A Description of Reverse Osmosis using Practical Kedem-Katchalsky Equations

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Abstract. The work is concerned with an analytical description of reverse osmosis using the Kedem-Katchalsky equations. The process has been considered for well-mixed solutions. We have obtained formulas describing the concentration of a solution (purified by reverse osmosis) as a function of the transport parameters of a membrane, concentration of the initial solution, and the mechanical pressures on the membrane. The formulae are illustrated by numerical computations. Our results may be applicable to biophysical studies concerning reverse osmosis in biological membrane systems.

Key words: Membrane, Solution, Transport, Reverse osmosis, Transport equations

1. Introduction

Reverse osmosis has been a subject of numerous papers. From the mathematical point of view it has been analyzed mainly either using Fick's law [1–6], or by thermodynamical methods with an application of Fick's law [7–12]. By thermodynamical methods we mean here the Kedem-Katchalsky equations [13]. In this work we consider reverse osmosis using so-called practical Kedem-Katchalsky equations. They have the form:

$$J_v = L_p \sigma \Delta \Pi - L_p \Delta P, \quad (1)$$

$$j_s = -\omega \Delta \Pi + (1 - \sigma) \bar{c} J_v, \quad (2)$$

where J_v = volume flux, j_s = solute flux, L_p = filtration coefficient, σ = reflection coefficient, ω = permeation coefficient, $\Delta \Pi$ = osmotic pressures difference, and ΔP = mechanical pressures difference. The quantity $\bar{c}$ is given by:

$$\bar{c} = \frac{c_2 - c_1}{\ln \frac{c_2}{c_1}} \approx \frac{c_2 + c_1}{2}, \quad (3)$$

where c_1, c_2 = concentrations. Equation (2) can also be written as:

$$j_s = j_d + j_u, \quad (4)$$

where

$$j_d = -\omega \Delta \Pi \quad (5)$$

is a diffusion flux, and

$$j_u = (1 - \sigma)\bar{c}J_v \quad (6)$$

is the solute flux carried by the volume flux J_v in the membrane pores.

The above equations apply to systems of thin membranes with solutions sufficiently diluted and well mixed. In this work we analyze reverse osmosis occurring in such conditions. We obtain new formulas for the concentration of the solution purified by means of reverse osmosis as a function of the transport parameters of the membrane, the initial concentration, and the mechanical pressures difference across the membrane. We illustrate the formulas with some numerical results obtained using experimental data.

Our results may be applicable to biophysical studies concerned with biological membrane systems in which a reverse osmosis occurs. As an example one can consider the mass transport of water and assimilates in the plant phloem. The transport can be explained by several mechanisms comprising the so-called Münch model [14]. Reverse osmosis is one of these.

The formulas may also be of some significance in membrane technology, in particular in design of purification devices which function by removing from solutions substances with small molecular masses [6, 7, 11]. The efficiency of such devices could be estimated using our formulae in the design phase.

2. Analysis and numerical results

2.1. ANALYTICAL DESCRIPTION OF THE REVERSE OSMOSIS

We consider a membrane system shown schematically in Figure 1. In the system a membrane M with transport parameters L_p , σ , and ω separates two compartments: A (of large volume) and B (of small volume), both with well mixed solutions. At the initial time the compartment A is filled with a solution of concentration c_r , while the compartment B is empty. Since there is a mechanical pressure difference ΔP , a volume flux J_v flows through the membrane M (to the compartment B). After a certain time the latter fills with a solution of concentration $c_0 < c_r$, provided the reflection coefficient σ of the membrane is greater than zero. The inequality $c_0 < c_r$ means that there is an osmotic pressure difference $\Delta\Pi$ across the membrane:

$$\Delta\Pi = RT(c_r - c_0) \quad (7)$$

acting against the mechanical pressure ΔP . However, $\Delta P > \Delta\Pi$ hence reverse osmosis occurs in the system. One should add here that besides the flux J_v there is a solute flux j_s (if $\sigma < 1$). Both fluxes flow in the same direction, and can be described using the Kedem-Katchalsky equations in the following form:

$$J_v = L_p[\Delta P - \sigma RT(c_r - c_0)], \quad (8)$$

$$j_s = \omega RT(c_r - c_0) + (1 - \sigma) \frac{c_r + c_0}{2} J_v. \quad (9)$$

Division gives:

$$\frac{j_s}{J_v} = \frac{\omega RT(c_r - c_0)}{L_p[\Delta P - \sigma RT(c_r - c_0)]} + (1 - \sigma) \frac{c_r + c_0}{2}. \quad (10)$$

