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OSMOMETRY WITH MEMBRANES PERMEABLE TO SOLVENT AND SOLUTE

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by A. J. STAVERMAN, Ch. A. KRUISSINK and D. T. F. PALS

[*]) A.K.U., Institute for Cellulose Research, Utrecht

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By A. J. Staverman, Ch. A. Kruissink and D. T. F. Pals

Central Laboratory TNO, Delft, The Netherlands

An explanation of the anomalous osmosis described in the preceding paper [7] is given in terms of friction coefficients in the glass membrane. It is shown that anomalous osmosis may be expected when the friction coefficients are constant and positive provided that the membrane absorbs solute strongly and the outside concentration of solute is small. These were exactly the conditions prevailing in the case described.

MACROSCOPIC PERMEABILITY EQUATIONS

Permeability phenomena of an n-component liquid with respect to a given membrane can be described completely by either of the following sets of equations [1, 3, 4]

$$J_i = \sum_k L_{ik} X_k, \tag{1}$$

or

$$X_i = \sum_k R_{ik} J_k, \tag{2}$$

where J_i is the flux of component i; X_i is the force operating on a molecule of component i, generally of the nature (in non-electrolyte systems),

$$X_i = v_i \Delta P + \Delta \mu_i^c, \tag{3}$$

where v_i is the molecular volume, P the pressure and μ_i the chemical potential of component i and Δ indicates the difference of a quantity from one side of the membrane to the other. The L_{ik}, the permeability coefficients, and the R_{ik}, the resistance coefficients, form reciprocal matrices. These matrices can be made symmetrical.[2, 3]

The attractive feature of eqn. (1) and (2) is that a number of conclusions can be drawn from them without knowing or assuming anything about the composition of the membrane and the processes occurring inside it.[1] However, they have one serious disadvantage in that the coefficients R_{ik} or L_{ik} depend on the concentration outside and inside the membrane in an unpredictable way. As a result, the equations may only be used for stationary states in which all concentrations are constant. If the coefficients are known at one set of concentrations nothing is known about their value at another composition of the liquid, as a result of which their usefulness to describe a system is much restricted.

MICROSCOPIC PERMEABILITY EQUATIONS

If we call the description (1) or (2) a macroscopic description of the permeability behaviour of the system, we can define a microscopic description, an equivalent description of the phenomena, without both the advantages and the disadvantages of the macroscopic description. Such a description is given in terms of microscopic friction coefficients r_{ik} inside the membrane as proposed by Onsager,[2] Klemm [4]

and Laity.[3] Following these authors we write

$$X_i' = \sum_k r_{ik} c_k (u_i - u_k), \tag{4}$$

where X is the force acting upon molecules of component i inside the membrane in a definite layer of constant composition, c_k is the concentration of component k in that layer, and u_i and u_k are the average velocities of the molecules of the respective components. The coefficient r_{ik} is the friction coefficient between components i and k in the membrane. In view of the physical meaning of these coefficients, one expects that they will not depend very strongly on the composition of the medium. Generally they will not be constant over a large range of concentrations except perhaps in "ideal" mixtures where the interaction between molecules does not depend on the concentrations. Since $r_{ik} c_i c_k$, the force exerted by all molecules k on all molecules i, must equal $r_{ki} c_i c_k$, $r_{ik} = r_{ki}$.

CONFRONTATION OF THE TWO DESCRIPTIONS [5]

Since (2) and (4) describe essentially the same phenomenon, we may express the r_{ik} in the R_{ik} and vice versa. We do this here [5] for a system consisting of two components, 0 and 1, and a membrane indicated by m. In this case we have $u_m = J_m = 0$, $J_0 = u_0 c_0$ and $J_1 = u_1 c_1$ giving

$$X_0' = (r_{0m} c_m + r_{01} c_1) u_0 - r_{01} c_1 u_1,$$
$$X_0' = (f_{0m} + r_{01} c_1 J_0 / c_0) - r_{01} J_1,$$
$$X_0' = R_{00}' J_0 - r_{01} J_1, \tag{5}$$

where

$$R_{00}' = (f_{0m} + r_{01} c_1 / c_0 \tag{6}$$

and $f_{0m} = r_{0m} c_m$.   Completely analogously we find

$$X_1' = -r_{01} J_0 + R_{11}' J_1 \tag{7}$$

with

$$R_{11}' = (f_{1m} + r_{01} c_0)/c_1 \tag{8}$$

and $f_{1m} = r_{1m} c_m$.   The X_i are related to the X_i' by the equation

$$X_i = \int^m X_i' dz, \tag{9}$$

where z is the space co-ordinate in the membrane parallel to the direction of flow and the integration extends from one face of the membrane to the other.

