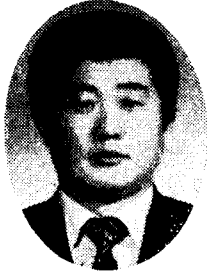# Theory and Applications on Reverse Osmosis

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요　약

역삼투의 공업적 응용은 최근 수처리 관계 뿐만아니라 식품 공업, 전자 공업, 약품 공업 및 유전자 공업에 까지 그 범위가 넓어지고 있다.

현재 국내에서도 상당 수 보급되었고, 앞으로 점점 그 이용도가 증가하리라고 전망된다. 이와같은 역삼투에 대하여 지금까지 발표된 기본원리와 삼투막의 제조 및 성질을 논하고, 역삼투조작에 있어서 물질전달방정식과 유동방정식을 유도하고 이를 이용하여 역삼투조작의 처리용량과 분리능력을 추정할 수 있는 방법을 고찰 하였다.

I. Introduction

Reverese osmosis is a general process for the separation of substances in fluid(liquid or gaseous) solution by permeation under pressure through an appropriate membrane.

To understand how reverse osmosis works, consider natural osmosis. In Figure 1, pure water is separated from a salt solution by a semipermeable membrane, which passes water readily, but retards the flow of dissolved solids.

Osmosis is the natural process whereby pure water flow through the membrane from a dilute solution into more concentrated solution. Water flow continues until the pressure created by the osmotic head equals osmotic pressure of the salt solution, which is osmotic equilibrium as shown in Figure 2. If the osmotic pressure is overcome as in Figure 3 by application of the external pressure, the flow is reversed. and purified water is removed from the concentrated solution. This is the process of reverse osmosis.

II. Mechanisms.

Several mechanism for reverse osmosis has been suggested. [1]~[10] The origin of the current
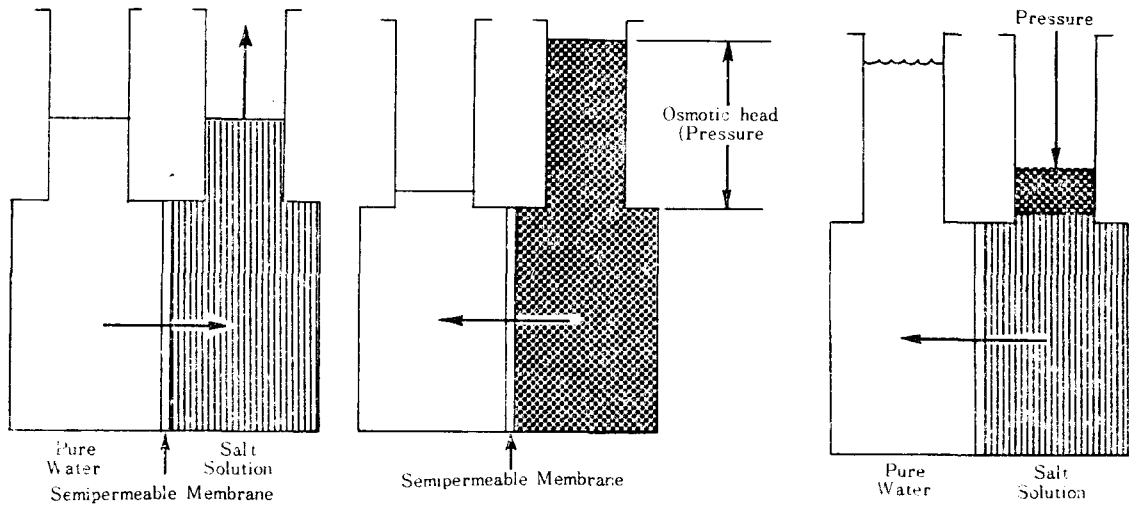

| Fig. 1. Osmotic Flow | Fig. 2. Osmotic Equilibrium | Fig. 3. Reverse Osmosis |

world-wide interest and activity in the field of reverse osmosis is the original development of the porous cellulose acetate membranes which have proved useful for many water treatment and other applications.

This development was the result of approach, described as "the preferential sorption capillary flow mechanism" [11] for revese osmosis.