This ratio has a certain physical interpretation. Consider the following expression [13]:

$$J_v = j_w \overline{v_w} + j_s \overline{v_s}, \quad (11)$$

where $\overline{v_w}$ and $\overline{v_s}$ are the molar volumes. The fluxes j_w and j_s are given by:

$$j_w = \frac{\Delta m_w}{S \Delta t}, \quad (12)$$

$$j_s = \frac{\Delta m_s}{S \Delta t}, \quad (13)$$

where Δm_w and Δm_s are masses (of water and of the solute), S is the active surface of the membrane, and Δt is the time. From Equations (11)–(13) we obtain:

$$\frac{j_s}{J_v} = \frac{\Delta m_s}{\Delta m_s \overline{v_s} + \Delta m_w \overline{v_w}} = \frac{\Delta m_s}{V} = c_0, \quad (14)$$

where V is the volume. Equation (10) can now be rewritten as:

$$c_0 = \frac{\omega RT(c_r - c_0)}{L_p[\Delta P - \sigma RT(c_r - c_0)]} + (1 - \sigma) \frac{c_r + c_0}{2}. \quad (15)$$

This equation can be immediately solved for c_0 , yielding:

$$c_0 = \frac{-L_p[\Delta P(1 + \sigma) - 2\sigma RT c_r] - 2\omega RT + \sqrt{\Delta}}{2L_p\sigma RT(1 + \sigma)}, \quad (16)$$

where

$$\begin{aligned} \Delta = & \{L_p[\Delta P(1 + \sigma) - 2\sigma RT c_r] + 2\omega RT\}^2 \\ & - 4L_p\sigma RT(1 + \sigma)[L_p c_r(1 - \sigma)(\sigma RT c_r - \Delta P) - 2\omega RT c_r] \end{aligned} \quad (17)$$

Equation (16) gives an explicit dependence of the concentration c_0 on the mechanical pressure difference ΔP , the concentration of the initial solution c_r (see Figure 1) and the transport parameters of the membrane L_p , σ , and ω . We wish to emphasize that Equation (16) has been derived with the assumption that $0 < \sigma < 1$,

Figure 1. The membrane system (M = membrane; c_r and c_0 = concentrations; P_r and P_0 = mechanical pressures; m and m = mixing devices; A and B = compartments).

Table 1. Values of transport parameter of different membranes

Membrane	Solute	$L_p \left[\frac{m^3}{N \cdot s} \right]$	σ	$\omega \left[\frac{mol}{N \cdot s} \right]$
M_A	Sucrose	$9.7 \cdot 10^{-12}$	0.036	$7.7 \cdot 10^{-10}$
M_B	Methanol	$1.1 \cdot 10^{-12}$	0.5	$11 \cdot 10^{-10}$
M_C	Melonamide	$0.92 \cdot 10^{-12}$	0.83	$0.04 \cdot 10^{-10}$
M_D	Acetamide	$0.4 \cdot 10^{-12}$	0.89	$0.0041 \cdot 10^{-10}$

Source: Katchalsky and Curran, 1965 [13].

therefore it is not applicable to semipermeable membranes ($\sigma = 1$). However it is obvious directly from Equation (9) that if $\sigma = 1$ (and henceforth $\omega = 0$), then $j_s = 0$, which implies $c_0 = 0$. On the other hand if $\sigma = 0$, then Equation (15) shows $c_0 = c_r$. For $0 < \sigma < 1$ we have $0 < c_0 < c_r$, and the larger the reflection coefficient σ , the smaller the concentration c_0 obtained in the process of reverse osmosis. This point is illustrated by curves 1 in Figures 2, 3, 4, and 5. They show the relation $c_0 = f(\Delta P)$ for membranes M_A , M_B , M_C , and M_D , with reflection coefficients equal to 0.036, 0.5, 0.83, and 0.89, respectively. Other parameters of the membranes are given in Table 1.

These exemplary graphs, as well as others which we do not reproduce here, suggest that the concentration c_0 decreases with increasing pressure difference ΔP (for ΔP in the interval $0 < \Delta P < 50 \cdot 10^3$ Pa). For membranes with reflection coefficient $\sigma < 0.5$ the concentration drop is relatively small (see curve 1 in the Figures 2 and 3). However, for membranes with $\sigma > 0.5$ the observed decrease in

Figure 2. Relations: $c_0 = f(\Delta P)$ -curve 1, and $c'_0 = f(\Delta P)$ -curve 2, for a membrane with $\sigma = 0.036$.

Figure 3. Relations: $c_0 = f(\Delta P)$ -curve 1, and $c'_0 = f(\Delta P)$ -curve 2, for a membrane with $\sigma = 0.5$.

c_0 (with an increase in ΔP) is significant. It is illustrated by curve 1 in Figures 4 and 5.

It follows from these graphs that for any constant pressure difference ΔP , the concentration c_0 is the smallest for a membrane with the largest reflection coefficient σ and vice versa.

In the remaining part of this paper we consider conditions under which certain simplifications in the description of reverse osmosis presented here can be made. It is particularly important in an analysis of reverse osmosis modified by a gravitational field. It allows an explicit mathematical description. This phenomenon

Figure 4. Relations: $c_0 = f(\Delta P)$ -curve 1, and $c'_0 = f(\Delta P)$ -curve 2, for a membrane with $\sigma = 0.83$.

