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Comparisons of Reverse Osmosis and Pervaporation Membrane Processes. I. Theoretical Interpretations.

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Abstract : Reverse osmosis(RO) and pervaporation(PV) membrane processes were compared with each other theoretically by using Paul and Ebra-Lima model. From this model the concentrations of liquid within the membrane when pressure was applied to the upper compartment(for PV case, the applied pressure is infinite) were calculated for rubber membrane-n-hexane and rubber membrane-benzene systems. The permeabilities of RO and PV were also calculated and compared for polyethylene film-n-hexane and polyethylene film-benzene systems. Theoretically, the permeabilities of PV membrane were greater than those of RO membrane.

요 약 : 본 논문에서는 역삼투막 공정과 투과 증발막 공정이 Paul과 Ebra-Lima 모델을 사용하여 이론적으로 서로 비교되어졌다. 이 모델로부터 막내에 있는 액의 농도를 역삼투 공정의 경우 압력이 막의 윗쪽에 가하여졌을 때 (반면에 투과 증발 공정의 경우는 가하여진 압력이 무한대일 때) 막-n-hexane 그리고 rubber 막-benzene 계들에 대하여 계산되어졌다. 또한 polyethylene-n-hexane 그리고 polyethylene-benzene 계들에 대하여 역삼투 및 투과 증발 공정의 투과도가 계산되어졌고 비교되어졌다. 이론적으로는, 투과 증발 공정의 투과도가 역삼투 공정의 투과도보다 더 컸음을 알 수 있었다.

1. Introduction

Pervaporation (PV) differs from all other membrane processes because of the phase change of the pervaporate. However, it has been considered that both PV and reverse osmosis (RO) processes are based on the same transport mechanism, sorption-diffusion-desorption [1].

Shelden and Thompson [2] investigated the effects of upstream and downstream processes on the permeation rates on the basis of solution-diffusion mechanism and compared between RO

and PV processes. Rautenbach and Albrecht [1] also discussed transport equations for PV, and furthermore PV is compared with RO. Recently, Kimura et al.[3] investigated the ethanol permselective RO membrane and the comparison of RO and PV processes.

In this paper, RO and PV processes were discussed in terms of solubility and activity of feed component within the membrane by using Paul and Ebra-Lima solution-diffusion model [4,5].

2. Theory

RO and PV can be considered to have the same transport mechanism, sorption - diffusion - desorption. The pressure difference in RO process leads to a chemical potential difference across the membrane, while the chemical potential difference in PV process across the membrane is achieved by applying a vacuum to the downstream compartment. Therefore, it is possible to compare this two processes by using the solution-diffusion mechanism.

According to Paul and Ebra-Lima [4,5], the chemical potential of i in either solution or the membrane is a function of the pressure and the concentration i at constant temperature. For the two solutions, it can be expressed as

$$\mu_{i,0}^{s} = \mu_i^{o} + RT \ln a_{i,0}^{s} + V_i(P_0 - P_r) \quad (1)$$

$$\mu_{i,l}^{s} = \mu_i^{o} + RT \ln a_{i,l}^{s} + V_i(P_l - P_r) \quad (2)$$

where μ_i^{o} refers to pure i at arbitrary reference pressure, P_r, and other nomenclatures are shown at the end part of this paper.

The pressure distribution, P_m, within the membrane is required. Rosenbaum and Cotton [6,7] have considered three possible membrane pressure distributions as follows :

(a) $P_m = P_0$

(b) $P_m = P_l$

(c) $P_m = P_0 - [(P_0 - P_l)(x/\ell)]$

In case where the membrane is dense or non-porous, and the diffusing species is not dissolved in it, Rosenbaum and Cotton [7] showed that $P_m = P_0$ throughout the membrane to a good approximation was consistent. Therefore, in this paper, the distribution $P_m = P_0$ will be used.