According to this mechanism, reverse osmosis separation is the combined result of preferential sorption of one of the components of the fluid mixture at the membrane-solution interface and fluid permeation through the microporous membrane. Figure 4 is schematic representation of above mechanism for the separation of sodium chloride in aqueous solution in reverse osmosis system, where water is preferentially sorbed (i.e. solute is negatively adsorbed) at membrane-solution interface.
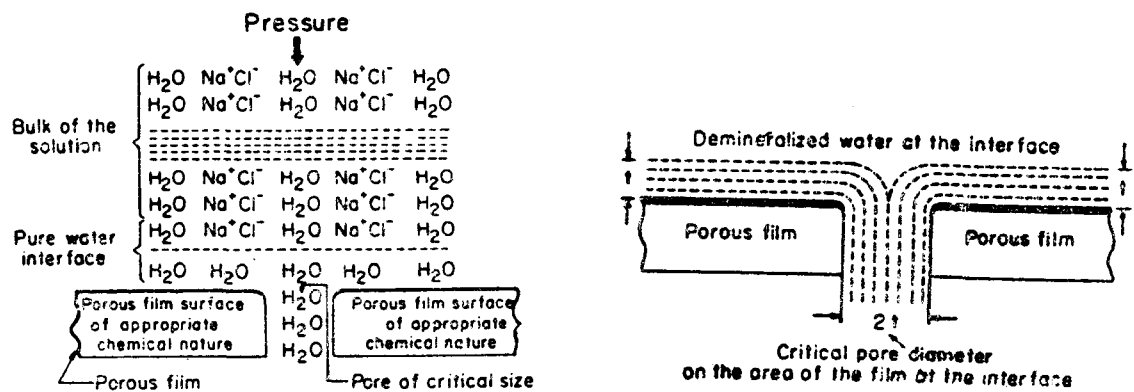

Fig. 4. Schematic representation of preferential sorption capillary flow mechanism

There is a critical pore diameter for maximum solute separation and fluid permeability for each system. The magnitude of this critical pore diameter is a function of the strength and magnitude of preferential sorption at the membrane-solution interface. Thus reverse osmosis is not size separation. With respect to a given membrane material-solution system, solute and

solvent flux through the membrane depend on the size, number and distribution of pores and the thickness of the surface, layer of the membrane; thus solute separation and membrane flux are two independent variables in reverse osmosis processes.

The forgoing consequences of the ntial prefere sorption capillary flow mechanism have far reaching scientific and technological significance.

Preferential sorption at the membrane-solution interface is a funtion of solute-solvent-membrane material interactions. These interaction arise in general from polar, steric, nonpolar and ionic character of each one of the above components.

For example, considering reverse osmosis systems with cellulose acetate, membranes and aqueous feed solutions involving organic solutes, the solvent (water) is polar, the solute may have polar, steric, nonpolar and ionic character, and the polymer (membrane material) has both polar and nonpolar character. Now three case arise;

(a) When the polymer attracts water more than solute, water is preferentially sorbed at membrane-solution interface resulting in positive solute separation.

(b) When the polymer attracts water to the same extent as the solute, neither water nor solute is preferentially sorbed at membrane-solution interface, in which case no solute separation is possible in reverse-osmosis whatever the porous structure of the membrane.

(c) When the polymer attracts the solute more than water, the solute is preferentially sorbed at the membrane-solution interface, in this case solute separation in reverse osmosis can be positive, negative or zero depending on the relative mobility of the solute molecule, compared to water, under operating conditions.

III. Characteristics of solution

The polar character of solute molecule can be expressed in quantitative terms as the following parameters.

(i) the hydrogen bonding ability of the solute (basicity or acidity)

(ii) the PKa (dissociation constant)

(iii) the Taft or Hammett number for the substituent group in the solute molecule

(iv) interfacial free energy parameter

(v) steric parameter and nonpolar parameter

Cellulose acetate molecule behaves as a net proton acceptor (base), therefore a solute which is a proton donor (such as alcohols, phenols, and acids) is attracted foward the membrane surface, and a solute which is a proton acceptor (such aldehyde, ketone, ethers, esters and tertiary amine) is repelled away from the membrane surface.

Consequently, higher basicity ($\triangle\nu_s$ (basicity)), lower acidity ($\triangle\nu^s$(acidity)), high PKa, lower $\Sigma\sigma$ (Hammett number) or $\Sigma\sigma^*$ (Taft parameter) increase preferential sorption of water at membrane-solution interface.

When the acidity of solute is less than that of the water ($\triangle\nu_s$ (acidity)$=250\text{cm}^{-1}$, $\Sigma\sigma^*=0.49$), the latter is preferentially sorbed at the membrane-solution interface. Numerical values of the polar parameters are available in the literature for many organic solutes.[12]

Polar interfacial free energy parameter ($-\Delta\Delta G/RT$) is operational parameter for predicting reverse osmosis separation from minimum of experimental data, but it does not offer any

criterion for preferential sorption at the interface.

