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Reverse Osmosis in an Unstirred Batch System. II. Analysis on Transport Phenomena across Membrane

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Abstract

Transport behavior across a membrane in a reverse osmosis unstirred batch system is analyzed by simulation of a mathematical model developed in a previous paper. The effects of a phenomenon termed "concentration polarization" on the throughput rate and on % *SR* are postulated by information generated. A simple determination method of the membrane constants via the model simulation is proposed.

INTRODUCTION

A number of theoretical analyses have been published on the transport phenomena of reverse osmosis flow systems (1, 2). The motivation for the theories is to develop a sufficient understanding of the flow field and of the troublesome phenomenon termed "concentration polarization" for engineers to be able to improve the performance of a desalination system on the basis of rational design procedures. An unstirred batch cell may be the simplest apparatus in the laboratory for testing the accuracy of theory and obtaining the characteristic constants of the membrane. An improved experimental piece of equipment has been introduced by Liu and William (3) which aids in understanding the performance of desalination. The role played by the flow rate in the concentration polarization phenomenon was shown by Alfani and Drioli (4). A semiempirical model was developed by them in order to describe this phenomenon (5). However, the model cannot be used to predict this phenomenon, since it needs the aid of experimental data in order to evaluate the salt concentration profile. A mathematical model proposed by authors in a previous report (6) has succeeded in the development of a

theoretical expression to predict the transport phenomena across the membrane in an unstirred batch cell. In this paper the behavior of reverse osmosis transport is analyzed via model simulation which aids in a better understanding to the flow field of such a system.

MODEL SIMULATION

The model consists of a two parameter membrane transport mechanism of Eqs. (1) and (2) in combination with a one-dimensional time-dependent diffusion equation of Eq. (3):

$$N_A^* = B(\rho_{A0} - \rho_{A1}) \quad (1)$$

$$N_B^* = A(\Delta P - \Delta \pi) \quad (2)$$

$$\frac{\partial X_A^*}{\partial \tau^*} + \bar{v}^* \frac{\partial X_A^*}{\partial Z^*} = D_{AB} \frac{\partial^2 X_A^*}{\partial Z^{*2}} \quad (3)$$

The resultant nonlinear differential equations are then reduced to a family of equations involving several dimensionless parameters which are summarized in Table 1 of a previous paper (6). The numerical integration by finite difference procedure can be carried out along the dimensionless time axis to solve this dimensionless mass balance equation. The parameter F represents the dimensionless group of the solvent flux. Therefore V/F represents the normalized dimensionless throughput rate, where $V/F = \bar{v}^* \rho / A \Delta P$. When $V/F = 1$, the liquid is the pure solvent. The parameter E represents a dimensionless group of the solute flux. When $E = 0$, it means 100% salt rejection by the membrane.

The percent salt rejection, % SR , is a basic measure of the membrane performance for desalination, which can be derived by

$$\% SR = \frac{100}{1 + \frac{\rho B}{A(\Delta p - \Delta \pi)}} \quad (4)$$

where A and B are the two "membrane constants," and ρ is the density of liquid in terms of concentration. In the experimental equipment, one can only measure the rate of effluent and its salt concentration, from which one obtains the apparent percent of salt rejected, which is defined as

$$\% SR_a = \frac{\rho^0 - \rho_{A1}}{\rho^0} \times 100 \approx (1 - X_{A1}) \times 100 \quad (5)$$

where ρ^0 is the concentration at feed and ρ_{A1} is the concentration of effluent downstream of the membrane.

Another physical quantity obtainable is the accumulated apparent per cent of salt rejected, $\% SR_{aa}$, defined as

$$\% SR_{aa} = 1 - \frac{\int_0^\tau N_A^* d\tau^*}{\rho^0} \times 100 \quad (6)$$

The first quantity ($\%SR$) is obtainable theoretically, while the later two quantities ($\%SR_a$ and $\%SR_{aa}$) are obtainable both theoretically and experimentally.

