Osmotic Concentration by Using Reverse Osmosis Membranes

INTRODUCTION

It is well known since about two centuries ago that when a more dilute aqueous solution and a more concentrated one are placed on both sides of a semipermeable membrane, osmotic flow of water occurs from the more dilute solution to the other. Recently, reverse osmosis is rapidly becoming popular as a promising process to obtain desalted water or to concentrate dilute solutions. This process depends on the application of the principle of osmosis.[1,2] By applying higher pressure than osmotic pressure on the more concentrated phase, water permeates to the more dilute phase through the membrane. Recently, membrane performance has been rapidly improved.[3] Many membranes are made of acetylcellulose and have a skin layer on one side. The skin layer has a compact microstructure and is very effective in rejecting the permeation of salts or other solutes when this layer is placed to be facing the more concentrated phase. In order to separate solutes or water from solutions, application of external energy is always necessary, and relatively higher pressure is applied in reverse osmosis. Many studies on reverse osmosis have been concerned with desalination of brackish waters (concentration of brackish waters) or concentration of various solutions, as shown below:
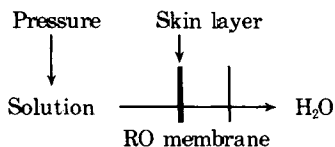
So far, no study has been found concerning with the osmotic flow of water and the migration of the solutes through the RO membranes as follows:
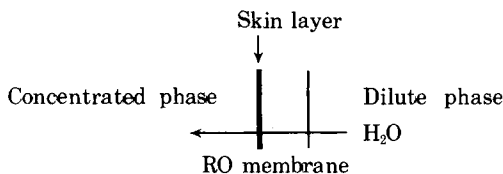
In this system, water flows from the dilute phase to the concentrated phase, and it might be expected at the same time that the skin layer could reject the migration of the solute through the membrane from the concentrated phase to the other. The experimental results evidently showed that the expectation was right only when RO membrane was used. So, concentration of dilute phase may be done without any serious contamination of the solutes from the concentrated phase. Some examples were then investigated to evaluate the practical applicability of the osmotic concentration by using RO membranes.

EXPERIMENTAL

Materials

The membranes used were made of acetylcellulose by Eastman Kodak Co., Ltd., (RO-97, KP-98, KP-90, and HF-35 for ultrafiltration). Cellophane for dialysis from Arther H. Thomas Co. was used as a control. All reagents were of chemical grade.

Apparatus and Procedures

The apparatus is shown in Figure 1. All experiments were done at 25°C. After putting a more dilute solution (D solution, 100 ml) and a more concentrated solution (C solution, 200 ml)

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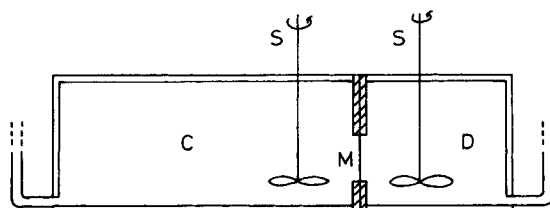
C: C-COMPARTMENT
D: D-COMPARTMENT
S: STIRRER
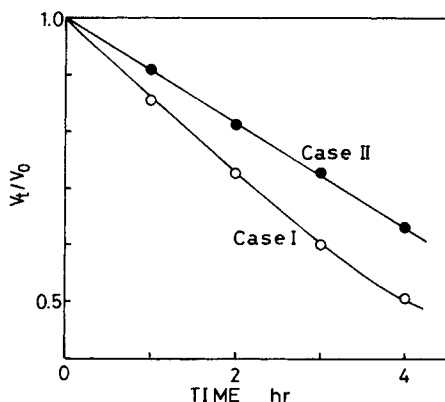M: MEMBRANE (10 cm²)

Fig. 1. Apparatus.