The final relationship resulted from the scientific research[13]~[15] for this parameter is following equation.

$$\frac{D_{AM}}{K\delta} = C^* \exp\left[\Sigma\left(\frac{-\Delta\Delta G}{RT}\right)_i\right] \qquad (1)$$

where, $\frac{D_{AM}}{K\delta}$ is solute transport parameter,

Steric parameter (Es) for the substituent group in a polar organic molecule is defined by Taft as equation 2.[15]

$$Es = \log(k/k_0)_A \qquad (2)$$

where k and ko are rate constants in the acidic hydrolysis of RCOOR' and CH_3COOR' respectively.

The value of Es for the substituent group in the solute molecule depends only on the chemical structrure of the group.

Just as $\Sigma\sigma^*$, a decrease in the value of Σ Es for solute molecule yields a lower value of $D_{AM}/K\delta$, and hence higher solute separation in reverse osmosis under otherwise identical experimental conditions.

A direct measure of hydrophobicity or nonpolar character of a hydrocarbon molecule is given either by its molar solubility in water or by its molar attraction constant as given by Small.[16] The Small's number(S^*) versus logarithm of solubility is a straght line which is different for different reactive series of compounds of similar chemical nature.

The nonpolar parameter ΣS^* for a hydrocarbon molecule or the hydrocarbon backbone of polar organic molecule is obtained from chemical structure using the additive property of S^* for different structual groups.

The numerical values of ΣS^* give quantitative measure of the relative mutual attraction of organic molecules to one another as a result of dispersion force.

Ⅳ. Membrances

Material science of reverse osmosis is concerned with the physicochemical basis for the choice of
(i) the membrane material
(ii) the film casting conditions for the chosen membrane material.

Ions in aqueose solution are repelled in the vicinity of membrane materials of low dielectric constant by the so-called electrical image forces arising at the membrane-solution interface.

As a result of these repulsions, solute separations in reverse osmosis tend to increase with decrease in dielectic constant of membrane material.

The polar (α_p) and nonpolar (α_n) parameter representing the hydrogenbonding and hydrophobic characters of the polymer material have been derived as following relationships from experiment on the liquid solid chromatograpy using different polymeric materials in the columns, and benzyl alcohol (benz.alc), phenol, and phenethyl alcohol (phen. alc) as the reference solutes and potassium biphthalate as the unretained component (u_c).[17]

$$\alpha_p = 0.812(\ln r_1 - \ln r_2) \qquad (3)$$

$$\alpha_n = 0.188 \ln r_1 + 0.812 \ln r_2 \qquad (4)$$

$$r_1 = \frac{t_{ben.alc} - t_{uc}}{t_{phe} - t_{uc}} = \frac{K_{benz.alc}}{K_{phe.}} \tag{5}$$

$$r_2 = \frac{t_{phen.alc} - t_{uc}}{t_{benz.alc} - t_{uc}} = \frac{K_{phen.alc}}{K_{benz.alc}} \tag{6}$$

The values of α_p and α_n are higher for the aromatic polyamide materials than for the cellulose acetate material.

With the same average pore size on the membrane surface, reverse osmosis separations for polar orginic solutes can be expected to be relatively higher with membranes made from materials whose α_p and α_n values are higher.

Further the nonpolar (hydrophobic) force of the polymer material, besides being an attractive force for the organic solute, has an additional effect on reverse osmosis tansport.

The increase in the value of α_n tend to increase the mobiliity of the preferentially sorbed water through the membrane pores when water is preferentially sorbed, and to decrease the mobility of the solute when the latter is preferentially sorbed.

Using t-butyl alcohol, s-butyl alcohol, sodium thio-cyanate and raffinose as the arbitrarily chosen reference solutes in liquid solid chromatograpy, several polymer materials have been characterized by a parameter called the β parameter, defined as following equation.[18]

$$\beta = (\ln r_1 + \ln r_2)/2 \tag{7}$$

where,

$$r_1 = \frac{t_{t-BuOH} - t_{raffinose}}{t_{NaSCN} - t_{raffinose}} \tag{8}$$

$$r_2 = \frac{t_{s-BuOH} - t_{raffinose}}{t_{NaSCN} - t_{raffinose}} \tag{9}$$

The β parameter may be more sensitive than both the polar and the nonpolar characters of polymer and exhibits unique correlations with the other parameters governing solute separations in reverse osmosis systems where water is preferentially sorbed at the membrane-solution interface.

A fudamental understanding of mechanism of pore formation and development in the process of making asymmetric porous membranes should be physicochemical basis for the choice of film casting conditions for use in a given reverse osmosis operation.[19]~[22]

Film casting solution is usually a mixture of polymer P(e. g. cellulose acetate), a solvent S(e.g. acetone) and nonsolvent swelling agent N(e.g. aqueous solution of magnesium perchlorate or formamide).[26]~[30]

The film making procedure involves generally the following steps.