In a stationary state the fluxes J_i in the two descriptions are identical. In order to compare the sets of coefficients, eqn. (5) and (7) are integrated over the membrane thickness.

$$\int^m X_0' dz = X_0 = J_0 \int^m R_{00}' dz - J_1 \int^m r_{01} dz,$$

or, by writing $\overline{R_{00}'} = \frac{1}{d} \int^m R_{00}' \, dz$ and similarly for r_{01} and R_1' , we get

$$X_0 = d(\overline{R_{00}'} J_0 - \overline{r_{01}} J_1), \tag{10}$$

$$X_1 = d(-\overline{r_{01}} J_0 + \overline{R_{11}'} J_1), \tag{11}$$

leading to the desired relations

$$R_{00} = d\overline{R_{00}'}, \quad R_{01} = -d\overline{r_{01}}, \quad R_{11} = d\overline{R_{11}'}. \tag{12}$$

ANOMALOUS OSMOSIS

One way to describe the phenomenon of anomalous osmosis or negative reflection coefficient is to note that at zero pressure difference, J_0 and X_0 differ in sign

$$(J_0/X_0)_{\Delta P=0} < 0. \tag{13}$$

In a two-component system with $\Delta P = 0$ the Duhem-Margules rule gives

$$X_1 = -n_0 X_0/n_1, \tag{14}$$

where n_0 and n_1 are the concentrations in the liquid outside the membrane.

Eqn. (2) then becomes

$$X_0 = R_{00}J_0 + R_{10}J_1,$$
$$-n_0 X_0/n_1 = R_{10}J_0 + R_{11}J_1,$$

giving

$$\frac{J_0}{X_0} = \frac{R_{11} + (n_0 R_0'/n_1)}{R_{11}R_{00} - R_{10}^2}. \tag{15}$$

Since the denominator of (15) is positive, (13) can be satisfied only if

$$R_{11} + n_0 R_{10}/n_1 < 0, \tag{16}$$

It follows from (12) that the R_{ik} are proportional to the $\overline{R_{ik}'}$ so we may write instead of (16),

$$R_{11}' - n_0 r_{01}/n_1 < 0,$$

or with (8),

$$f_{1m} < (n_0 c_1/n_1 - c_0)r_{01} \tag{17}$$

is the condition for anomalous osmosis. The factor $F = n_0 c_1/n_1 - c_0$ is a measure of the selectivity of absorption of the two components by the membrane. In the absence of selectivity it is zero. For preferential absorption of solute it is positive $c_1/n_1 > c_0/n_0$.

This was clearly the case in the experiments described in the preceding paper. From (17), anomalous osmosis occur with a positive concentration-independent friction coefficient provided F is positive and not too small. We know from absorption studies that F may become large for high selectivity and tends to increase strongly at high dilution. This is in accordance with the observation in the preceding paper that the reflection coefficient is negative only in high dilution and increases sharply with increasing concentration of solute. Thus the experimental observations are in complete agreement with theoretical predictions derived from constant friction coefficients. It might be argued that " absorbed " and " free " solute in the membrane are in different states with different friction coefficients and, therefore, may not be treated as a single component as we have done. It can be shown, however, that the essentials of our results are not affected if the solute is treated as consisting of two components with different friction coefficients.

Cases of anomalous osmosis reported so far have been with electrolyte solution. Their explanation is also based upon the preferential absorption of electrolyte by the membrane,[5] while Kedem and Katchalsky [6] have shown that in these cases heteroporosity can cause a decrease of the coefficient eventually towards negative values.

[1] Staverman, Trans. Faraday Soc., 1952, 48, 176.

[2] Onsager, Ann. N.Y. Acad. Sci., 1945, 46, 241.

[3] Laity, J. Physic. Chem., 1959, 63, 80.

[4] Klemm, Z. Naturforsch., 1953, 8a, 397.

[5] Kedem and Katchalsky, J. Gen. Physiol., 1961, 45, 143.

[6] Kedem and Katchalsky, Trans. Faraday Soc., 1963, 59, 1931.

[7] Talen and Staverman, preceding paper.