The chemical potential of i ainside the membrane using $P_m = P_0$ may be written as

$$\mu_{i,l}^{m} = \mu_i^{o} + RT \ln a_{i,l}^{m} + V_i(P_0 - P_r) \quad (3)$$

The equilibrium should exist at both surfaces so that

$$\mu_{i,0}^{s} = \mu_{i,0}^{m}$$

$$\mu_{i,l}^{s} = \mu_{i,l}^{m}$$

Applications of the above conditions to Eqs. (1), (2), and (3) yield the following relationships between the activities in the solutions and just inside of the membrane.

$$a_{i,0}^{m} = a_{i,0}^{s} \quad (4)$$

$$a_{i,l}^{m} = a_{i,l}^{s} \exp[-V_i(P_0 - P_l)/RT] \quad (5)$$

The pressure applied to the feed solution does not change the activity of i within the membrane at $x = 0$, however it decreases the activity of i in the membrane at $x = \ell$. This is a main point in this theory. From Eq.(5) it can be realized that the sorption capacity of solvent in the membrane is dependent on the pressure differences between two surfaces.

The acitivity of component i can be derived from Flory-Huggins mixing equation and the rubber elasticity theory :

$$\ln a_{i,l}^{m} = \ln(1 - v_{p,l}) + v_{p,l} + \chi_i v_{p,l}^{2} + [V_i \nu_i / V_0)(v_{p,l}^{4/3} - v_{p,l}/2)] \quad (6)$$

Combination of Eqs. (5) and (6) gives finally

$$-V_i(P_0 - P_l)/RT = \ln(1 - v_{p,l}) + v_{p,l} + \chi_i v_{p,l}^{2} + [V_i \nu_i / V_0)(v_{p,l}^{4/3} - v_{p,l}/2)] \quad (7)$$

If the solubility is obtained from the swelling measurement, the concentration of solvent in the

membrane can be calculated from Eq.(7). Substantially, the activities of component i just inside of the membrane and the solution can be obtained from Eqs. (5) and (6).

Also the theoretical concentration profile in the membrane can be estimated from the following relationship [6] :

$$1-v_i = (1-v_{i0})[(1-v_{i\ell})/(1-v_{i0})]^{x/\ell} \quad (8)$$

The volumetric flux from Fick's equation is generally given as

$$n_i V_i = (D/\ell)\ 1n[(1-v_{i\ell})/(1-v_{i0})] \quad (9)$$

Based on the above theoretical background, it will be discussed how the solubility and activity are affected by the applied pressure in RO and PV for the binary systems such as rubber membrane-hexane, rubber membrane-benzene, polyethylene film-hexane, and polyethylene film-benzene systems.

3. Results and Discussion

Figs. 1 and 2 show the calculated volume fractions and activities of pure components, n-hexane and benzene, just inside of the rubber membrane at $x=\ell$ when pressure was applied to the feed solution in RO. As the applied pressure increases, the volume fractions of n-hexane and benzene in rubber membrane at $x=\ell$ decrease and the activities of both components also decrease. The activity of pure component in the membrane at $x=0$ can be considered as 1 ,i.e., the activity gradient across the membrane in RO increases with the increase of the pressure difference. Therefore, the flux increases by increasing the pressure difference. In other words, the maximum concentration gradient in RO can be obtained at which the applied pressure to the feed solution is infinite so that $v_{i\ell}$ goes to 0. This $v_{i\ell}$ situation can be easily achieved by applying a very high vacuum to the downstream side. The activity of the component within the membrane at $x=\ell$ is then given by

$$a^m_{i\ell} = P_i/P_i^* \quad (10)$$

where P_i is the partial pressure of the solvent and P_i^* is its vapor pressure. The vacuum state at the downstream side makes $a^m_{i\ell}$ zero, since P_i is very small compared to P_i^*. As $a^m_{i\ell}$ approaches zero, $v_{i\ell}$ also goes to 0 (See Eq.(6)). Consequently $v_{i\ell}=0$