(i) casting the polymer solution as a thin film on a surface

(ii) evaporation (or removal) of solvent from the surface

(iii) immersion of the film in the appropriate gelation medium such as cold water or an aqueous ethanol solution

(iv) thermal shrinking, pressurization and other pretreatment.

Smaller size of polymer aggregates in the casting solution tends to create a large number of smaller size nonsolvent droplets in the interdispersed phase, resulting ultimately in larger number of smaller size pores on the membrane surface. The size of the supermolecular polymer aggregate in the casting solution is decreased by

(i) increasing S/P ratio

(ii) decreasing N/S ratio

(iii) increasing the temperature of the casting solution

Gelation control is an effective means of changing pore size, and pore size distribution on the membrane surface.[31]~[32]

V. Transport

The engineering of reverse osmosis transport is concerned with the development of basic equations governing such transport.

With respect to reverse osmosis systems involving aqueous solutions and preferential sorption of water at the membrane solution interface, such transport equations have been developed as follows.

At any given operating temperature and pressure, the experimental reverse osmosis data on pure water permeation rate (PWP), product rate (PR) and fraction solute separation (f) at any point in the reverse osmosis system can be analyzed on the basis that (PWP) is directly proportional to operating pressure, the solvent water transport (N_B) through the membrane is proportional to effective pressure, the solute transport (N_A) through the membrane is due to pore diffusion through the membrane capillaries and hence proportional to the concentration difference across the membrane, and mass transfer coefficient k on the high pressure side of the membrane is given by the "film theory" on mass transport. This analysis which is applicable to all membrane materials and membranes at all levels of solute separation, gives rise to the following basic reverse osmosis equations.[33]

$$A = (PWP)/(M_B \times S \times 3,600 \times P) \quad \text{[mol } H_2O/cm^2 \cdot s. \text{ atm]} \qquad (10)$$

$$N_B = A[P-\pi(X_{A2})+\pi(X_{A3})] \quad \text{[mol}H_2O/cm^2 \cdot s] \qquad (11)$$

$$= \left(\frac{D_{AM}}{K\delta}\right) \left(\frac{1-X_{A3}}{X_{A3}}\right) \ (C_2 X_{A2} - C_3 X_{A3}) \qquad (12)$$

$$= kC_1(1-X_{A3}) \ln \frac{X_{A2}-X_{A3}}{X_{A1}-X_{A3}} \qquad (13)$$

where A=pure water permeability constant

P=operating pressure, C molar density of solute

X_A=mole fraction of solute

k=mass transfer coefficient for the solute

D_{AM}=solute diffusivity through the membrane

δ=effective film thickness, π=osmotic pressure

K=equilibrium constant at equilibrium between solution phase and membrane phase

Equation 13 enables one to calculate the mass transfer coefficient k on the high pressure side of membrane.

The magnitude of k is a function of the nature of solute, concentration of feed solution, feed flow rate, porosity of membrane and the geometry of the apparatus used.

Under steady state operating condions, a single set of experimental data on (PWP), (PR) and f enables one to calculate the quantities $A, X_{A2}, \frac{D_{AM}}{K\delta}$, and k at any point in the reverse

osmosis system using equations 10—13.

Combining equations 11, 12 and 13

$$A[P-\pi(X_{A2})+\pi(X_{A3})]=\left(\frac{D_{AM}}{K\delta}\right)\left(\frac{1-X_{A3}}{X_{A3}}\right)(C_2X_{A2}-C_3X_{A3}) \qquad (14)$$

$$\frac{(C_2X_{A2}-C_3X_{A3})}{X_{A3}}=\frac{k}{(D_{AM}/K\delta)}C_1\ln\left(\frac{X_{A2}-X_{A3}}{X_{A1}-X_{A3}}\right) \qquad (15)$$

A membrane must be specified in terms of A and $D_{AM}/K\delta$.

Equations 14 and 15 enable one to predict solute separation and membrane flux for any feed concentration X_{A1}, and any chosen feed flow condition specified in terms of k.

