fluxes, but the decrease is less than that obtained from coating the tube surface with cosmoline only.

5. *The results of this testing indicate that extraordinary care should be exercised in plant operations to prevent the introduction of petroleum-based compounds into the heat exchangers which can result in the fouling of the heat transfer surfaces.*

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Interfacial Distribution Between a Membrane and the Adjoining Free Solution

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This paper deals with the interfacial equilibrium between the membrane surface and the adjacent homogeneous liquid/gaseous solution.

In membrane separation processes, such as reverse osmosis, ultrafiltration and pervaporation, there is a liquid/gaseous solution under high pressure on one side of the membrane and liquid or gas at low pressure on the downstream side. All permeate molecules move under the combined influence of concentration and pressure gradients. The description of this process requires the flux equations in the membrane phase and the interfacial distribution relations between the membrane phase and the adjacent solution phase (interfacial equilibrium).

The flux equations have been derived based upon irreversible thermodynamics, where the flux is described as the linear combination of independent driving forces such as chemical potentials (Kedem and Katchalsky, 1958; Spiegler and Kedem, 1966). Lightfoot (1968, 1974) derived the flux equations under the framework of the Stefan-Maxwell equations, which relate the driving force as the linear combination of the fluxes. The Kedem Katchalsky equations (1958) were also justified by Lightfoot (1974) based upon the Stefan-Maxwell equation with the Kirkwood formulation. The diffusion theory, which is the most simplified version of the flux equations mentioned above, has been developed and widely used especially in describing solvent permeation through a polymeric membrane (Merten, 1966; Paul and Ebra-Lima, 1970).

To integrate the flux equations, appropriate boundary conditions should be specified at the points within membrane on the upstream and on the downstream side. The boundary conditions are the pressure and the pressure-independent activities of the permeate species at both membrane surfaces. It is very difficult to measure and then specify the boundary values. However, the boundary values can be related to the measured pressures and concentrations of the solutions adjacent to the membrane surfaces, by assuming interfacial equilibrium. At both membrane surfaces, the abrupt

changes in concentration and pressure occur across the boundary between a membrane and the adjoining solution. Concentration and pressure gradients in the two solution phases are negligible compared to the interfacial gradients across the boundary. Therefore, the resistance to flux across the boundary is negligibly small, so that equilibrium should exist between the species i just inside the membrane and i in the adjacent solution (Rosenbaum, 1968; Lightfoot, 1974). It should be noted that interfacial equilibrium does not necessarily imply the continuity of pressure across the boundary (Gregor, 1948, 1951; Lightfoot, 1974). However, Paul and Ebra-Lima (1970) suggested the approximation that the pressure within the membrane is constant and equal to that in the solution on the upstream side. This approximation was used in modelling the pervaporation processes (Greenlaw et al., 1977a,b). Rosenbaum (1968) suggested that in a nonporous membrane the pressure within the membrane is independent of location and is of a constant value, P_m. Several authors have derived interfacial equilibrium equations under the various constraints imposed upon the standard chemical potentials and the reference pressures.

The purpose of this paper is to present a generalized interfacial equilibrium equation which can be simplified for special cases to give previously reported equations, Table 1. It is also shown that the proper choice of the standard chemical potentials and the reference pressures gives an interfacial equilibrium equation which can be conveniently used to calculate the distribution (partition) coefficient between the membrane-solution boundary. The equations derived in this paper can be applied to ultrafiltration, reverse osmosis and gas separation by a polymeric membrane.

GENERALIZED INTERFACIAL EQUILIBRIUM EQUATIONS

When the concentration and pressure gradients in the solution are negligible compared to the interfacial gradients across the