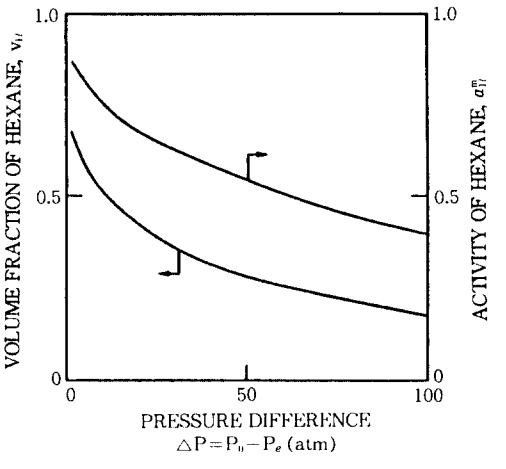

Fig. 1. Calculated volume fraction and activity of n-hexane in the rubber membrane at $x=\ell$ caused by the applied pressure.

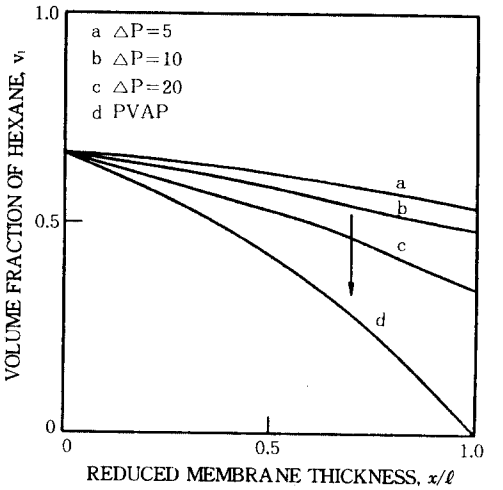

Fig. 2. Calculated volume fraction and activity of benzene in the rubber membrane at $x=\ell$ caused by the applied pressure.

situation can be obtained in both ways ; (i) by applying pressure infinitely to upstream side and (ii) by applying a sufficient vacuum to the downstream side. Thus, it might be said that the pervaporation flux is the upper limit for any reverse osmosis flux. Another observation can be arised that the introduction of high pressure on upstream part would not affect the pervaporation flux since the lowest activity in the membrane at $x=\ell$ was already formed in this process.

Fig. 3 shows the calculated concentration profile of n-hexane in the rubber membrane vs. normalized membrane thickness. As can be seen, the concentration gradient tends to form a deeper curvature with increasing the pressure difference, ΔP.

In summary, despite the fact that both processes are based on the same transport mechanism, the separation potential of PV is higher than that of RO. In order to get the same selectivity and flux as in PV, the infinite pressure must be applied in RO. The membrane quality must be extremely high with respect to compaction and imperfections in RO.

And next, we have compared RO and PV processes in terms of permeabilities. In order to caalculate the permeabilities of pure component using the model discussed in '2. Theory' section, the binary interaction parameters between the polymer membrane material and feed component should be known. In general, this parameter is known as 0.5 in the polymer solution. Fig. 4 shows the calculated concentration of benzene in the polyethylene (PE) membrane using $\chi=0.5$ for the ΔP ranging from 1 atm to 100 atm at 30℃. In detail, the concentration of benzene was calculated ① numerical calculation of v_{ri} by using proper binary interaction parameter value and the pressure difference, ΔP, from Eq.(7) ② then, the concentration profile can be estimated from Eq.(8). As can be seen, the concentration of benzene at $x=0$ is lower than that at $x=\ell$. In this case there is no flux as expected because $\chi=0.5$ was obtained from the infinite dilute solution. Fig.5 shows again the concentration of benzene in the PE membrane using $\chi=1.348$ calculated from Eq.(7) for the ΔP ranging from 1 atm to 100 atm at 30℃. In this case there will be some flux since the concentration of benzene at $x=0$ is larger than that at $x=\ell$. Therefore, the binary interaction parameters are calculated from Eq.(7). Table 1 shows the calculated binary interaction parameters from the known solubilities of n-hexane and benzene in PE membrane at various temperatures and the diffusion coefficients.

