Chen-Chong Lin[ab]; Min-Kung Chiang[a]
[a] DEPARTMENT OF CHEMICAL, ENGINEERING NATIONAL TAIWAN UNIVERSITY, TAIWAN, REPUBLIC OF CHINA [b] Division of Chemical Engineering, Department of Chemical Engineering and Chemistry, New Jersey Institute of Technology, Newark, New Jersey

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A Mathematical Model for Composite Membranes for Reverse Osmosis

CHEN-CHONG LIN* and MIN-KUNG CHIANG

DEPARTMENT OF CHEMICAL ENGINEERING
NATIONAL TAIWAN UNIVERSITY
TAIPEI, TAIWAN, REPUBLIC OF CHINA

Abstract

A mathematical model based on two characteristic membrane parameters, A and B, is developed to describe the transport phenomena in the reverse osmosis process of the composite membrane, which consists of two components having different value of A and B. It is found possible to fabricate a high performance membrane by casting a film composed of a dispersed phase with a small particle size of Component II possessing a high water flow (i.e., large value of A) and a very thin matrix phase of Component I possessing a small solute permeation (i.e., small value of B) in the practical separation technique.

INTRODUCTION

After intensive study on reverse osmosis desalination membranes for the past two decades, many theoretical treatments and mathematical models have been proposed (e.g., Ref. *1*). Cellulose acetate is generally used as the desalination membrane, which has an active separating layer and porous support layer (*2*). Thus composite membranes have recently received considerable attention (*3–5*). However, very few theoretical treatments have been reported to describe the membrane transport mechanism of this type of membrane in spite of its practical importance. Several theoretical discussions on the homogeneous membranes have appeared (*6, 7*). In this paper we

*Present address: Division of Chemical Engineering, Department of Chemical Engineering and Chemistry, New Jersey Institute of Technology, Newark, New Jersey 07102.

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develop a mathematical model for the composite membranes to describe their potential in reverse osmosis application. Though the model developed evaluates the performance of composite membranes in the production of fresh water, the development of composite membranes is practically certain to be important in other processes where a pure solvent must be removed from a solution either to recover the solvent or to concentrate the solution.

MODEL DEVELOPMENT

There are several theoretical treatments in common use to describe membrane transport phenomena (*8*). We would like, however, to use the two parameter model as follows:

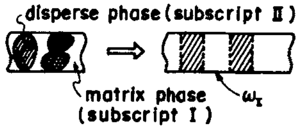
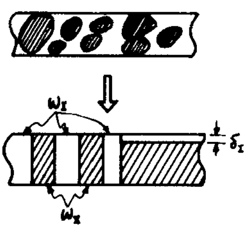
$$N_1 = B(\rho_{1u} - \rho_{1d}) \quad (1)$$

$$N_2 = A(\Delta P - \Delta\pi) \quad (2)$$

where A is a membrane constant for water flow and B is a solute permeation constant. The constants A and B thus provide a complete practical description of membrane performance.

The permeate concentration is generally determined by r_B and a large value of r_A in order to get high % SR and water flux in parallel-type membranes. It is supposed to be of little practical significance in reverse osmosis because very poor mechanical properties of the membrane are expected in the wet conditions used for such structures. On the contrary, there is a good region for high % SR and water flux in the series type which does not sacrifice mechanical strength. Figures 2 and 4 show that both high salt rejection and water flux can be achieved if the effective thichness of matrix phase, ξ, is essentially small. The effect of r_B on the % SR is also minimum. The asymmetric membrane fabricated by Loeb and Sourirajan (*2*) belongs to this type. As seen in Table 1, the series type can be achieved by making a membrane composed of a dispersed phase and a matrix phase. The HSPAN/PVA membrane (*9*) showed a sufficiently encouraging performance in desalination, which can be regarded as an example of this type. According to the mathematical modeling, high salt rejection (small value of B) and high water flow (large value of A) through a membrane can be obtained by making a series type of membrane. It is therefore recommended that a membrane which consists of a dispersed phase with a small size of particles of Component II with a large value of A and a very thin matrix phase of Component I with a small value of B be fabricated. Figure 5 shows a case of a combined type of membrane. It is seen that high performance

