Modeling of reverse osmosis flux of aqueous solution containing glucose

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Abstract−The aim of the paper is to model the permeate flux during reverse osmosis (RO) of a highly concentrated glucose solution using the osmotic pressure model. Such a model accounts for the effect of the concentration polarization phenomenon on the permeate flux. To apply this model the viscosity, the osmotic pressure of solution and the diffusion coefficient of glucose were estimated. Using mathematical simulation software, the values of mass transfer coefficient for different concentrations of glucose (5, 10, 15 and 20 wt%) and at different feed flow rate were determined. The experimental permeate flux values conducted on flat RO membranes (Type HR-99) agreed well with the values calculated by the osmotic pressure model, as shown by statistical analysis.

Keywords: Mass Transfer Coefficient, Reverse Osmosis, Glucose, Permeate Flux

INTRODUCTION

Reverse osmosis (RO) is a mature technology widely used all over the world. In the food industry, its application has been developed successfully and many investigations have been carried out to remove water from juices and other liquid foods with high efficiency [1,2].

In the food industry, solutions treated by reverse osmosis usually contain many kinds of solutes and their concentrations are relatively high. Therefore, the prediction of permeate flux, which is necessary for designing plant configurations and operating conditions, is an important issue. Despite its success in several industries, the reverse osmosis mass transfer mechanism and modeling still attracts interest [3-8]. In this context, the mass transfer coefficient determination is important for designing membrane separation modules. The problem with Sherwood number relationships [9,10] is that they are depending on many parameters, such as equivalent hydraulic diameter, module length of flow channel, kinematic viscosity of solution. To overcome this difficulty, Sherwood number correlations require a known flow correlation.

To predict permeate flux through RO membrane, the osmotic pressure model was applied. This model considers the increase of osmotic pressure at the membrane surface caused by the concentration polarization phenomenon. It requires knowledge of the solution properties, such as viscosity, density and diffusivity of the solute that affect the concentration polarization phenomenon, and therefore the permeate flow. The dependence of these properties to the solute concentration was not estimated sufficiently. Therefore, permeate flux during reverse osmosis of highly concentrated solutions has not been predicted accurately.

In the present work, we used, based on the literature, semi-empir-

ical relationships linking the viscosity, osmotic pressure and the diffusion coefficient to glucose concentration, solute were selected as a model. From these relationships, we determined the mass transfer coefficient. Then we carried out modeling of the flow of permeate.

In the present study, glucose was used as solute solution model, simulating the component of fruit juice. Besides, it is a component that usually exists in the food industry with quite high concentration. Solutions were filtrated through RO and mass transfer coefficient was estimated. Then the permeate flux during RO of a highly concentrated glucose solutions was estimated using the osmotic pressure model and compared with experimental data

THEORETICAL

1. Osmotic Pressure Model

The effect of the concentration polarization phenomenon on the permeate flux in reverse osmosis can be described by the osmotic pressure model. The effective driving pressure, according to this model, is reduced as the osmotic pressure of the solution at the membrane surface increases. The permeate flux J_v is expressed as follows:

$$J_v = L_p \cdot (\Delta P - \sigma \Delta \Pi) \tag{1}$$

where σ and $\Delta \Pi$ are the reflection coefficient and the osmotic pressure difference across the membrane, respectively. When rejection is sufficiently high, σ can be assumed to be unity and the osmotic pressure difference across the membrane can be determined by the concentration at the membrane surface C_m as

$$\Delta \Pi = \Pi(C_m) - \Pi(C_p) \approx \Pi(C_m) \tag{2}$$

where C_m and C_p are the solute concentrations at the membrane surface and in the permeate, respectively. Then Eq. (1) can be rewritten as

$$J_v = L_p \cdot (\Delta P - \Pi(C_m)) \tag{3}$$

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According to the concentration polarization equation [11], C_m can be expressed as

$$C_m = C_b \exp (J_v/k) \qquad (4)$$

where C_b and k are the solute concentration in the bulk retentate and the mass transfer coefficient, respectively. Thus, by knowing k, L_p and $\Pi(C_m)$ J_v can be obtained by the resolution of Eqs. (3) and (4).