Table 2 shows the calculated permeabilities at

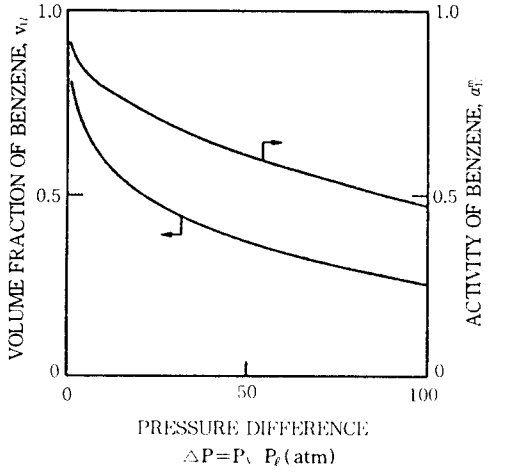

Fig. 3. Calculated concentration profiles of hexane in the rubber membrane at various pressures (atm) in RO(a, b, c) and PVAP (d).

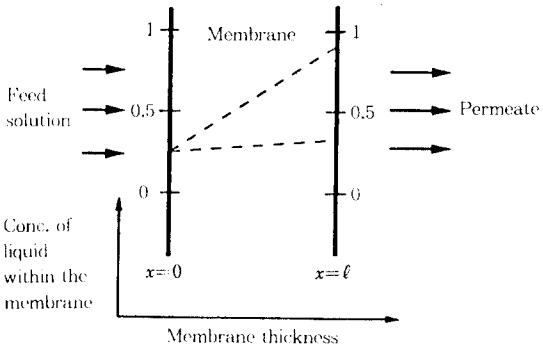

Fig. 4. Calculated concentration of benzene in the polyethylene membrane using $\chi=0.5$ for the ΔP ranging from 1 atm to 100 atm at 30 ℃.

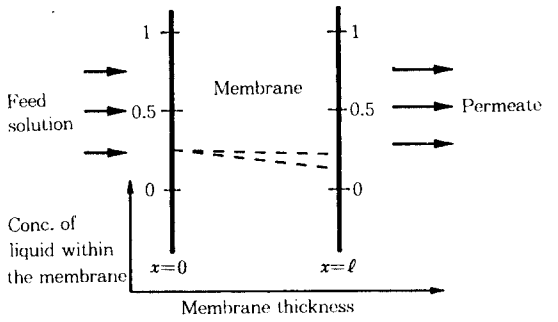

Fig. 5. Calculated concentration of benzene in the polyethylene membrane using $\chi=1.348$ for the ΔP ranging from 1 atm to 100 atm at 30℃.

Table 1. Calculated binary interaction parameters and diffusion coefficients for PE-Benzene and PE-n-hexane systems

System	Temp. (℃)	Solubility[a]	χ	Calculated diffusion coeff.[b], $\times 10^{-6}$ cm²/sec
PE-Benzene	25	0.1483	1.4569	1.3752
	30	0.1751	1.3483	1.9943
	35	0.1991	1.2675	2.1627
	40	0.2225	1.1999	3.7258
	45	0.2343	1.1692	3.5631
PE-n-Hexane	25	0.1611	1.4022	0.5757
	30	0.1766	1.3393	0.7015
	35	0.1927	1.2878	0.9024
	40	0.2116	1.2302	1.2303
	45	0.2284	1.1842	1.5791

[a]Solubility=liquid cc/(liquid cc+polymer cc), adapted from ref. [8].

[b]Adapted from ref. [9].