ANALYTICAL RESULTS AND DISCUSSION

The normalized dimensionless throughput rate, V/F , vs dimensionless time, τ , is plotted for different F values in Fig. 1 under the conditions of $E = 9$ (i.e., $\% SR = 100\%$). It is seen that the larger the F value, the smaller the throughput rate will be. The driving force of solvent permeation (i.e., $\Delta P = \Delta \pi$) will be greatly diminished as time elapses because of the buildup of excessive amounts of dissolved salt adjacent to the membrane. This is known as "concentration polarization." For a smaller F value (e.g., Curves c and d), the salt accumulation in the neighborhood of the membrane can be offset by diffusion of salt solute, resulting in a higher V/F value in the beginning. Moreover, the dependency of the throughput rate on time is flatter than that of a large F value (e.g., Curves a and b). When the concentration polarization approaches the upper boundary layer, however, a sudden decrease in throughput rate is observed at a finite time, say $\tau > 10^{-2}$. On the other hand, for a large F value, which has a lower V/F value at the beginning, the throughput rate decreases progressively as time elapses as in Curves a and b. In Fig. 2 the throughput rate vs time is now plotted for different E values under the conditions of a constant F value (i.e., $F = 83.33$) and a constant pressure (i.e., $\Delta P = 50$ atm). The time needed to reach a V/F value of zero caused by the complete concentration polarization is quicker for higher E values in spite of a flatter dependency of throughput rate on time. Figure 3 shows now the dependency of throughput rate for different operational pressures under the conditions of constant E value (i.e.,

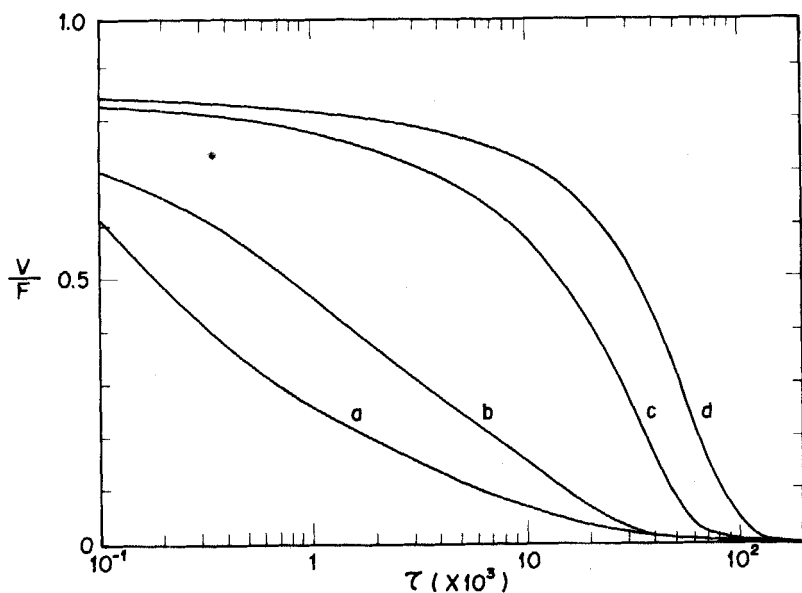


FIG. 1. Predicted plot of normalized throughput rate vs time for F varied ($\Delta P = 50$ atm, $X_A^0 = 0.01$, $E = 0$.) (a) $F = 166.7$, (b) 83.33 , (c) 16.67 , (d) 8.333 .

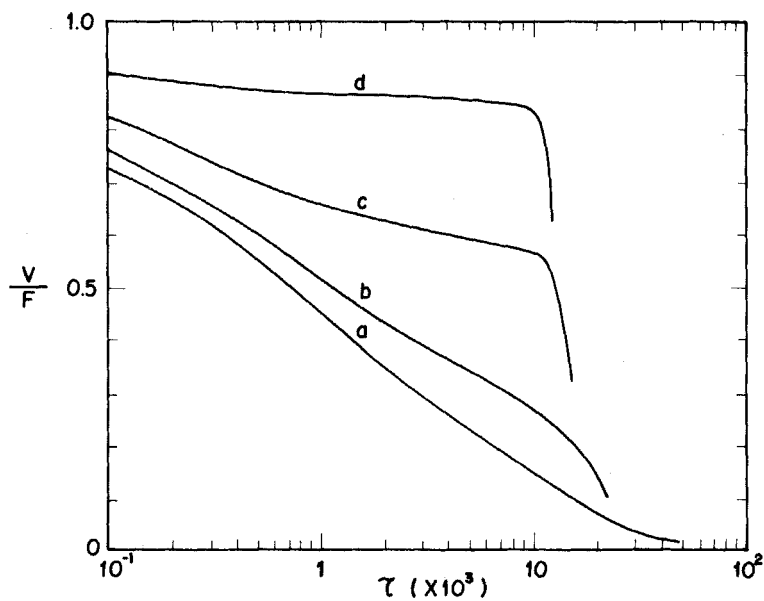


FIG. 2. Predicted plot of normalized throughput rate vs time for E varied. ($\Delta P = 50$ atm, $X_A^0 = 0.01$, $F = 83.33$.) (a) $E = 0$, (b) 0.0333 , (c) 0.1667 , (d) 0.6667 .