TABLE 1.
Table 1. Three models of composite membrane

Parallel Type		$A = A_I\omega_I + A_{II}(1 - \omega_I)$ $B = B_I\omega_I + B_{II}(1 - \omega_I)$ $C = C_I\omega_I + C_{II}(1 - \omega_I)$
Series Type		$\frac{1}{A} = \frac{\xi}{A_I} + \frac{1-\xi}{A_{II}}$ $\frac{1}{B} = \frac{\xi}{B_I} + \frac{1-\xi}{B_{II}}$ $\frac{1}{C} = \frac{\xi}{C_I} + \frac{1-\xi}{C_{II}}$
Combined Type		$A = A_I\omega_I + A_{II}\omega_{II} + (1-\omega_I-\omega_{II})(\frac{\xi}{A_I} + \frac{1-\xi}{A_{II}})^{-1}$ $B = B_I\omega_I + B_{II}\omega_{II} + (1-\omega_I-\omega_{II})(\frac{\xi}{B_I} + \frac{1-\xi}{B_{II}})^{-1}$ $C = C_I\omega_I + C_{II}\omega_{II} + (1-\omega_I-\omega_{II})(\frac{\xi}{C_I} + \frac{1-\xi}{C_{II}})^{-1}$

desalination is very difficult to achieve even with a very small value of ξ. % *SR* shows a maximum of about 45% under such conditions. If we set $\xi = 0.1$, for example, then the transport mechanism shows almost the same relative flows of solute and water. According to our definition,

$$\%\ SR = \left(1 - \frac{\rho_{1d}}{\rho_{1u}}\right) \times 100 \qquad (3)$$

Salt rejection analogous to Eq. (3) can be obtained for a two parameter model:

$$\%\ SR = \left[1 + \frac{\rho B}{A(\Delta P - \Delta\pi)}\right]^{-1} \times 100 \qquad (4)$$

We now consider a composite membrane which consists of two other immiscible components with different values of A and B. Furthermore, it is supposed that the composite membrane is composed of a dispersed phase of Component I and a matrix phase of Component II. The transport mechanism is now classified into the following three types according to the morphological point of view (Table 1).

(1) Parallel type: If the particle size of the dispersed phase is large compared to the thickness of the membrane or the particles are contacted one by one so that the normal direction of the phase is equivalent to the thickness of membrane, then the transport mechnism can be described by this type.
(2) Series type: If the thickness of membrane is larger than the size of particles which are dispersed homogeneously in the matrix phase, then this is morphologically analogous to the series type of geometrical structure.
(3) Combined type: If the above two types exist at the same time in the membrane structure, the transport mechanism can be described by this type.

Any membrane can be one of the above three types depending on the geometrical factors of its structure. The overall values of A and B for each types of membrane are obtainable theoretically as shown in the third column of Table 1. A large value of A means high solvent flow and a small value of B indicates small solute permeation.