Table 2. Calculated permeabilities at various ΔP for PE-Benzene and PE-n-hexane systems

System	Temp. (℃)	Calc. Permeabilities, $\times 10^{-4}$ g · cm/cm²hr				
		40[a]	50	60	70	80
PE-Benzene	25	1.75	2.07	2.37	2.63	2.87
	30	3.24	3.82	4.33	4.80	5.22
	35	4.28	5.01	5.66	6.25	6.78
	40	8.78	10.23	11.51	12.65	13.67
	45	9.07	10.55	11.84	12.99	14.03
PE-n-Hexane	25	0.83	0.96	1.08	1.18	1.28
	30	1.16	1.35	1.50	1.64	1.77
	35	1.67	1.92	2.14	2.34	2.51
	40	2.60	2.99	3.32	3.62	3.88
	45	3.74	4.28	4.74	5.15	5.50

[a]$\Delta P=P_0-P_1$ (uni : atm)

Table 3. Comparison of calculated permeabilities at various ΔP and experimental permeabilities by PV

System	Temp. (℃)	Ratio[a]				
		40[b]	50	60	70	80
PE-Benzene	25	1.55	1.83	2.09	2.33	2.54
	30	1.86	2.19	2.49	2.76	3.00
	35	1.58	1.85	2.09	2.31	2.50
	40	2.08	2.42	2.73	2.99	3.24
	45	1.42	1.65	1.85	2.03	2.19
PE-n-Hexane	25	1.29	1.50	1.69	1.85	1.99
	30	1.16	1.35	1.50	1.64	1.77
	35	1.06	1.22	1.37	1.49	1.60
	40	1.09	1.26	1.40	1.52	1.63
	45	1.08	1.24	1.37	1.49	1.60

[a]Ratio=Calculated permeability/experimental permeability by PV

[b]$\Delta P=P_0-P_1$ (unit : atm)

various ΔP for PE-benzene and PE-n-hexane systems. As expected, the permeabilities increase by increasing the pressure differences, i.e., concentration differences. However, as can be seen in Table 3 which illustrates the calculated permeabilities in RO divided by the ex-perimental permeabilities from PV(=Ratio), the ratio is larger than 1 for all cases. In other words, the theoretically calculated permeabilities in RO using the model mentioned earlier in this paper are larger than the experimentally determined permeabilies in PV. In the calculation of the permeabilities in PV using the same diffusion coefficients, the calculated permeabilities in PV are larger than the experimental permeabilities[9]. The diffusion coefficients used in this calculation could be slightly larger than the actual values. And also, the membrane compaction effect probably leads to larger permeabilities in RO than the permeabilities in PV.

4. Conclusions

We have tried to compare the reverse osmosis

membrane process and the pervaporation membrane process using Paul and Ebra - Lima model. Several important points obtained were as followings :

1) Theoretically, the slope of the concentration profile for PV is steeper than that for RO. (More flux)

2) The Flory - Huggins interaction parameter for calculating the concentration of the permeates in the membrane is very important factor.

3) Using this model, the concentration profile of the permeates within the membrane and the flux could be roughly predicted.

4) At various ΔP, the selectivity and the permeability in both RO and PV processes for the binary feed mixture could be predicted.

Nomenclatures

a^i : activity of species i
D : diffusion coefficient
ℓ : membrane thickness
R : gas constant
T : absolute temperature
P_0 : pressure at $x=0$
P_ℓ : pressure at $x=\ell$
P_m : pressure in membrane
P_r : arbitrary reference pressure
v_i : volume fraction of i
V_0 : volume of dry membrane
V^i : molar volume of i

Greek Symbols

μ : chemical potential
ν : moles of elastically effective chains
χ : Flory - Huggins binary interaction parameter

Subscript

i : species i
ℓ : conditions at $x=\ell$
0 : conditions at $x=0$
r : rubber or membrane

Superscript

m : membrane phase
0 : reference state
s : solution, or liquid phase

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