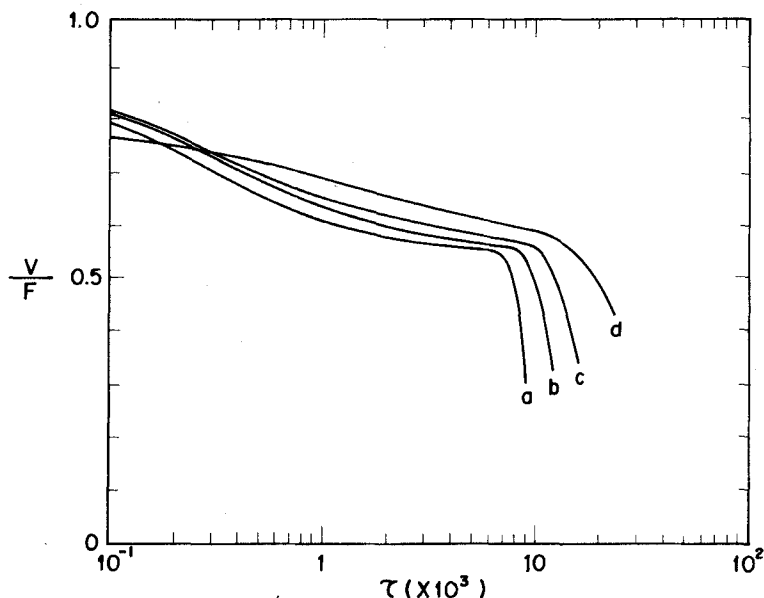


FIG. 3. Predicted plot of normalized throughput rate vs time for the operation pressure varied. ($E = 0.1667$, $X_{A1}^0 = 0.01$, $F/\Delta P = 1.667 \text{ atm}^{-1}$.) (a) $\Delta P = 100 \text{ atm}$, (b) 75 atm , (c) 50 atm , (d) 25 atm .

$E = 0.1667$) and a constant value of $F/\Delta P = 1.667 \text{ atm}^{-1}$. It is apparent that the higher the pressure, the quicker complete concentration polarization is achieved. Curve d has a smallest value of throughput rate at $\tau < 2 \times 10^{-4}$. This is attributable to the very low solvent driving force under such a low operational pressure. The influence of the initial salt concentration on the throughput rate under the conditions of a constant pressure of $\Delta P = 50.0 \text{ atm}$ and an F value of 3000 is shown in Fig. 4. It is apparent from Fig. 4 that the larger the salt concentration, the larger and quicker is the influence of the concentration polarization. The influence of the initial concentration on the interface concentration upstream of the membrane and downstream of the membrane in terms of the weight percent are shown in Figs. 5 and 6, respectively. For a 1% concentration represented by Curve c, the trend of a sudden increase in X_{A0}^*/X_{A1}^* is observed at $\tau > 7.5 \times 10^{-2}$ where complete concentration polarization occurs. For a higher concentration of liquid, the value of X_{A0}^* or X_{A1}^* increases quicker, indicating a large influence of the concentration polarization. Our model simulation can develop a sufficient detailed understanding of the flow field in such reverse osmosis. Finally, the influences of salt concentration and operation pressure on % SR are shown in Figs. 7 and 8, respectively. It is concluded that the lower the NaCl