1-1. Determination of L_p

When pure water is filtered, there is no osmotic pressure and Eq. (1) can be written as:

$$J_v = L_p \cdot \Delta P \qquad (7)$$

This equation permits the calculation of pure water permeability L_p.

1-2. Determination of Osmotic Pressure Π_g (C)

In a previous work [13], the osmotic pressure of the glucose solution Π_g was measured up to a concentration of 50 wt%. The data indicate that the difference of the osmotic pressure measured from that of an ideal solution could be related to hydration. If the hydration number of glucose is assumed to be 2, the data is explained well. Therefore, Π_g can be expressed in terms of solute concentration C by Eq. (8).

$$\Pi_g (C) = -(RT/V_w) \ln \{[(100 - C/M_w) - (2C/M_g)]/ \\ [(100 - C/M_w) - (C/M_g)]\} \qquad (8)$$

where R and T are the gas constant and the temperature of the solution, respectively. M_w, and M_g are the molar masses of water and glucose, whose values are 18.016 and 180.16 g·mol^{-1}, respectively. The partial molar volume of water, V_w, can be assumed to be equal to the molar volume of pure water ($= 18.07 \times 10^{-6}$ m^3·mol^{-1}).

1-3. Determination of Mass Transfer Coefficient k

The mass transfer coefficient k is calculated by using a mass transfer correlation that is a function of feed flow velocity (v), height of flow channel, hydraulic diameter (d_h), diffusion coefficient (D) and kinematic viscosity of solution (ν).

In the case of laminar regime [9], k is obtained using the Leveque mass transfer correlation

$$N_{Sh} = 1.62 (N_{Re} N_{Sc} d_h/L)^{1/3} \qquad (5)$$

In the case of turbulent regime [10], k is obtained using the Deissler mass transfer correlation:

$$N_{Sh} = 0.023 N_{Re}^{0.875} N_{Sc}^{0.25} \qquad (6)$$

N_{Sh}, N_{Re} and N_{Sc} are Sherwood, Reynolds and Schmidt numbers, respectively, defined as: $N_{Sh} = kd_h/D$, $N_{Re} = d_h v/\nu$; $N_{Sc} = \nu/D$ [12].

To estimate the mass transfer coefficient k, the viscosity and diffusion coefficient were obtained from the work of Gladden et al. [14]. According to these authors the logarithm of the relative viscosity ln (μ_g/μ_w) was a linear function of the solute molar fraction:

$$\ln(\mu/\mu_w) = AC/(100 - BC) \qquad (9)$$

μ and μ_w are the solute and water viscosities (Pa·s), respectively; C the solute concentration expressed in wt%; the empirical coefficients A and B are functions of temperature.

Using the relationship (9), the following equation was derived:

$$\mu_g(C_b) = \mu_w \exp \{2.41 C_b/100 - C_b\} \qquad (10)$$

where μ_w is the viscosity of water (8.94×10^{-4} Pa·s). This equation can be used in the concentration ranges up to 50 wt% with an error of ±1.5%. Constela et al. used Eq. (9) to evaluate the apple juice viscosity [15], and the values predicted fitted well with the experimental measurements.

Gladden and Dole [14] reported also a linear relationship between the logarithm of the diffusion coefficient ratio, ln (D_0/D), and the

Fig. 1. Schematic of the experimental set up.

molar fraction of solute. From this relationship, the following equation has been derived.

$$D_g(C_b) = D_{0,g} \{\mu_w/\mu_g(C_b)\}^{0.45} \tag{11}$$

where $D_{0,g}$ is the diffusion coefficient of glucose in dilute solution which value is $6.75 \times 10^{-10} \, m^2 \cdot s^{-1}$. This equation has an error of $\pm 7\%$ in the concentration range up to 50 wt%.

Eq. (11) was used [1,16] to estimate diffusion coefficient of sucrose, glucose and malic acid at 298 K. Their values are 6.75×10^{-10}, 5.24×10^{-10} and $7.05 \times 10^{-10} \, m^2/s$, respectively.