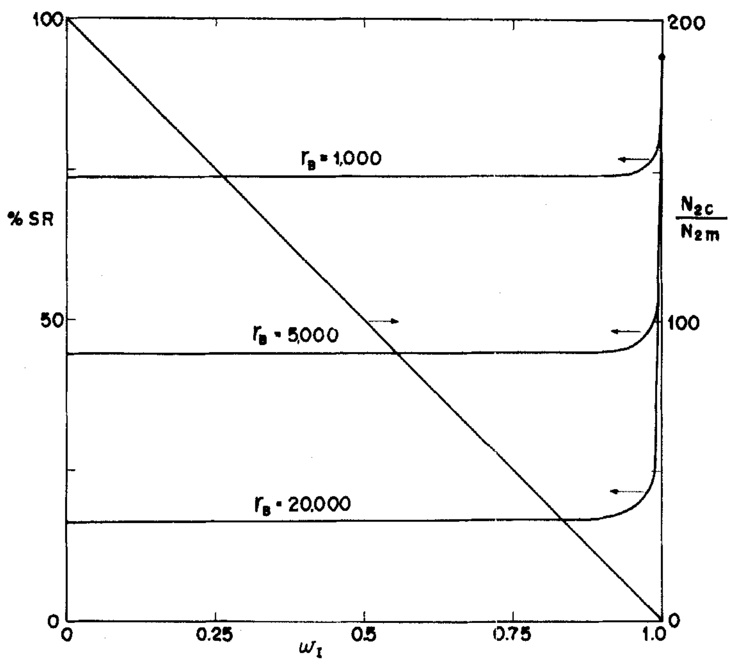


FIG. 1. Effect of r_B on the relationship between % *SR* or water flux and w_I in the parallel-type membrane. $r_A = 200$, $\rho B_I/A_I(\Delta P - \Delta\pi) = 0.05$.

RESULTS AND DISCUSSION

Let us define two new parameters as follows: The parameter ratio of constant A between two components:

$$r_A = A_{II}/A_I$$

The parameter ratio of constant B between two components

$$r_B = B_{II}/B_I$$

Table 1 shows three types of model describing the relationships between the overall values and the individual characteristic membrane constants. Substituting these overall value of constants into Eq. (4), the % SR of the composite membrane can be satisfactorily discussed. The simulations of the models proposed are shown in Figs. 1–6. Figures 1 and 2 illustrate the effect of r_B on the % SR and water flux for parallel and series type membranes,

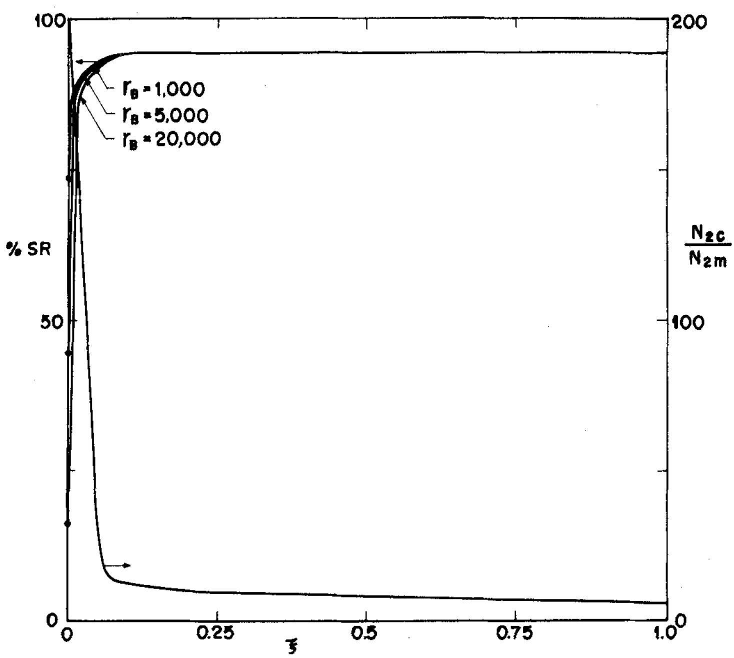


FIG. 2. Effect of r_B on the relationship between % SR or water flux and ξ in the series-type membrane. $r_A = 200$, $\rho B_I/A_I(\Delta P - \Delta\pi) = 0.05$.