Solute separation (f) and membrane flux (PR) are calculated by following equations with the aid of X_{A2}, X_{A3}, N_B obtained from equations 11, 14, 15.

$$f=\frac{m_1-m_2}{m_1}=1-\left(\frac{X_{A3}}{1-X_{A3}}\right)\left(\frac{1-X_{A1}}{X_{A1}}\right)=1-\frac{X_{A3}}{X_{A1}} \qquad (16)$$

$$(PR)=\frac{N_B\times M_B\times S\times 3,600}{\left[1-\cfrac{1}{1+\cfrac{1,000}{m_1(1-f)M_A}}\right]} \quad [g/hr] \qquad (17)$$

In any reverse osmosis process, the membrane-solution-operating system may be specified by three fundamental nondimensional parameter γ, θ and λ defined as follows.

$$\gamma=\frac{\pi(X^0{}_{A1})}{P}=\frac{\text{osmotic pressure of initial feed solution}}{\text{operating pressure}} \text{(osmotic pressure characteristic)} \qquad (18)$$

$$\theta=\frac{D_{AM}/K\delta}{V_w{}^*}=\frac{\text{solute transport parameter}}{\text{pure water permeation velocity}} \text{(membrane characteristic)} \qquad (19)$$

$$\lambda=\frac{k}{D_{AM}/K\delta}=\frac{\text{mass transfer coefficient on the high pressure side of membrane}}{\text{solute transport parameter}}$$

$$\text{(mass transfer coefficient characteristic)} \qquad (20)$$

$$V_w{}^*=\frac{AP}{C}, \quad \lambda\theta=\frac{K}{V_w{}^*} \qquad (21)$$

For feed solutions, the molar density of the solution is essentially that of pure water, and osmotic pressures involved during reverse osmosis are negligible compared to the usual operating pressure, which means that $(PR)=(PWP)$

Under these conditions, $k=k_{ref}[D_{AB}/(D_{AB})_{ref}]^{2/3}$ [34], where D_{AB} and $(D_{AB})_{ref}$ are diffusivity of the solute respectively in water.

$$\frac{D_{AM}}{K\delta}=\frac{(PR)}{3,600S\rho}\frac{1-f}{f}\left[\exp\left(\frac{PR}{3,600Sk\rho}\right)\right]^{-1} \qquad (22)$$

$$\text{and } f=\left[1+\frac{(D_{AM}/K\delta)\,3,600S\rho}{(PR)}\exp\left(\frac{PR}{3,600Sk\rho}\right)\right]^{-1} \qquad (23)$$

Let V_s represent the permeation velocity (cm/s) of product solution expressed by

$$V_s=\frac{PR}{3,600S\rho} \qquad (24)$$

Equation 22 can then be written as

$$D_{AM}/K\delta = V_s \left(\frac{1-f}{f}\right) [\exp (V_s/k)]^{-1} \tag{25}$$

When V_s/k is sufficiently small, equation 25 can be written as

$$f = \frac{V_s}{V_s\left(1 + \dfrac{D_{AM}/K\delta}{k}\right) + D_{AM}/K\delta} \tag{26}$$

When $\dfrac{D_{AM}}{K\delta}$ and k are constants and V_s is proportional to P, equation 26 becomes

$$f = \frac{K'P}{K''P + 1} \tag{27}$$

where K' and K'' are constants.

Equation 27 has the same form as the familier Langmuir adsorption equation which of course should be expected on the basis of the preferential sorption capillary flow mechanism for reverse somosis.

The most general expression for $D_{AM}/K\delta$ for a nonionized polar organic solute can be given by the relation.

$$D_{AM}/K\delta \propto \exp[\rho^*\Sigma\sigma^* + \delta^*\Sigma E_i + \omega^*\Sigma S^*] = C^*\exp[\Sigma(-\Delta\Delta G/RT) + \delta^*\Sigma E_i] \tag{28}$$

The coefficients ρ^*, δ^* and ω^* associated with the parameters $\Sigma\sigma^*$, ΣE_i and ΣS^* respectively are characteristic of the membrane-solution interface, i. e. chemical nature of the membrane material, solvent, and functional group in the solute molecule, in addition, the value of δ^* depends on the porous structure of the membrane surface.

With respect to completely ionized inorganic and simple organic solutes, it was found that

$$D_{AM}/K\delta \propto \exp \Sigma(-\Delta\Delta G/RT)_{ion} \tag{29}$$

On the basis of Equations 28 and 29, following equation has been established.[35]~[37]

$$\ln(D_{AM}/K\delta)_{NaCl} = \ln C^*_{NaCl} + \Sigma[(-\Delta\Delta G/RT)Na^+ + (-\Delta\Delta G/RT)cl^-] \tag{30}$$

where $\ln C^*_{NaCl}$ is constant respectively the porous structure of the membrane surface.