TABLE 1. INTERFACIAL EQUILIBRIUM EQUATIONS

Authors	Constraints	Interfacial Equilibrium
Gregor (1948, 1951)	$P^* = P_m$ $P^\square = P_e = P_o$ and define $P_m - P_e = \pi$	$RT \ln \left(\dfrac{a_{i,m}}{a_{i,e}}\right)_{P_e} = - \int_0^\pi \overline{V}_{i,m} d\pi$
Rosenbaum (1968)	$P_o = 1$ atm	$RT \ln \left(\dfrac{a_{i,m}}{a_{i,e}}\right)_1 + \int_1^{P_m} \overline{V}_{i,m} dp$ $- \int_1^{P_e} \overline{V}_{i,e} dp + (\mu_{i,m}^* - \mu_{i,s}^\square) = 0$
Paul and Ebra-Lima (1970)	$P^* = P^\square = P_o,\ P_m = P_e,\ \overline{V}_{i,m} = \overline{V}_{i,e} = v_i$	$\left(\dfrac{a_{i,m}}{a_{i,e}}\right)_{P_o} = 1$ (on the upstream side)
Paul and Paciotti (1975)	$P^* = P^\square = P_o = P_m = P_e,\ \overline{V}_{i,m} = \overline{V}_{i,e} = \overline{V}_i$	$(a_{i,m})_{P_e} = (a_{i,e})_{P_e} = 1$ (on the upstream side)
Greenlaw et al. (1977a,b)	$P_o = P^* = P^\square = P^o$ (saturation pressure of pure liquid) $\overline{V}_{i,m} = \overline{V}_{i,e} = v_i, P_m = P_e$ $a_{i,e} = 1.0$	$(a_{i,m})_{P^o} = (a_{i,e})_{P^o} = 1$ (on the upstream side)
Lightfoot (1968, 1974)	$P^* = P^\square,\ \overline{V}_{i,m} = \overline{V}_{i,e} = \overline{V}_i$	$RT \ln \left(\dfrac{a_{i,m}}{a_{i,e}}\right)_{P_o} + \int_{P_e}^{P_m} \overline{V}_i dp = 0$
Lightfoot* (1974)	$P^* = P^\square,\ \overline{V}_{i,m} = \overline{V}_{i,e} = \overline{V}_i$ $P_o = P_e$	$RT \ln \left(\dfrac{a_{i,m}}{a_{i,e}}\right)_{P_e} + \int_{P_e}^{P_m} \overline{V}_i dp = 0$ or $RT \ln \dfrac{(a_{i,m})_{P_m}}{(a_{i,e})_{P_e}} = 0$

* Note that Eq. 1.5.4 in Lightfoot's book (1974) is $RT \ln(a_{i,m}/a_{i,e})_{P_e} = 0$, which is corrected to $RT \ln(a_{i,m})_{P_m}/(a_{i,e})_{P_e} = 0$ in this paper.

boundary, instantaneous equilibrium can be assumed; this is the definition of interfacial equilibrium. From the equilibrium criterion of thermodynamics, the interfacial equilibrium is described simply with

$$\mu_{i,e} = \mu_{i,m} \tag{1}$$

The chemical potential of component i just inside the membrane, $\mu_{i,m}$, and the chemical potential in the adjacent solution, $\mu_{i,e}$, respectively, are

$$\mu_{i,e} = \mu_{i,e}^\square + RT \ln (a_{i,e})_{P_e} \tag{2}$$

and

$$\mu_{i,m} = \mu_{i,m}^* + RT \ln (a_{i,m})_{P_m} \tag{3}$$

where $\mu_{i,e}^\square$ is the standard chemical potential at the pressure $P^\square$, $\mu_{i,m}^*$ is the standard chemical potential at P^*, $(a_{i,e})_{P_e}$ is the activity of component i in the solution at the pressure P_e and $(a_{i,m})_{P_m}$ is the activity just inside the membrane at the pressure P_m. The chemical potential changes with pressure and the rate of this change is given by;

$$RT \left(\frac{\partial \ln a_i}{\partial P}\right)_{T,X} = \overline{V}_i, \text{ when } P_\text{standard} \neq P \tag{4}$$

where $\overline{V}_i$ is the partial molar volume. For the special case when the standard pressure is equal to the pressure at which the chemical potential is determined, Eq. 4 takes the following form;

$$RT \left(\frac{\partial \ln a_i}{\partial P}\right)_{T,X} = \overline{V}_i - v_i, \text{ when } P_\text{standard} = P \tag{5}$$

where v_i is the molar volume of component i. By intergrating Eqs.

4 and 5 and combining with Eq. 2, we can write the chemical potential in the solution in terms of the activity at P_o (arbitrary pressure) as:

for $P^\square \neq P_e$, $\mu_{i,e} = \mu_{i,e}^\square + RT \ln (a_{i,e})_{P_o} + \int_{P_o}^{P_e} \overline{V}_{i,e} dp$

$$\tag{6}$$

and for $P^\square = P_e$, $\mu_{i,e} = \mu_{i,e}^\square + RT \ln (a_{i,e})_{P_o}$

$$+ \int_{P_o}^{P_e} (\overline{V}_{i,e} - v_i) dp \tag{7}$$

where $\overline{V}_{i,e}$ is the partial molar volume at the concentration of the solution.

Similarly, just inside the membrane,

for $P^* \neq P_m$, $\mu_{i,m} = \mu_{i,m}^* + RT \ln (a_{i,m})_{P_o}$

$$+ \int_{P_o}^{P_m} \overline{V}_{i,m} dp \tag{8}$$

and for $P^* = P_m$, $\mu_{i,m} = \mu_{i,m}^* + RT \ln (a_{i,m})_{P_o}$

$$+ \int_{P_o}^{P_m} (\overline{V}_{i,m} - v_i) dp \tag{9}$$

where $\overline{V}_{i,m}$ is the partial molar volume at the concentration just inside the membrane. Substituting these equations (Eqs. 6, 7, 8 or 9) into the interfacial equilibrium equation (Eq. 1), we obtain for the case of $P^\square \neq P_e$ and $P^* \neq P_m$,