EXPERIMENTAL

1. Apparatus and Materials

A flat sheet thin film composite polyamide reverse osmosis membrane (type HP-99) was used for the experimental studies. It was supplied by DDS and has effective filtration area of 360 cm^2. The schematic diagram of a cross flow filtration setup equipped with a plate and frame type module used in this work is shown in Fig. 1.

Glucose was supplied by Wako Pure Chemical Industries Ltd.

2. Conditions and Procedures

The reverse osmosis tests were performed in total recirculation mode with both the retentate and the permeate recirculated to the feed tank. In fact, the permeate collected is returned to the feed tank after measuring permeate flow and glucose concentration. This mode adopted reduces change in feed concentration.

The experimental conditions were as follows:

Feed concentration of glucose C_b: 5, 10, 15 and 20 wt%

Applied pressure ΔP: 2, 3, 4 and 5 MPa;

Feed temperature T: 25 °C;

Feed flow rate Q: 2, 3, 4, 5, 6, 7, 9, 10, 11, and 13 L·min^{-1}.

After circulating the RO water and measuring the pure water permeate flux J_w, the feed water was replaced with the test solution. Permeate fluxes and observed rejections were measured when a steady state was reached. The concentrations of glucose in the permeate C_p were determined by a hand refractometer (accuracy of $\pm 0.2\%$). The observed rejection R_{obs} was calculated by using the following equation.

$$R_{obs} \, (\%) = \{1 - (C_p/C_b)\} \times 100 \tag{12}$$

where C_b is the feed concentration of glucose.

By the end of each experiment, the RO membrane was washed by circulating pure water in the module and pure water permeability was checked.

3. Software Program & Statistical Analysis

In this study, mathematical simulation software, Equatran-G, was used to solve simultaneously the three Eqs. (3), (4) and (8). This software permits:

• To estimate the experimental data of mass transfer coefficient k using permeate flux measurements in order to know the form of mass transfer correlation;

Input variables are ΔP, Q and experimental J_v. Output variables are experimental data of k, C_m and Π.

• To deduce the theoretical values of J_v;

The applied pressure ΔP, feed flow rate Q and mass transfer coefficient k (deduced from mass transfer coefficient correlation) consti-

tuted the input variables. Theoretical values of permeate flux J_v, solute concentration at the membrane surface C_m, and osmotic pressure Π correspond to output variables.

Statistical analysis was carried out to check the validity of the used mathematical model. Correlation coefficient between experimental and calculated J_v is defined using function "Correl" from Excel. It is a statistical measurement of the correlation (linear association) between two sets of values. It is given by the formula:

$$\text{Correl} \, (X, Y) = \{\Sigma(x - \bar{x})(y - \bar{y})/(\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2)^{0.5}\} \tag{13}$$

where $\bar{x}$ and $\bar{y}$ are the sample means of the two arrays of values.

Correlation coefficient is expressed as value between +1 and −1. A coefficient of +1 indicates a perfect positive correlation.

In addition, Kolmogorov-Smirnov Test was used to examine whether two samples come from the same distribution. To do this, the difference between observed cumulative distribution of experimental and theoretical values of permeate was calculated using Excel. Then, statistical value (D_{stat}) was defined as the maximum of this difference. And it was compared to critical value (D_{crit}).

$$D_{crit} = 1.36 \{(m+n)/mn\}^{0.5} \tag{14}$$

where m and n are the size of the two data;

The null hypothesis is H_0: both samples come from a population with the same distribution. The null hypothesis was confirmed (at significance level $\alpha = 0.5$) if $D_{stat} < D_{crit}$.

RESULTS

1. Rejection Ability and Pure Water Permeability

The observed rejection R_{obs} for glucose was 100% for all reverse osmosis experiments.

The value of the water permeability of the reverse osmosis membrane at temperature 25 °C deduced from Eq. (7) was 6.5×10^{-12} m^3/s·m^2·Pa.

2. Estimation of Model Parameters

Four series of experiments were performed at constant temperature 25 °C and fixed glucose concentration while varying the applied pressure ΔP and the feed flow rate Q.