For completely ionized inorganic solutes,

$$\ln(D_{AM}/K\delta)_{Solute} = \ln C^*_{NaCl} + \Sigma n_{ion}(-\Delta\Delta G/RT)_{ion}$$
$$= \ln C^*_{NaCl} + \{n_c(-\Delta\Delta G/RT)_c + n_a(-\Delta\Delta G/RT)_a\} \tag{31}$$

and for nonionized polar organic solute,

$$\ln(D_{AM}/K\delta)_{Solute} = \ln C^*_{NaCl} + \ln\Delta^* + (-\Delta\Delta G/RT)$$
$$+ \delta^*\Sigma E_i + \omega^*\Sigma S^* \tag{32}$$

Δ^* = a function of chemical nature of membrane material and the porous structure of the membrane surface (= scale factor)

For a given membrane, a single set of reverse osmosis experiments with a reference feed solution NaCl-H$_2$O at a chosen operating pressure and temperature, yields values of A, $(D_{AM}/K\delta)_{NaCl}$, C^*_{NaCl} and k_{NaCl}.

From the value of $(D_{AM}/K\delta)_{NaCl}$, the value of $D_{AM}/K\delta$ for any other solute can be calculated,

and we can predict the performance of membrane (f and PR) with respect to any other solute for any specified value of k.

These illustrate the practical utility of both the transport equations and the related correlations and the concept of specification of membrane and membrane materials.

For mixed solute systems, the application of the basic transport equations may be cited as follows.

For case of inorganic solute which is partially hydrolyzed, equation 30 becomes[37]

$$\ln(D_{AM}/K\delta)_{Solute} = \ln C^*_{NaCl} + (1-\alpha_H)[n_c(-\Delta\Delta G/RT)_c + n_a(-\Delta\Delta G/RT)_a]$$
$$+ \alpha_H[n_{hy}(-\Delta\Delta G/RT)_{hy} + (-\Delta\Delta G/RT)_{OH^- \text{or} H^+}] \tag{33}$$

where α_H represents degree of hydrolysis, and subscripts hy and OH$^-$ or H$^+$ refer to the hydrolysis reaction and hydroxyl or hydrogen ion respectively.

For the case of an aqueous solution of an inorganic solute where both dissociation and ion pair formation occur, Equation 30 becomes[37]

$$\ln(D_{AM}/K\delta)_{Solute} = \ln C^*_{NaCl} + \alpha_D[n_c(-\Delta\Delta G/RT)_c + n_a(-\Delta\Delta G/RT)_a]$$
$$+ (1-\alpha_D)(-\Delta\Delta G/RT)_{ip}$$
$$+ (1-\alpha_D)(n_c - n_{ipc})(-\Delta\Delta G/RT)_c$$
$$+ (1-\alpha_D)(n_a - n_{ipa})(-\Delta\Delta G/RT)_a \tag{34}$$

where α_D represents degree of dissociation, subscrpt ip refer to the ion pair formed, and, n_{ipc} and n_{ipa} are number of moles of cations and anions respectively in one mole of ion pair.

Recently, a new approach to analysis of experimental reverse osmosis data have been presented by Sourirajan.[38]

In this analysis, the relative solute-membrane material interactions at the membrane-solution interface are expressed in terms of electrostatic or Lennard-Jones type potential functions as follows.

$$\frac{\phi}{RT} = \frac{A}{d} \tag{35}$$

$$R = r + d \tag{36}$$

$$\Phi(\rho) = \frac{A/R}{1-\rho} \tag{37}$$

$$\phi_{overall} = \phi_{attractive} + \phi_{repulsive} = -\frac{B}{d^6}RT + \frac{C}{d^{12}}RT \tag{38}$$

$$\phi_{overall} = -\frac{B}{d^3}RT \, (d>D)$$
$$= 10RT \, (d \leq D) \tag{39}$$

$$\Psi = \frac{E}{d} \, (d>D)$$
$$= 10 \, (d \leq D) \tag{40}$$

$$b(\rho) = e^{\Psi(\rho)} = e^{10} \quad (1-\rho \leq D/R)$$
$$= \exp\left(\frac{E/R}{1-\rho}\right) \quad (1-\rho > D/R) \tag{41}$$

$$\Phi(\rho) = -\frac{B/R^3}{(1-\rho)^3} \quad (1-\rho > D/R)$$
$$= 10 \quad (1-\rho \leq D/R) \tag{42}$$

where, ϕ=potential function of force exerted on solute molecule by pore wall [J/g-mol]

Ψ=frictional function of force restricting movement of solute molecule.

$\Phi(\rho)$=dimensionless quantity $(=\phi^{(r)}/RT)$

D=distance between the polymer surface and solute molecule at which ϕ_{over} becomes very large [m]

R=pore radius [m]

r=radial distance in cylindrical coordinate [m]

d=distance between pore wall and center of solute molecule [m]

ρ=dimensionless quantity $\left(=\dfrac{r}{R}\right)$

$b(\rho)$=dimensionless parameter

A, B, C, E=constants.