$$RT \ln \left(\frac{a_{i,m}}{a_{i,e}}\right)_{P_o} + \int_{P_o}^{P_m} \overline{V}_{i,m} dp$$

$$- \int_{P_o}^{P_e} \overline{V}_{i,e} dp + (\mu_{i,m}^* - \mu_{i,e}^\square) = 0 \quad (10)$$

and for the special case of $P^\square = P_e$ and $P^* = P_m$,

$$RT \ln \left(\frac{a_{i,m}}{a_{i,e}}\right)_{P_o} + \int_{P_o}^{P_m} \overline{V}_{i,m} dp - \int_{P_o}^{P_e} \overline{V}_{i,e} dp = 0 \quad (11)$$

since

$$\mu_{i,m}^* - \mu_{i,e}^\square = \int_{P_e}^{P_m} v_i dp \quad (12)$$

These generalized interfacial equilibrium equations (Eqs. 10 and 11) contain three arbitrarily chosen parameters. Those are the standard pressures, P^* and $P^\square$, and the reference pressure, P_o. Now we examine how the generalized equations can be simplified for special cases to give previously reported equations (Table 1). For example, Gregor (1948, 1951) used the pressure inside the membrane as the standard pressure for the chemical potential within the membrane ($P^* = P_m$), and the pressure in the solution phase as the standard pressure for the chemical potential in the solution and the reference pressure ($P^\square = P_e = P_o$, Table 1). For this situation the interfacial equilibrium equation (Eq. 11) becomes

$$RT \ln \left(\frac{a_{i,m}}{a_{i,e}}\right)_{P_e} = - \int_{P_e}^{P_m} \overline{V}_{i,m} dp \quad (13)$$

which is equivalent to that Gregor (1948, 1951) derived. He showed how to predict ion exchange phenomena, in particular distribution coefficient, from measurable physical quantities. It should be noted that the same equation as Eq. 13 can also be obtained for the case of $P^* = P^\square$, $P_o = P_e$ and $\overline{V}_{i,m} = \overline{V}_{i,e} = \overline{V}_i$ (Lightfoot, 1974). (See the last row of Table 1.) However, the derivations by Gregor are thermodynamically consistent whereas those by Lightfoot are not except when the partial molar volume in the membrane phase is equal to the partial molar volume in the solution ($\overline{V}_{i,m} = \overline{V}_{i,e}$). The five other interfacial equilibrium equations by Rosenbaum (1968), Paul and Ebra-Lima (1970), Paul and Paciotti (1975), Greenlaw et al. (1977a,b) and Lightfoot (1968, 1974) can be easily derived from Eq. 10 or 11 and are shown in Table 1.

We now conclude this article with a brief discussion involving the choice of the reference pressure, P_o, and the convenience in the determination of the activity within the membrane. Gregor chose the pressure in the solution phase as the reference pressure and derived the interfacial equilibrium equation (Eq. 13). He also showed how to determine the thermodynamic osmotic pressure π which is $P_m - P_e$. Rearranging Eq. 13 with the definition of π gives

$$(a_{i,m})_{P_e} = (a_{i,e})_{P_e} \exp\left[- \int_o^\pi \frac{\overline{V}_{i,m}}{RT} d\pi\right] \quad (14)$$

The above equation indicates that the activity within the membrane at P_e can be determined if $\overline{V}_{i,m}$ is known as a function of pressure (or osmotic pressure). However, it is very difficult to measure the partial molar volume of a permeate in the membrane phase. This is particularly true for a nonporous membrane. Furthermore, the activity which is needed as a boundary condition for the integration of the transport equation through a membrane is $(a_{i,m})_{P_m}$, not $(a_{i,m})_{P_e}$. It will be shown that *these difficulties* can be easily avoided by choosing the pressure within the membrane,

P_m, as the reference pressure, P_o. Equation 11 with $P_o = P_m$ becomes

$$RT \ln \left(\frac{a_{i,m}}{a_{i,e}}\right)_{P_m} - \int_{P_m}^{P_e} \overline{V}_{i,e} dp = 0 \quad (15)$$

Rearranging Eq. 15 with the definition of $\pi = P_m - P_e$ gives

$$(a_{i,m})_{P_m} = (a_{i,e})_{P_e + \pi} \exp\left[- \int_o^\pi \frac{\overline{V}_{i,e} d\pi}{RT}\right] \quad (16)$$

which indicates that the activity within the membrane at P_m can be determined with measurable quantities (π, $\overline{V}_{i,e}$, P_e and $(a_{i,e})$-$_{P_e + \pi}$). Therefore, Eq. 16 is a more useful alternative form of Eq. 13. In the above argument, it is assumed that the osmotic pressure, π, can be directly measured or indirectly determined [as Gregor (1948, 1951) demonstrated]. It is evident that the choice of P_m as the reference pressure is *advantageous* over the choice of P_e.

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