Reverse Osmosis Separations of Aqueous NaCl–Organic Solute Systems

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(Received September 13, 1984)

Synopsis. Some of alcohols, amides, aromatic hydrocarbons and surfactants were used as organic solute. Addition of NaCl increased the rejections of aromatic hydrocarbons and decreased the rejections of amides. It was also found that the permeability of NaCl was influenced by organic solutes.

In reverse osmosis process, it is well known that the solute permeability in multi-component solution system is different from that in single solute system. The results of bisolute systems containing only inorganic salts indicate that univalent ions may permeate more easily by addition of multivalent ions, and that rejections of multivalent ions are increased.[1,2] However, very little are known concerning the effects of inorganic salts on the permeabilities of nonionic organic solutes. As the effective forces between membrane and organic solutes are different from the forces between membrane and ions, it is difficult to evaluate the effects of salt addition on the permeabilities of nonionic organic solutes. The object of this work is to examine the effects of NaCl addition on the rejections of organic solutes (*i.e.* alcohols, amides, aromatic hydrocarbons and surfactants).

Experimental

Cellulose acetate membranes were prepared by the previous method.[1] The membranes were anealed in a water bath at 351—357 K for 10 min followed by precompaction under 7 MPa during 24 h. The reverse osmosis cell used was batch type one reported previously.[1] The experiments were carried out at 4.0 MPa at 303 K. The concentrations of the solutions used in feed solution except aqueous aromatic hydrocarbon and surfactant solutions were 10×10^{-3} mol dm^{-3}. The concentrations of surfactant solutions were above the critical micell concentration. The organic solutes used in this work were listed in Table 1. Na^+ ion was analysed by an atomic flame spectrometer and the concentrations of organic solutes were measured by a total organic carbon (TOC) analyser and a UV-spectrometer. NaCl rejections (R_{NaCl}) and solution flux (J_v; g cm^{-2} s^{-1}) of the used membranes were as follows: Memb. 1 (R_{NaCl}=97.3%, $J_v=4.565\times10^{-4}$), Memb. 2 (R_{NaCl}=89.3%, $J_v=9.276\times10^{-4}$, and Memb. 3 (R_{NaCl}=83.9%, $J_v=7.879\times10^{-4}$).

Results and Discussion

When R^S_{org} and R^M_{org} denote the rejections of single organic solutes and of organic solutes with NaCl, respectively, the relationship between R^S_{org} and R^M_{org} is shown in Fig. 1. Although difference between R^S_{org} and R^M_{org} were not large, it was found that each group of organic solutes indicated different tendency. The addition of NaCl reduced the rejections of aromatic hydrocarbons by 1.1—10.2% and the largest depression of rejection was found in biphenyl whose rejection in a single solute system was the highest in all of this group. On the other hand, the rejections of amides were increased by NaCl addition. The results of the experiment on the effect of NaCl concentration on the rejection of amides are shown in Fig. 2. It was recognized that the rejection of amides increased as increasing NaCl concentrations and that this effect appeared clearly in formamide and acetamide whose rejections in single solute systems were lower than others. The rejections of alcohols and surfactants, however, were not affected very much by NaCl addition.

When R^S_{NaCl} and R^M_{NaCl} mean the NaCl rejection in single solute system and mixed solute system, respectively, the relationship between ΔR_{org} ($=R^M_{org}-R^S_{org}$) and ΔR_{NaCl} ($=R^M_{NaCl}-R^S_{NaCl}$) is shown in Fig. 3. Although ΔR_{NaCl} is smaller than ΔR_{org}, the sign of ΔR_{NaCl} also varies by the group of organic solute. The effects of NaCl addition on the solute rejection were summarised as follows: as to aromatic hydrocarbons and surfactants $\Delta R_{org}<0$ and $\Delta R_{NaCl}>0$, amides $\Delta R_{org}>0$ and $\Delta R_{NaCl}<0$, and alcohols $\Delta R_{NaCl}<0$.

If, even in the mixed solutes system, the diffusibities of solutes in the pore of membrane remain the same as in single solute systems, the solute permeabilities may be influenced by the partition of solute between bulk solution and membrane surface or pore of membrane.

TABLE 1. ORGANIC SOLUTES

No.	Solute	conc.[a]	memb.No.	No.	Solute	conc.[a]	memb.No.
1	Ethyl alcohol	10	1	11	Benzene	14.3	2
2	Propyl alcohol	10	1	12	Toluene	4.71	3
3	Isopropyl alcohol	10	1	13	*o*-Xylene	1.76	3
4	Isobutyl alcohol	10	1	14	1,3,5-Trimethyl-		
5	*t*-Butyl alchol	10	1		benzene	1.72	2
6	Formamide	10	1	15	Chlorobenzene	6.29	2
7	Acetamide	10	1	16	Biphenyl	0.031	2
8	Butyramide	10	1	17	SDS[b]	10	1
9	*N,N*-Dimethyl-			18	SDBS[c]	5	1
	formamide	10	1	19	Brij-35	10	1
10	*N,N*-Dibutyl-						
	formamide	10	1				

a) mmol dm^{-3}. b) Sodium dodecyl sulfate. c) Sodium dodecylbenzenesulfonate.