Fig. 2. Comparison of concentrating rates in cases I and II by using RO-97: C solution, 0.5M NaCl; D solution, 0.01M CaCl₂; V_0, initial volume of D solution (100 ml); V_t, volume of D solution after a definite time.

into the D and C compartments, respectively, the changes in volume and concentration of the D solution were measured after 1 hr or every 1 hr by replacing the C solution with a new one. The rotating speed of the stirrers was kept at 1500 rpm, if not otherwise noted. The skin layer was placed as follows:

Case I

C solution ‖ D solution

↑

Skin layer

Case II

↓
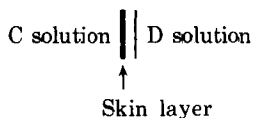
C solution ‖ D solution

J_{H_2O} shows the flux of water permeating from the D solution to the C solution through the membrane, and J_{NaCl} or J_{CaCl_2}, if not otherwise noted, shows the quantity of the salt diffusing from the C solution to the D solution through the membrane.

RESULTS AND DISCUSSION

Figure 2 shows an example of the osmotic concentration in relation to the direction of the skin layer of the membrane. Evidently, the decrease in the V_t/V_0 value in case I was larger than that in case II, and the V_t/V_0 value in case II linearly decreased with time; but the decrease in case I

TABLE I
Concentration by Osmosis Using Various Membranes for 1 Hour[a]

Membrane	Case no.	$J_{H_2O} \times 10^2$, mol/hr·cm^2	$J_{NaCl} \times 10^4$, mol/hr·cm^2	$(J_{NaCl}/J_{H_2O}) \times 10^4$
RO-97	I	7.84	0.55	7.0
	II	5.20	0.41	7.9
KP-98	I	8.33	0.32	3.8
	II	5.90	0.33	5.6
KP-90	I	9.18	1.20	13.1
	II	7.72	1.06	13.7
HF-35	—	0.89	6.09	685
Cellophane	—	0.28	1.06	382

[a] C Solution: 0.5M NaCl; D solution: 0.01M $CaCl_2$; diffusion of $CaCl_2$ to C solution was negligible.

was not linear at the later stage, probably because of the increase in concentration of the D solution. Namely, concentration of the D solution in case I was more rapid than that in case II. Table I shows the results obtained by using various membranes. The membranes for reverse osmosis were clearly more advantageous with regard to J_{H_2O} and J_{NaCl} values than cellophane or the membrane for ultrafiltration, HF-35. The J_{H_2O} values in case I were larger than those in case II, but the J_{NaCl} values in case I were a little larger than those in case II. It was clearly demonstrated that case I was preferable to case II, because the J_{H_2O} value in case I was larger and the J_{NaCl}/J_{H_2O} ratio in case I was smaller, in comparison to those in case II. These results clearly show the effectiveness of the skin layer of the RO membranes.

Figure 3 shows the effect of concentration of the D solution on the concentrating rate. The concentrating rate increased with decrease in concentration of the D solution. Table II shows an example of the effect of the concentration of the C solution on osmotic concentration. When the concentration of the C solution was larger (4M), the J_{NaCl} value was, of course, larger than the other, and diffusion of $CaCl_2$ through the membrane was also observed, probably due to the flow of much more water from the D solution to the C solution. Furthermore, the J_{NaCl}/J_{H_2O} ratio was larger, and this means that much more NaCl diffused into the D solution through the membrane. These results shown in Figure 3 and Table II can be reasonably explained: both the decrease in concentration of the D solution shown in Figure 3 and the increase in concentration of the C solution shown in Table II mean an increase in osmotic pressure between the C and D solutions, so the J_{H_2O} value increased.
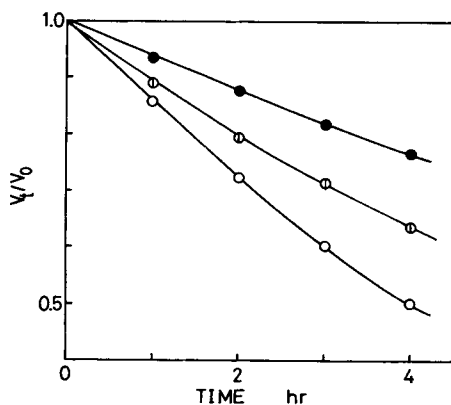

Fig. 3. Effect of $CaCl_2$ concentration in D compartment on concentrating rate; membrane, RO-97: C solution, 0.5M NaCl; D solution, (O) 0.01M $CaCl_2$, (⦵) 0.05M $CaCl_2$, (●) 0.1M $CaCl_2$; V_0 and V_t are the same as those in Fig. 2.