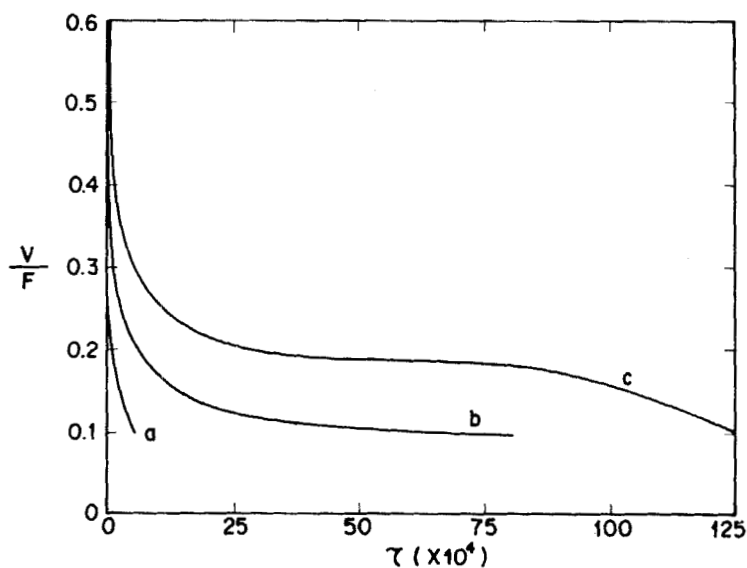


FIG. 4. Predicted plot of normalized throughput rate vs time for the concentration varied. ($\Delta P = 50$ atm, $E/X_A^0 = 10$, $F = 300$.) (a) 4 wt-%, (b) 2 wt-%, (c) 1 wt-%.

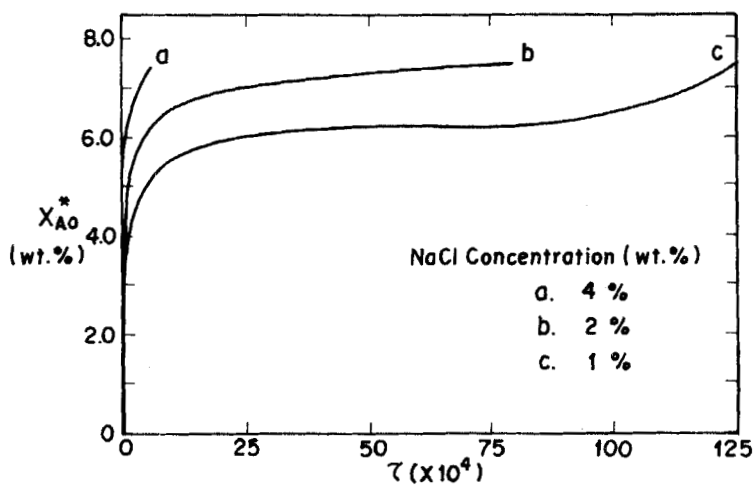


FIG. 5. Predicted plot of salt concentration upstream of the membrane vs time for the concentration varied. ($\Delta P = 50$ atm, $E/X_A^0 = 10$, $F = 300$.)

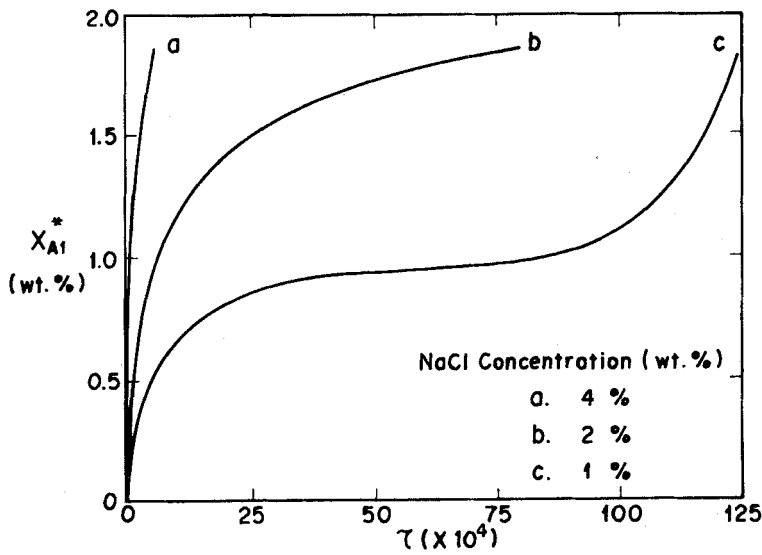


FIG. 6. Predicted plot of salt concentration downstream of the membrane vs time for the concentration varied. ($\Delta P = 50$ atm, $E/X_A^0 = 10$, $F = 300$.)