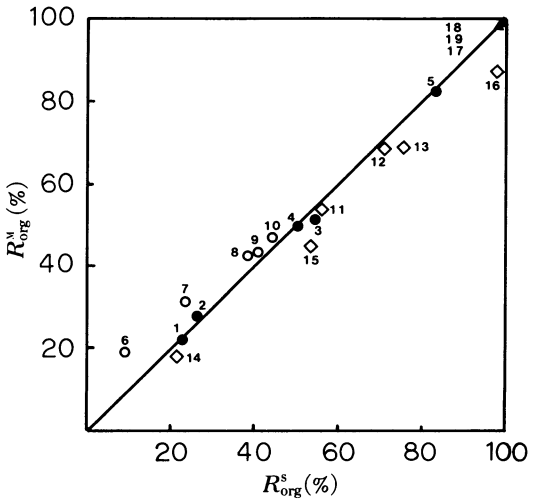

Fig. 1. R^M_{org} *vs.* R^S_{org}.
●: Alcohols, ○: Amides, ◇: Aromatic hydrocarbons, ▲: Surfactants.

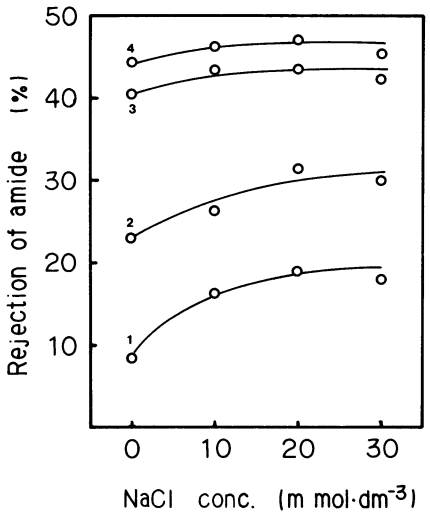

Fig. 2. The effect of NaCl concentration on the rejection of amides.

Kesting *et al.*[3] and Kamizawa and Ishizaka[4] previously indicated that surfactants are adsorbed on the surface of cellulose acetate membrane. Matsuura and Sourirajan[5] mentioned that the preferential sorption layer of aromatic hydrocarbon was formed on the membrane surface. As the solubilities of aromatic hydrocarbons decrease by NaCl addition, these solutes may be adsobed more easily on the membrane and therfore

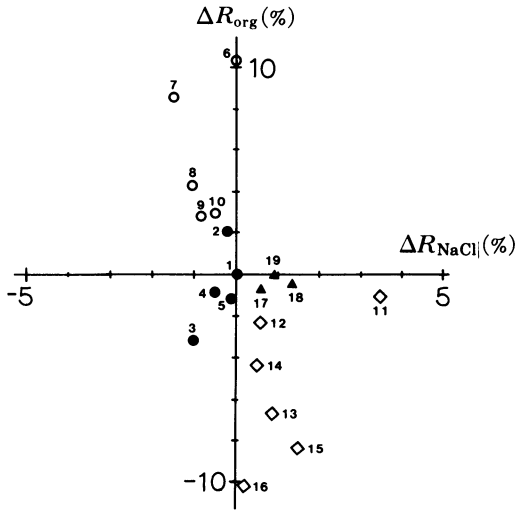

Fig. 3. ΔR_{org} *vs.* ΔR_{NaCl}.
●: Alcohols, ○: Amides, ◇: Aromatic hydrocarbons, ▲: Surfactants.

the rejection of the aromatic hydrocarnons may decrease. On the other hand, it is considered that the sorption layer of the aromatic hydrocarbons or surfactants hindered the permeation of ions through the membrane by following reasons: 1) The pore size of membrane decreases by sorption of organic solute, 2) ionic solutes are difficult to come near the membrane due to the increase of hydrophobic hydration, and 3) the sorption layer of ionic surfactant particularly acts as a kind of ionic membrane. As to amides, the mechanism of the effect of NaCl addition on solute rejection are not clear. The results, however, suggested that ionic solute might hindered the transport of amides into the pore of membrane. From the results of this work, it is concluded that the effect of NaCl addition on the rejection of organic solute depended on the permeation mechanism of the organic solute.

References

1) M. Sugahara, Y. Kiso, T. Kitao, Y. Terashima, and S. Iwai, *J. Chem. Eng. Jpn.*, **11**, 366 (1978).
2) J. P. Agrawal and S. Sourirajan, *Ind. Eng. Chem. Process Des. Dev.*, **9**, 12 (1970).
3) R. E. Kesting, W. J. Subcasky, and D. J. Paton, *J. Colloid Interface Sci.*, **28**, 156 (1968).
4) C. Kamizawa and S. Ishizaka, *Bull. Chem. Soc. Jpn.*, **45**, 2967 (1972).
5) T. Matsuura and S. Sourirajan, *J. Appl. Polym. Sci.*, **17**, 3683 (1973).