2-1. Type of Flow in the Membrane Module

Using the permeate flux measurements in RO, experimental values of mass transfer coefficients were calculated by Eqs. (3), (4) and (8). From the analysis of these mass transfer coefficient values, it is proposed that the influence of permeate flux J_v, solute concentration C_b and feed flow rate Q on mass transfer coefficient k may be represented by a correlation. To choose a relationship for the mass transfer coefficient that describes the system accurately, we needed to know the type of flow in the membrane module. So, a plot of ln(k) vs. ln(Q) was made for each feed glucose concentration and applied pressure.

In the present work, straight lines were obtained with a slope value equal to 1/3 (0.33) and with a regression coefficient R^2 of 0.99. Therefore, the type of flow in the membrane module is laminar rather than turbulent. The experimental data of mass transfer coefficients agreed well with Leveque Eq. (5).

2-2. Estimation of Parameter E

By replacing in the Eq. (5) the dimensionless numbers, Reynolds

number N_{Re}, Schmidt number N_{Sc} and Sherwood number N_{Sh} by their definition $(u\,d_h/\nu)$, (ν/D) and $(k\,d_h/D)$, respectively, as below:

$$\frac{kd_h}{D}=1.62\left(\frac{\left(\frac{du_h}{\nu}\right)\left(\frac{\nu}{D}\right)d_h}{L}\right)^{1/3} \tag{15}$$

the mass transfer coefficient equals to:

$$k=1.62\times d_h^{-1/3}\times L^{-1/3}\times u^{1/3}\times D^{2/3} \tag{16}$$

$$k=1.62\times d_h^{-1/3}\times L^{-1/3}\times\left(\frac{10^{-3}}{60}\times\frac{Q}{s}\right)^{1/3}\times D^{2/3} \tag{17}$$

Here u, the flow velocity $(\mathrm{m\cdot s^{-1}})$,was replaced by Eq. (18),

$$u=\left(\frac{10^{-3}}{60}\times\frac{Q}{s}\right) \tag{18}$$

where Q and s are the feed flow rate $(\mathrm{L\cdot min^{-1}})$ and the effective area of membrane $(\mathrm{m^2})$, respectively.

$$\text{We set } E=41.38\times10^{-3}\times(d_h\times L\times s)^{-1/3} \tag{19}$$

An expression from which this parameter E depends on equivalent hydraulic diameter d_h, module length of flow channel L and effective surface area of the membrane s.

The value of E was estimated by the method of least square using the experimental data. In the present work, E equals to $12.98\,\mathrm{m^{-4/3}}$.

2-3. Estimation of Mass Transfer Coefficients

Substituting the feed solution concentration C_b in Eqs. (10) and (11), the viscosity of the feed solution and the diffusion coefficient of glucose were calculated. These values obtained for different feed concentrations are presented in Table 1. Thereafter, substituting these values, viscosity and diffusion coefficient, and the feed flow rate in equation Eq. (20), the mass transfer coefficient k for glucose was obtained.

$$k=E\times D^{2/3}\times Q^{1/3} \tag{20}$$

Table 2 displays the theoretical values of mass transfer coefficient for different feed concentrations of glucose (5, 10, 15 and 20 wt%) at different feed flow rate. These values are independent of applied pressure ΔP.

3. Validation of the Model with Experimental Data

Once the values of k are known, predicted permeate flux values can be obtained by solving simultaneously Eqs. (3), (4), and (8) for each solution using a program Equatran G as described in section "Software Program & Statistical Analysis."

Any mathematical model gets accepted as an appropriate analytical tool only if the model predictions match with the experimental measurements within some acceptable magnitude of error. Studies carried out in this work on validation of mathematical model with experimental data are presented in this section.