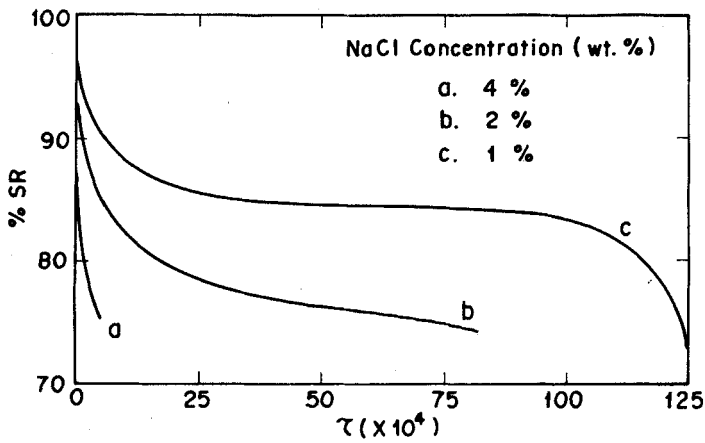


FIG. 7. Predicted plot of percentage of salt rejected vs time for the concentration varied. ($\Delta P = 50$ atm, $E/X_A^0 = 10$, $F = 300$.)

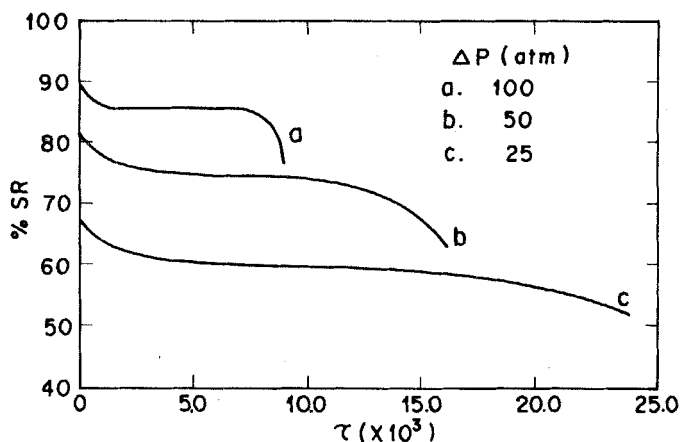


FIG. 8. Predicted plot of percentage of salt rejected vs time for the operation pressure varied. ($F/\Delta P = 1.667$, $E = 0.1667$, $X_A^0 = 0.01$.)

concentration, the larger % SR is. Moreover, the dependency of % SR on time is flatter for a lower concentration. On the other hand, the higher the pressure, the larger % SR is. However, the time needed to reach the concentration polarization, where a sudden decrease in % SR occurs, is reached sooner for a higher operational pressure. These facts offer a good basis of a rational design for engineers to improve the performance of a membrane for desalination.

Three types of salt rejection vs time are plotted in Fig. 9 under the conditions of $\Delta P = 50$ atm, $X_A^0 = 0.01$, $E = 0.00333$, $F = 83.333$, and % $SR^0 = 95.58\%$. The value of % SR is very little affected by the elapsed time as shown in Curve a. The value of % SR_{aa} , however, is significantly affected by the elapsed time as shown in Curve c and can take a negative value at a finite time.

The performance of desalination of a membrane is characterized by the "membrane constants" A and B .

In Fig. 10, % SR vs B is plotted, illustrating how the salt rejection does depend on the value B . By using our simulation model, one can get the value B for a membrane tested according to the following procedures.

- (1) Obtaining membrane constant A of Eq. (2) by performing experiment with pure solvent (i.e., distilled water).
- (2) Measuring the throughput rate and salt concentration of effluent to obtain % SR_a and % SR_{aa} .
- (3) Numerical analysis on the model by making use of membrane