TABLE II
Effect of Concentration of C Solution in Case I[a]

C Solution	$J_{H_2O} \times 10^2$, mol/hr·cm²	$J_{NaCl} \times 10$, mol/hr·cm²	$(J_{NaCl}/J_{H_2O}) \times 10^4$	$J_{CaCl_2} \times 10^4$, mol/hr·cm²[b]
0.5 M NaCl	8.22	0.34	4.1	undetected
4 M NaCl	19.9	3.89	20	0.02

[a] D Solution: 0.01M $CaCl_2$; membrane: KP-98; time: 1 hr.
[b] Diffused to C solution.

TABLE III
Concentration by Osmosis Using $CaCl_2$ or NaCl Solution as C Solution in Case I[a]

D Solution	C Solution	$J_{H_2O} \times 10^2$, mol/hr·cm²	J_{CaCl_2} or $J_{NaCl} \times 10^4$, mol/hr·cm²	(J_{CaCl_2}/J_{H_2O}) or $(J_{NaCl}/J_{H_2O}) \times 10^4$
0.001M	1M CaCl	18.3	0.09	0.54
NiCl₂	0.5M NaCl	8.85	0.34	3.78
0.5M	2M CaCl₂	5.06	0.19	3.78
Glucose	4M NaCl	5.83	5.81	99

[a] Membrane: KP-98; time: 1 hr.

TABLE IV
Concentration of Osmosis of Miscellaneous Solutions in Case I[a]

D Solution	$J_{H_2O} \times 10^2$, mol/hr·cm²	$J_{NaCl} \times 10^4$, mol/hr·cm²	$(J_{NaCl}/J_{H_2O}) \times 10^4$	$J_{solute} \times 10^4$, mol/hr·cm²[b]
0.1M CH₃COOH	9.40	0.55	5.9	2.09
0.1M HCl	7.58	0.73	9.5	1.73
0.05M Glucose	6.00	0.41	6.7	0.02[c]
5 wt-% Whey	4.11	4.3	104	—

[a] C Solution: 0.5M NaCl; membrane: KP-98; time: 1 hr.
[b] Diffused to C solution.
[c] Determined by the phenol-H_2SO_4 method.[5]

Table III shows the results obtained by using aqueous solution of NaCl or CaCl₂ in the C compartment. Clearly, the diffusion of CaCl₂ into the D solution is less than that of NaCl, probably because of the larger dimension of the hydrated Ca ion than that of the Na ion.[4,5] This is consistent with the order of nonpermeability through the membrane in reverse osmosis. Table IV shows examples of osmotic concentration for miscellaneous solutions.

As described above, there are two important factors in the osmotic concentration: (1) the diffusion of the solute in the C compartment into the D compartment, the rate of which is dependent on the difference between the concentrations of the two solutions; (2) the permeation of water from the D solution into the C solution, the rate of which is dependent on the osmotic pressure between the solutions. Therefore, these factors should be well balanced in practical uses. The merit of osmotic concentration is that no external energy is, in principle, necessary for the concentration of relatively more dilute solution itself; but there is a demerit in that perfect separation of solutes from water is difficult because of diffusion of the solutes in both compartments to the others through the membrane. In conclusion, this study suggests the practical use of osmotic concentration of various solutions, especially of dilute solutions of substances susceptible to heat such as amino acids, proteins, and other biomaterials.

References

1. C. E. Reid, in *Desalination by Reverse Osmosis,* U. Merten, Ed., MIT Press, Massachusetts Institute of Technology, Cambridge, Mass., 1966, p. 1.

2. J. S. Johanson, Jr., L. Dresner, and K. Kraus, in *Principles of Desalination,* K. S. Spiegler, Ed., Academic Press, New York, 1966, p. 345.

3. H. K. Lonsdale and H. E. Podall, Eds., *Reverse Osmosis Membrane Research,* Plenum Press, New York, 1972.

4. S. Sourirajan, *Ind. Eng. Chem.,* **3,** 206 (1964).

5. D. L. Erickson, J. Glater, and J. W. McCutchan, *Ind. Eng. Chem., Prod. Res. Devel.,* **5,** 205 (1966).

6. M. Dubois, K. A. Gilles, J. K. Hamilton, P. A. Revers, and F. Smith, *Anal. Chem.,* **28,** 350 (1956).

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