Membrane Transport Generated by the Osmotic and Hydrostatic Pressure. Correlation Relation for Parameters $L_p$, $\sigma$, and $\omega$

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Abstract. Standard approach to membrane transport generated by osmotic and hydrostatic pressures, developed by Kedem and Katchalsky, is based on principles of thermodynamics of irreversible processes. In this paper we propose an alternative technique. We derive transport equations from few fairly natural assumptions and a mechanistic interpretation of the flows. In particular we postulate that a sieve-type membrane permeability is determined by the pore sizes and these are random within certain range. Assuming that an individual pore is either permeable or impermeable to solute molecules, the membrane reflection coefficient depends on the ratio of permeable and impermeable pores. Considering flows through permeable and impermeable pores separately, we derive equations for the total volume flux, solute flux and the solvent flux across the membrane. Comparing the mechanistic equations to the Kedem-Katchalsky equations we find the former easier to interpret physically. Based on the mechanistic equations we also derive a correlation relation for the membrane transport parameters $L_p$, $\sigma$, and $\omega$. This relation eliminates the need for experimental determination of all three phenomenological parameters, which in some cases met with considerable difficulties.

Key words: Irreversible processes, Kedem-Katchalsky equations, membrane transport

1. Introduction

Passive membrane transport of nonelectrolytes across porous (sieve-type) membranes generated by hydrostatic ($\Delta P$) and osmotic ($\Delta \Pi$) pressure can be described by Kedem-Katchalsky formalism [1–4, 7]. The formalism is based on the so-called practical transport equations derived by these authors. The equations have the form:

$$J_v = L_p \Delta P - L_p \sigma \Delta \Pi,$$

$$j_s = \omega \Delta \Pi + (1 - \sigma) \bar{c} L_p (\Delta P - \sigma \Delta \Pi),$$

where: $J_v$, $j_s$ are the fluxes, $L_p$, $\sigma$, $\omega$ – coefficients of filtration, reflection and permeation, respectively, and $\bar{c}$ – the average concentration in membrane pores. The parameters $L_p$, $\sigma$, and $\omega$ are defined as:

$$L_p = \left( \frac{J_v}{\Delta P} \right)_{\Delta \Pi = 0}$$
The above definitions capture the physical meaning of the parameters and to some extent determine techniques for their experimental measurements [1, 4–6]. The volume flux $J_v$ is defined as:

$$J_v = j_w \nu_w + j_s \nu_s = J_{vw} + J_{vs},$$

(6)

where: $j_w, j_s$ are the solvent and solute fluxes, $\nu_w, \nu_s$ – molar volumes of the solvent and the solute, and $J_{vw}, J_{vs}$ – the solvent and solute volume fluxes.

The Kedem-Katchalsky formalism has been and still is an important tool in physico-chemical as well as technological and biophysical studies of membrane transport processes. Since its conception it has been expanded and modified in different ways [6–17]. This is also the subject of the present work.

We present a new approach to transport of nonelectrolytes across porous membrane generated both osmotically and hydraulically. It is based on a postulate that among all pores in a membrane, a certain number $n_a$ has radii sufficiently small to become totally impermeable to the given solute. The remaining $n_b = n - n_a$ pores are permeable. If we extend the notion of the reflection coefficient to a patch of a membrane, or even a single pore, we postulate that a single membrane pore has the reflection coefficient for a given solute equal to either 1 or 0. Our analysis led to three equations for: the volume flux $J_v$, the solute flux $j_s$, and the solvent volume flux $J_{vw}$. We reinterpret the classical Kedem-Katchalsky equations (1)–(2) and also present a new derivation of our previous result on the correlation relation of the membrane transport parameters $L_p, \sigma, \omega$.

2. Analysis and interpretation. Transport equations

2.1. POROUS MEMBRANE. AN EQUIVALENT MEMBRANE MODEL

We consider transport processes across porous membranes generated by hydrostatic and osmotic pressure gradients. A typical sieve-type membrane has a number $n$ of pores with random radii, from very small to a certain maximal value. The pores are distributed randomly in the entire membrane area. Examples of such membranes are: cellophane, colloid, or nephrophane membranes. We assume that all pores are permeable to the solvent, however a certain number, say $n_a$, is too small to allow the flow of solute molecules. These pores are then totally impermeable to the solute, while the remaining $n_b = n - n_a$ pores are permeable to both the solvent and the solute. Using the notion of the reflection coefficient, this postulate can be rephrased by saying that a single pore has the reflection coefficient equal either 1 or 0. Fractional values of $\sigma_p$ are not allowed. In other words, the membrane as a