Glueckauf[39] found the relationship between (PWP) and average value of R for cellulose acetate membrane and ionized solution system that

$$\ln PWP = \text{constant} + 1.5\ln R \tag{43}$$

The quantity A[m] represents ¦the electrostatic repulsive force between membrane material and ionized solute, the quantity B[m^3] and D[m] represent solute-membrane material interactions governed by the Lenard-Jones type potential functions, and the quantity E represents the frictional force on the solute molecule decreasing its mobility through the membrane pores.

The transport of solute and solvent through the membrane under the influence of surface forces is expressed through appropriate mass transport equation for individual circular cylindrical pores such as Figure 5.

From such expressions, equations for solute separation and $(PR)/(PWP)$ ratio are derived as following equations.

$$f' = \frac{C_{A2}-C_{A3}}{C_{A2}} = 1 - \int_0^1 [\exp(\alpha(\rho))/1 + \frac{b(\rho)}{e^{-\Phi(\rho)}} \{\exp(\alpha(\rho))-1\}]\alpha(\rho)\rho d\rho$$

$$\div \int_0^1 \alpha(\rho)\rho d\rho \tag{44}$$

$$(PR)/(PWP) = Q_{PR}/Q_{PWP} = \frac{2\int_0^1 \alpha(\rho)\rho d\rho}{\beta_2/8\beta_1} \tag{45}$$

where, $\alpha(\rho) = U_B(r)\delta X_{AB}/RT$ [$-$]

$\beta_1 = \eta/X_{AB}R^2C_{A2}$ [$-$]

$\beta_2 = (P_1-P_0)/RTC_{A2}$ [$-$]

η=solution viscosity [$P_a.s$]

X_{AB}=proportionality constant [Js/m²·g·mol]

U_B=velocity of solvent in the pore [m/s]

and the radial velocity profile can be expressed such as equation 46.

$$\frac{d^2\alpha(\rho)}{d\rho^2} + \frac{1}{\rho}\frac{d\alpha(\rho)}{d\rho} + \frac{\beta_2}{\beta_1} + \frac{1}{\beta_1}(1-e^{-\Phi(\rho)})(C_A(\rho)-1)$$

$$- (b(\rho)-1)\ \alpha(\rho)C_A(\rho)/\beta_1 = 0 \tag{46}$$

where $C_A(\rho) = \dfrac{C_{A3}(r)}{C_{A2}}$

Using the experimental f' and (PWP) data for given membrane, the value of A (which was kept the same for all the membranes used) and that of R for each membrane, which satisfied simultaneously equations 43, 44 and 46 were calculated.

The calculation procedure involves the following steps.

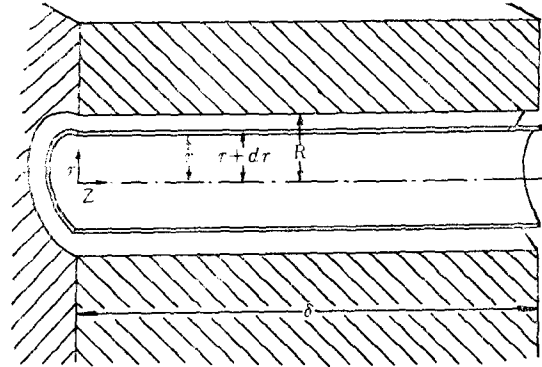step 1, assume a value of A applicable for
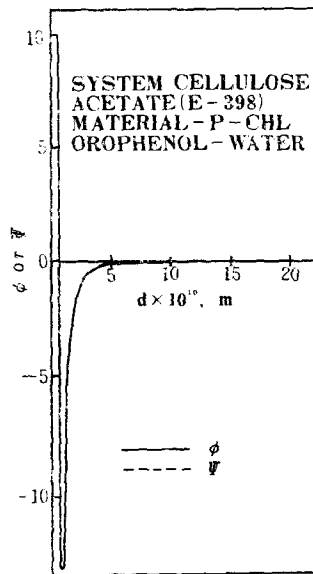

Fig. 5. Cylindrical coordinates in a membrane pore.