The comparison between experimental and calculated data obtained from the model is shown in Figs. 2 and 3. The solid lines represent the values of permeate flux predicted by the model, and the points represent the experimental values. The figures reveal a close agreement between the experimental and calculated flux values under all feed flow rate Q and feed concentrations. Indeed, the correlation coefficients corell(X, Y), are almost equal to value "+1" indicating a perfect positive correlation. The Kolmogorov-Smirnov

Table 1. The values of viscosity and the diffusion coefficient of glucose at different concentrations

C [wt%]	$\mu_g\,[\mathrm{Pa\cdot s}]\times10^3\pm0.015$	$D_g\,[\mathrm{m^2\cdot s^{-1}}]\times10^{10}\pm0.07$
5	1.015	6.37
10	1.168	5.98
15	1.368	5.57
20	1.633	5.15

Table 2. The theoretical values of mass transfer coefficient for different concentrations of glucose (5, 10, 15 and 20 wt%) and at different feed flow rates

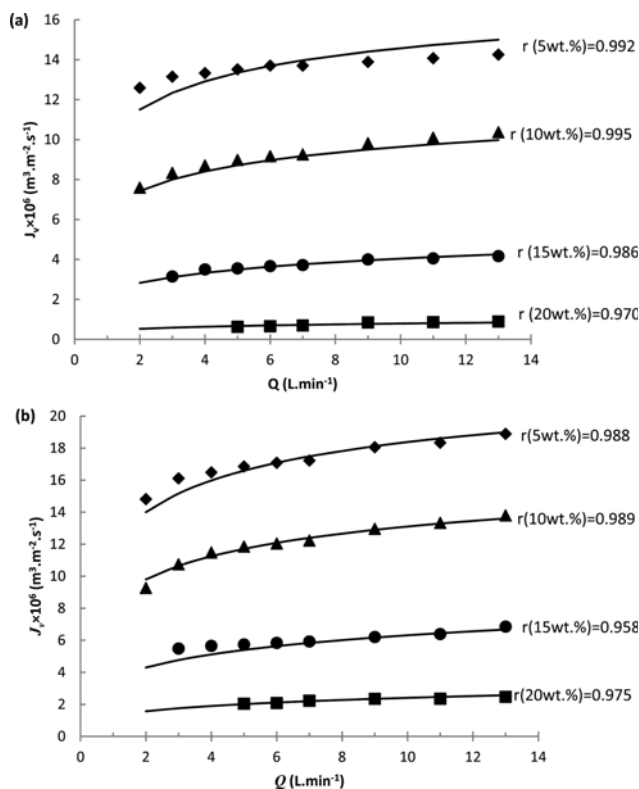| [Glucose] (wt%)	Feed flow rate Q $(l\cdot min^{-1})$	Mass transfer coefficient k $(\mathrm{m\cdot s^{-1}})\times10^6$
5	2	12.11
	3	13.87
	4	15.26
	5	16.44
	6	17.47
	7	18.39
	9	20.00
	11	21.38
	13	22.61
10	2	11.61
	3	13.29
	4	14.63
	5	15.76
	6	16.75
	7	17.63
	9	19.17
	11	20.50
	13	21.67
15	2	11.08
	3	12.68
	4	13.96
	5	15.03
	6	15.98
	7	16.82
	9	18.29
	11	19.55
	13	20.67
20	2	10.50
	3	12.02
	4	13.23
	5	14.26
	6	15.15
	7	15.95
	9	17.34
	11	18.54
	13	19.60

Fig. 2. Relationship between experimental and calculated values of permeate flux J_v for glucose solution as a function of feed flow rate Q, at different glucose concentrations (wt%): (◆) 5, (▲) 10, (●) 15 and (■) 20 and for two different applied pressure: (a) ΔP=4 MPa and (b) ΔP=5 MPa. T=25 °C.
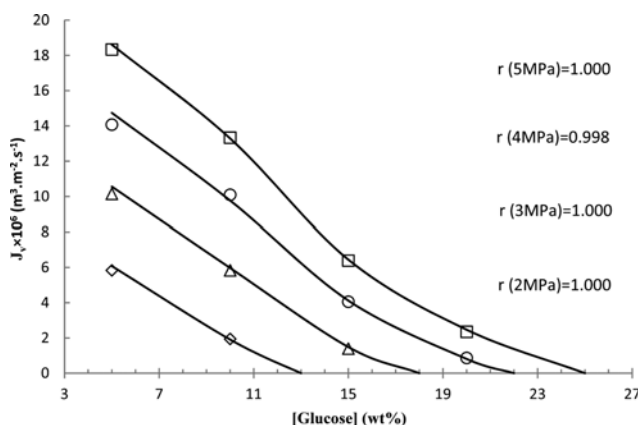