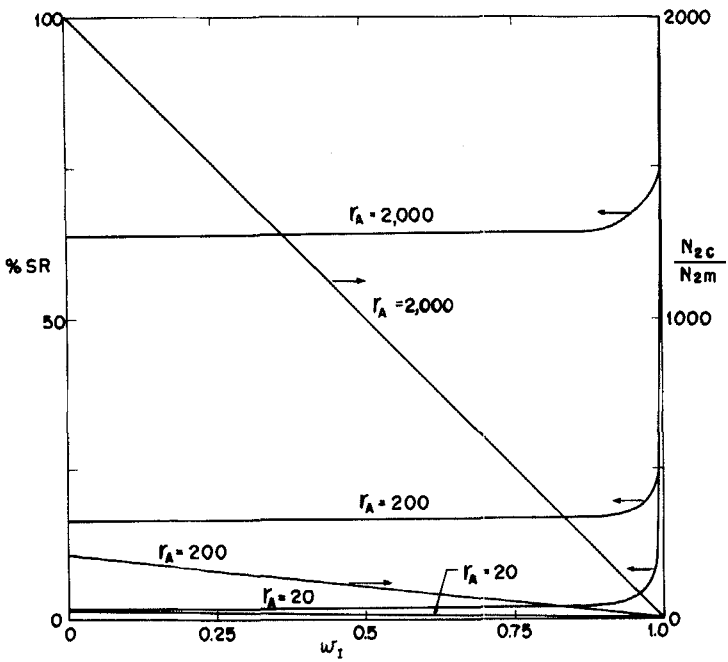


FIG. 3. Effect of r_A on the relationship between % SR or water flux and w_I in the parallel-type membrane. $r_B = 20{,}000$, $\rho B_I/A_I(\Delta P - \Delta\pi) = 0.05$.

respectively. Figures 3 and 4 illustrate the effect of r_A on the % SR and water flux for parallel and series type membranes, respectively.

SYMBOLS

A	characteristic membrane constant of water flow (g/cm$^2\cdot$s$\cdot$atm)
B	characteristic membrane constant of solute permeation (cm/s)
C	third membrane constant due to the pore flow (cm/s$\cdot$atm)
N	flux (g/s$\cdot$cm^2)
ΔP	pressure difference across the membrane (atm)
r	ratio of membrane constants for two components
w	fraction of occupied surface area

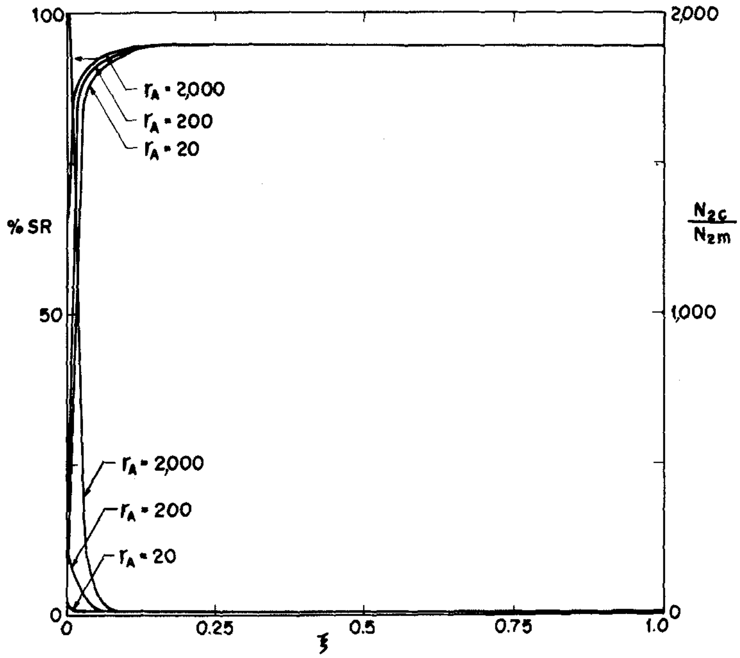


FIG. 4. Effect of r_A on the relationship between % SR or water flux and ξ in the series-type membrane. $r_B = 20{,}000$, $\rho B_I/A_I(\Delta P - \Delta\pi) = 0.05$.