Figure 5. Relations: $c_0 = f(\Delta P)$ -curve 1, and $c'_0 = f(\Delta P)$ -curve 2, for a membrane with $\sigma = 0.89$.

occurs if we have a horizontally oriented membrane and non-mixed solutions. A description of this problem can be found in [15–18].

2.2. SIMPLIFIED DESCRIPTION OF REVERSE OSMOSIS

We start our simplified analysis with Equation (9). The term:

$$\omega RT(c_r - c_0) = j_d \quad (18)$$

represents the diffusion flux of solute, and the term:

$$(1 - \sigma) \frac{c_r + c_0}{2} J_v = j_u \quad (19)$$

the solute flux carried in membrane pores by the volume flux J_v . Using the data from Table 1 and values of c_0 (found from Equation 16) we find the dependencies $j_d = f(\Delta P)$ and $j_u = f(\Delta P)$ from the above Equations (18) and (19). These relations are illustrated by curves 1 and 2 in the Figures 6, 7, 8 and 9, for membranes M_A , M_B , M_C , and M_D , respectively. It follows that $j_d < j_u$ for membranes with $\sigma < 0.5$. For $\sigma = 0.5$ we have $j_d = j_u$, while $j_d \gg j_u$ if $\sigma > 0.8$. Because of this strong inequality we can drop the second term of the right hand side of Equation (9) as negligibly small. As a result we obtain the following simplified version of Equation (16):

$$c'_0 = \frac{\omega RT(c_r - c'_0)}{L_p[\Delta P - \sigma RT(c_r - c'_0)]}. \quad (20)$$

The solution can be written as:

$$c'_0 = \frac{L_p(\sigma RT c_r - \Delta P) - \omega RT + \sqrt{\Delta}}{2L_p\sigma RT}, \quad (21)$$

where

$$\Delta = [L_p(\Delta P - \sigma RT c_r) + \omega RT]^2 + 4L_p\sigma\omega c_r(RT)^2. \quad (22)$$

From this formula we can find an approximate value of the concentration c_0 (which we denote as c'_0). To illustrate the accuracy of the simplified formula we plot the dependence $c'_0 = f(\Delta P)$ for the sample membranes M_A , M_B , M_C , and M_D . Again, we use the values of coefficients from Table 1. The results are shown as curves 2 in Figures 2, 3, 4, and 5. Comparing curves 1 and 2, we see that for membranes with $\sigma > 0.5$ there is a very good agreement between the values of c_0 and c'_0 . The discrepancy is less than 1%. The accuracy improves with a growing value of σ . For $\sigma > 0.8$ the values of c_0 and c'_0 are almost identical. A significant difference appears for membranes with $\sigma < 0.5$ (see curves 1 and 2 in Figure 2 obtained for $\sigma = 0.036$).

3. Conclusion

In this work we present a new mathematical description (exact and approximate) of reverse osmosis in a system with well mixed solutions. It is based on the practical Kedem-Katchalsky equations [13]. We obtained formulas (16) and (21) for the concentrations c_0 and c'_0 of a solution purified by means of reverse osmosis. These concentrations depend on the transport parameters of the membrane (L_p , σ , ω),

Figure 6. Relations: $j_d = f(\Delta P)$ -curve 1, and $j_u = f(\Delta P)$ -curve 2, for a membrane with $\sigma = 0.036$.

Figure 7. Relations: $j_d = f(\Delta P)$ -curve 1, and $j_u = f(\Delta P)$ -curve 2, for a membrane with $\sigma = 0.5$.

applied mechanical pressure difference (ΔP) and the concentration c_r of the initial solution. We illustrate the analytical results by numerical computations based on experimental data. In particular, we show that for membranes and solutes for which $\sigma > 0.5$ the exact and approximate results for the concentration c_0 and c'_0 are in good agreement. A meaningful difference appears when $\sigma < 0.5$.

The formulas (16) and (21) can be applied in biophysical studies concerning transport due to reverse osmosis occurring in biological membrane systems.

The results presented here can be extended to the reverse osmosis modified by a gravity force. This occurs in systems with a horizontally oriented membrane

Figure 8. Relations: $j_d = f(\Delta P)$ -curve 1, and $j_u = f(\Delta P)$ -curve 2, for a membrane with $\sigma = 0.83$.

Figure 9. Relations: $j_d = f(\Delta P)$ -curve 1, and $j_u = f(\Delta P)$ -curve 2, for a membrane with $\sigma = 0.89$.

on which near-membrane layers form [15–18]. These results will be presented elsewhere.

The formulas should be useful in estimating the efficiency of hyperfiltration devices. Moreover, the efficiency can be evaluated at the design stage.

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