Fig. 6. Potential curves of interfacial forces for the system cellulose acetate (E-398) membrane p-chlorophenol-water.
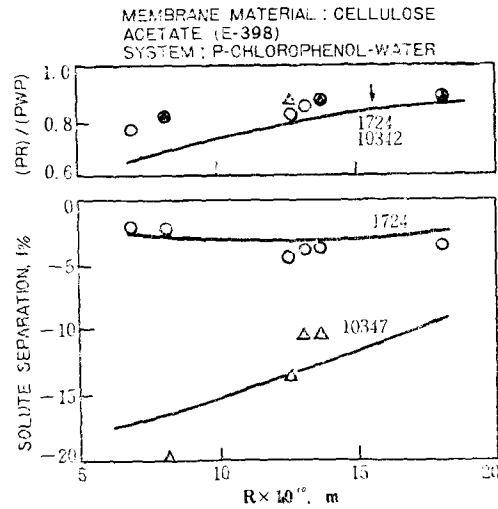

Fig. 7. Effect of pore radius on p-chlorophenol separation at $(PR)/(PWP)$ ratio. Membrane material, cellulose acetate (E398) feed concentration, 1 g-mol/m³, mass transfer coefficient $k = 15 \times 10^6$ m/s;—, calculated; o, $\triangle$ experimental.

all the membranes used

step 2, assume a value of R for each membrane

step 3, obtain the value of $\alpha(\rho)$ using equation 45 and boundary conditions.

step 4, using the above value of $\alpha(\rho)$, obtain f' from eq. 44

step 5, check the value of f' so obtained with the experimental value

On the other hand, for membrane-p-chlorophenol-water system, using the diffusivity data at infinite dilution ($e.g. D_{AB} = 0.974 \times 10^{-9} [\text{m}^2/\text{s}]$), the value of X_{AB} for the system was found to be $2.617 \times 10^{12} [\text{J} \cdot \text{s/m}^2 \text{ g-mol}]$ and applicable value of k for each membrane was obtained using 2/3 power relation, C_{A2} can be calculated from following relation.

$$C_{A2} = C_{A3} + (C_{A1} - C_{A3}) \exp(V_s/k) \qquad (47)$$

$$V_s = (PR)/3,600S\rho \qquad (48)$$

— 2 9 —

where S=effective area of membrane surface [m²]

ρ=density of solution

The numerical values of the constants B,D, and E were changed by trial and error, until the values of f' and $(PR)/(PWP)$ ratio calculated from equation 44,45 respectivly, were in reasonable agreement with the experimental values.

The values of B,D and E so determined were 13.5×10^{-30} [m³], 0.6×10^{-10} ₜ[m], and0.05×10^{-10}[m] respectively.

On the basis of the values of B,D and E given above, Figure 6 gives the polymer-solute interaction potential function (Φ, solid line) and the frictional force function(Ψ, dotted line).

Using this functions, Figure 7 shows the calculated values (solid line) of $(PR)/PWP$ ratio and f' for ellulose acetate membrane as a function of pore radius R.

Ⅵ. Applications

Applications of reverse osmosis process fall into four mayor areas[40],[41]

(a) portable application   (b) industrial application

(c) commercial application   (d) waste water application

(a) Portable applications

Condominiums, mobile home parks and hotels to produce water for portable use

(b) Industrial applications

Reverse osmosis process is used by industrial firms to prepare water for boiler make up, direct use as process.water and for rinsing of critical electronic component.

In normal high pressure boiler feed using raw water, reverse osmosis replaces cation and anion exchanger and is followed by a mixed bed demineralizer for polishing. The cost of reverse osmosis system is justified by eliminating the regeneration chemicals required for cation-anion exchangers and the associated water disposal problems.

For low pressure boilers, frequently reverse osmosis alone or in combination with sodium softening is adequate water treatment.

The chemical industry has found reverse osmosis useful in the preparation of process water. Typical uses include the production of USP (united states phamacopoeia) water for formulations, water for washing filter cake, water for rinsing and cleaning metals and water for polymerization reactions.

In addition to removing the majority of the dissolved oxygen from feed water, reverse osmosis produced water has been filtered to an extremely high degree.

The removal of colloidal matter and organics is of great interest to such firms as semiconductor and food, medical and phamaceutical processing.

- selective salt removal
- protein enrichment
- whey concentration
- maple sap concentration
- orange, tomato, apple juice concentration
- beer and wine concentration
- soft drink mixing

- low sodium diets
- mix water for medications
- separation of virus
- separation of enzym
- separation of components of body fluids
- artificial kidney

(c) Commercial applications
- hospitals and laboratories
- kidney dialysis treatment
- car washer
- small cooling tower and humidifiers
- flower raising
- water bottlers
- central home system
- restaurants
- ice manufacture
- camp ground

(d) Waste treatment application

Applications for waste treatment cover a wide spectrum of effluents from many type of manufacturing processes.

The main use has been the concentration of metallic salts in aqueous streams, permitting either reuse of both water and metal, or a significant reduction in volume for ultimate disposal, the processes frequently include other unit operations such as clarification, filtration, or ultrafiltration for pretreatment.

In addition to reuse, the concentration can be further reduced by evaporation or disposed of by chemical treatment lagoons or contact waste disposal.

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