Subscripts

1	solute
2	solvent (water)
I	Component I (matrix phase)
II	Component II (dispersed phase)
c	composite membrane
m	pure matrix membrane
d	downstream of membrane
u	upstream of membrane

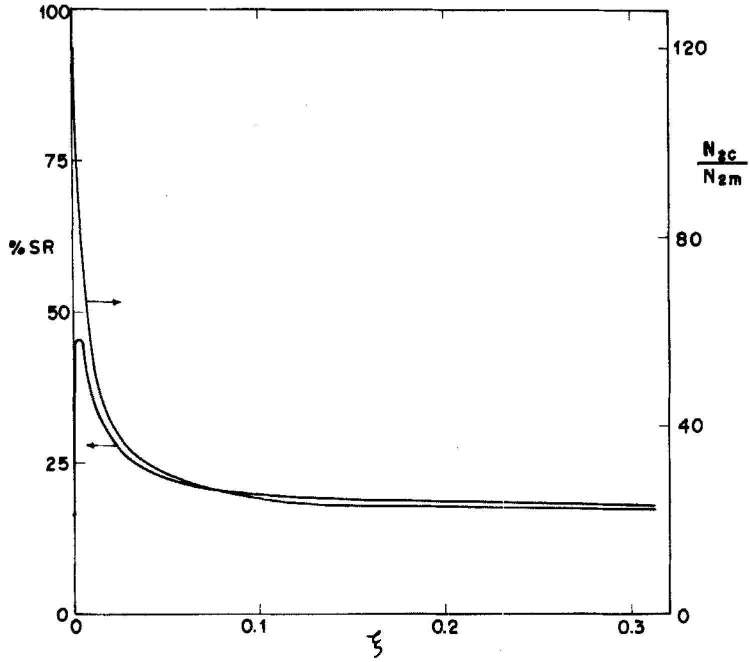


FIG. 5. The relationship between % *SR* or water flux and ω_I in the combined-type membrane at a definite value of ξ. $\xi = 0.1$, $w_I + w_{II} = 0.5$, $r_A = 200$, $r_B = 20{,}000$, $\rho B_I / A_I(\Delta P - \Delta\pi) = 0.05$.

Greeks

ρ	density or concentration (g/cm^3)
$\Delta\pi$	the difference between the osmotic pressure of saline solution at the membrane surface and product water (atm)
ξ	effective thickness fraction of matrix phase $= \delta_l/\delta_c$
δ	equivalent thickness in series-type membrane

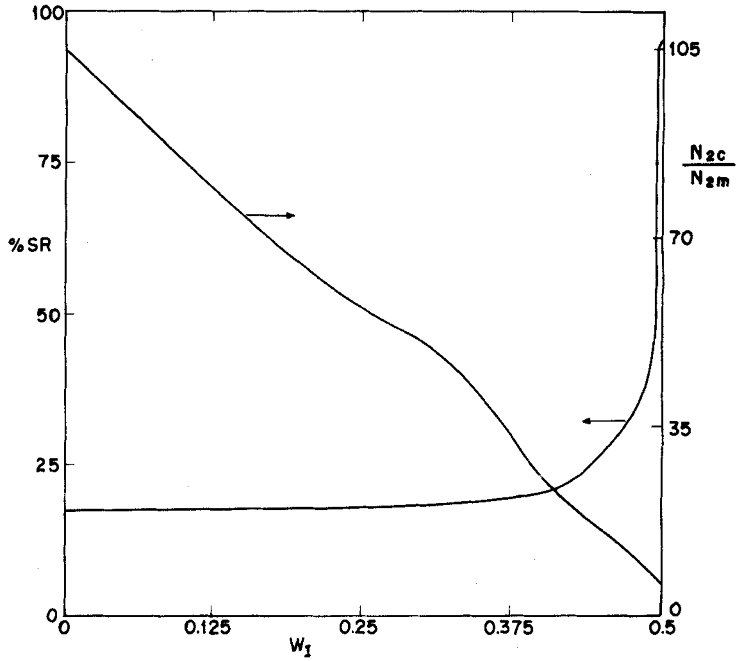


FIG. 6. The relationship between % *SR* or water flux and ξ in the combined-type membrane at a definite value of w_I. $w_I = 0.4$, $w_{II} = 0.1$, $r_A = 200$, $r_B = 20{,}000$, $\rho B_I A_I(\Delta P - \Delta\pi) = 0.05$.

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