Fig. 3. Relationship between experimental and calculated values of permeates flux J_v for glucose solution as a function of glucose concentration at different applied pressure ΔP (MPa): (◇) 2, (△) 3, (○) 4 and (□) 5. T= 25 °C, Q=11 L·min⁻¹.

test, a more efficient statistical analysis, confirms as well the fit goodness. When calculating the statistical value (D_{stat}) and the critical value (D_{crit}) as described in the "Programme and statistical analysis software" section, we get a value of (D_{crit}) lower than that of (D_{stat}). This indicates that both samples (experimental and the theoretical data) come from a population with the same distribution level of significance α=0.5.

Figs. 2(a) and 2(b) show the permeate flux as a function of feed flow rate at different feed concentrations of glucose at 4 MPa and 5 MPa, respectively. The permeate flux increased with the increase of flow rate, but this positive effect was reduced for higher flow rates. Beyond 6-7 L·min⁻¹ the flux increased slightly; this is related to the increase of osmotic pressure.

The variation of J_v for different applied pressures with glucose feed concentration is illustrated in Fig. 3. From these results, the permeate flux behavior of a solution containing glucose was found to be precisely predicted by the osmotic pressure model.

In addition, when ΔP increased, the limit concentration of glucose at which the water flux approaches zero increased; these concentrations are 13, 18, 22 and 25 wt% for 2, 3, 4 and 5 MPa, respectively. The applied pressure for these concentrations equals the osmotic pressure.

CONCLUSION

The permeate flux during reverse osmosis of glucose solution can be predicted by the osmotic pressure model, when the density, the viscosity and the osmotic pressure of solution and the diffusion coefficient of solute in solution can be defined by some relations of solute concentration.

The experimental values for glucose solutions agreed well with the calculated values under all feed flow rate, Q, and feed concentrations, C_b.

NOMENCLATURE

A : empirical coefficient in Eq. (9) [-]
B : empirical coefficient in Eq. (9) [-]
C : solute concentration [wt%]
D : diffusion coefficient [m²·s⁻¹]
E : parameter appearing in Eq. (19) [m⁻⁴ᐟ³]
d_h : equivalent hydraulic diameter [m]
J_v : permeate flux in volume [m³·m⁻²·s⁻¹]
J_w : pure water permeate flux [m³·m⁻²·s⁻¹]
k : mass transfer coefficient [m·s⁻¹]
L : RO module length of flow channel [m]
L_p : pure water permeability [m³·m⁻²·s⁻¹·Pa⁻¹]
M : molar mass [kg·mol⁻¹]
N_{Re} : Reynolds number=(u d_h/ν) [-]
N_{Sc} : Schmidt number=(ν/D) [-]
N_{Sh} : Sherwood number=(k d_h/D) [-]
P : pressure [Pa]
Q : feed flow rate [L·min⁻¹]
R : gas constant (=8.314) [J·K⁻¹·mol⁻¹]
R_{obs} : observed rejection [-]
s : effective area of membranes [m²]
T : temperature [K]
u : flow velocity=10⁻³ Q/60 s [m·s⁻¹]
V : partial molar volume [m³·mol⁻¹]

Subscripts
b : bulk

g	: glucose	
m	: membrane	
p	: permeate	
r	: retentate	
w	: water	
0	: dilute solution	

Greek Symbols

ν	: kinematic viscosity $= \mu/\rho$ $[\text{m}^{-2} \cdot \text{s}^{-1}]$
μ	: fluid viscosity [Pa·s]
ρ	: fluid density $[\text{kg} \cdot \text{m}^{-3}]$
Π	: osmotic pressure [Pa]
σ	: reflection coefficient [-]

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