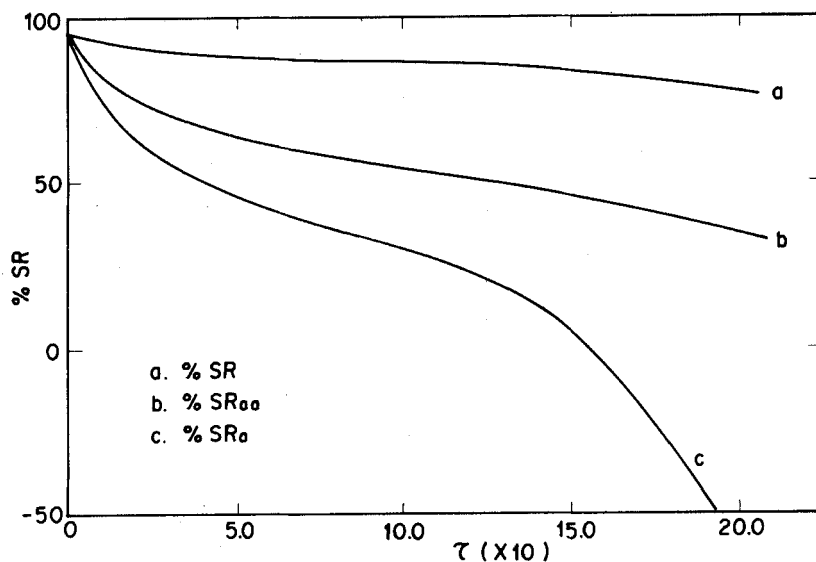


FIG. 9. Plot of three types of percentage of salt rejected vs time. ($\Delta P = 50$ atm, $X_A^0 = 0.01$, $E = 0.003333$, $F = 83.333$, % SR⁰ = 95.58.)

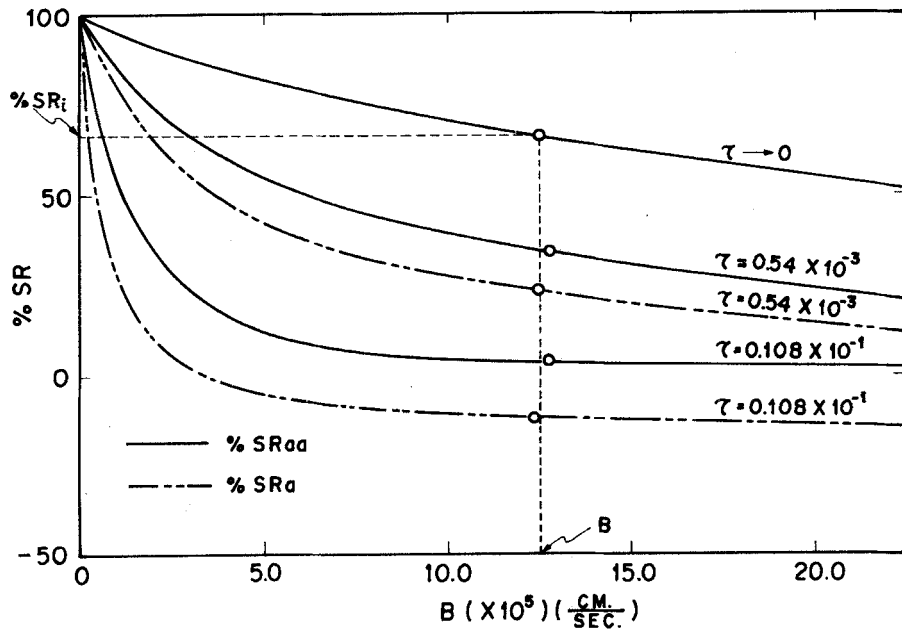


FIG. 10. Plot of percentage of salt rejected vs salt permeation constant B . ($\Delta P = 50$ atm, $X_A^0 = 0.01$, $F = 83.33$.) Experimental determination of B value.

constant A obtained according to Procedure (1) and other conditions, such as ΔP , L^* , and C^0 , and some arbitrary values of B . Constructing a diagram of % SR vs time plot like Fig. 10.

- (4) Fitting the experimental data of % SR_a and % SR_{aa} obtained in the Procedure (2) with the diagram obtained in Procedure (3) like Fig. 10 to obtain the corresponding points for each time as illustrated by circles. Make a straight line through the points. The intersection of the line and the abscissa is the value B for the membrane tested. The intersection of the line and the curve for $\tau = 0$ should be the value of % SR^0 .

CONCLUSION

An improved model based on a two-parameter membrane transport mechanism and a salt diffusion equation predicts transport phenomena across a membrane including concentration polarization in the reverse osmosis unstirred batch system. Membrane constants A and B can be easily obtained via a simulation model proposed in this kind of experimental equipment, from which the flow rate through the membrane usually can be measured with 5% accuracy in an unstirred batch cell.

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