Study on Reverse Osmosis. The Permeation Behavior of Surfactant Solutions through Cellulose Acetate Membranes

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Transport phenomena of some surfactants were investigated with Loeb-type skinned membranes annealed at 60, 70, 75, and 80°C, with the following results. (1) The rejection of cationic and anionic surfactants is larger than that of nonionic surfactants, especially at concentrations below CMC. (2) In the case of nonionic surfactants, their fluxes decrease with the increase of molecular weight. (3) The effect of CMC on the transport of surfactants is great, particulary in the case of nonionic surfactants. (4) Concentration polarization on the surface of the membrane can be predicted by taking into account the difference between surfactant fluxes below and above CMC.

Waste water contains various solutes of which surfactant is one of the most troublesome because of its harmfulness to human bodies. In this work, the behavior of anionic, cationic and nonionic surfactants was examined with Loeb-type skinned membranes. We intended to clarify the transport phenomena of various solutes with the membranes. However, in order to make the problem simpler a solution containing only one solute was examined in each case.

Expermental

Modified cellulose acetate (E-398-3) membranes were prepared by the method reported by Loeb and Manjikian[1] at annealing temperatures 60, 70, 75, and 80°C. The evaporation temperature was 18°±1°C, and evaporation time one minute. The membranes were placed in a stainless desalination cell described previously.[2] The pressurized (40 atm) solution was circulated along the surface of the membrane at 250 ml/min to reduce concentration polarization.

Solutions of sodium dodecylbenzenesulfonate (ABS) as anionics, tetradecylbenzylammonium chloride (TDBNC) as cationics and polyoxyethylene nonylphenyl ether (NP) as nonionics were tested at their various concentrations, since the surfactants have their critical micelle concentration (CMC). In the case of NP, NP-10 (C_9H_{19}-C_6H_4-O-(CH_2-$CH_2O)_n$ H; $n=10$), NP-16 (where : $n=16$) and NP-27 (where : $n=27$) were used to test the effects of the molecular weight on the permeation of surfactants. Analysis of surfactants was performed by photo-absorbance at 224 mμ for ABS, at 214 mμ for TDBNC and NP. The critical micelle concentrations were estimated from the plots of surface tension *vs.* surfactant concentration and from those of photo-absorption *vs.* surfactant concentration. Surface tensions were measured by the ring method.[3] Properties of the membrane were shown by water flux, salt flux, and salt rejection.[2,4]

Results

Rejection of Surfactants. The rejection of ABS was larger than that of the other two surfactants. The rejection of ABS was 88.9% even for the membrane annealed at 60°C and 99.8% for that annealed at 80°C (Table 1-1). The rejection was so large that no significant difference was observed between the solute fluxes below and above CMC. TDBNC also has a large rejection, *e.g.*, 86.5% and 93.4% for the membranes annealed at 60°C and 75°C, respectively. The rejection of NP–27 was the smallest, *e.g.*, 26% for the membrane annealed at 60°C (Fig. 1) and 86% for the membrane annealed at 80°C. The rejection of NP was almost the same as that of NaCl. The results obtained below CMC are given in Fig. 1.

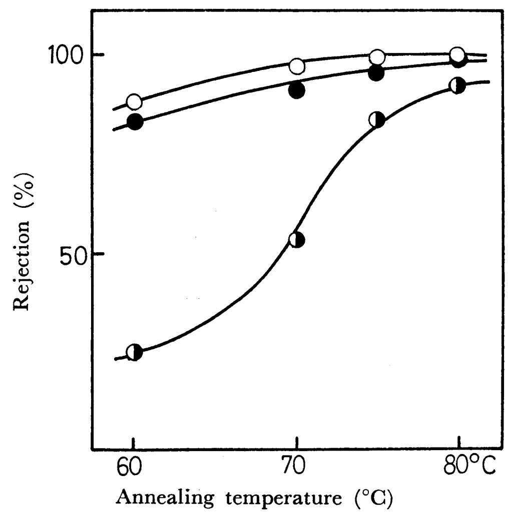

Fig. 1. Rejections of surfactants.
○: ABS 6.00×10^{-4} M
●: TDBNC 2.67×10^{-4} M
◑: NP-27 5.08×10^{-5} M

Effect of CMC. The effect of CMC on permeability through the membrane was measured. No detectable difference was found in the cases of ABS and TDBNC. The influence was remarkable in the case of NP, since its rejection was small below CMC, *e.g.*, the rejection of NP–10 was 42.1% below, and 83.9% above CMC for the membrane cured at 75°C (Table 1–2).

Effect of Molecular Weight. The influence of molecular weight on permeability through the membrane was examined for NP by changing the mole number of oxyetheylene unit. The flux of NP decreases with the increase of molecular weight of NP and

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TABLE 1-1 RESULTS OF REVERSE OSMOSIS EXPERIMENTS

Solute	Membrane	Concn of feed 10^{-4} mol/l	Water flux 10^{-3} g/cm²·sec	Solute flux 10^{-10} m mol/cm²·sec	Rejection %
ABS	60—1*[a]	6.0	2.04	17.8	85.5
	60—2	6.0	2.75	18.8	88.9
	70—1	6.0	1.74	3.53	96.7
	70—2	6.0	2.24	4.52	96.7
	75—1	6.0	1.61	0.65	99.3
	80—1	6.0	0.43	0.06	99.8
ABS	60—2	21.8	2.46	53.8	89.6
	70—2	21.8	2.01	13.4	97.0
	75—1	21.8	1.16	2.75	98.9
	75—2	21.8	1.43	2.02	99.4
	80—2	21.8	0.53	0.53	99.6
TDBNC	60—3	2.67	1.74	6.29	86.9
	60—4	2.67	2.53	14.2	78.9
	70—4	2.67	1.86	4.56	90.9
	75—3	2.67	1.44	2.54	93.4
	75—4	2.67	1.61	2.72	93.7

a) 60—1 (60: Annealing Temperature; 1: Identification Number of the Membrane)

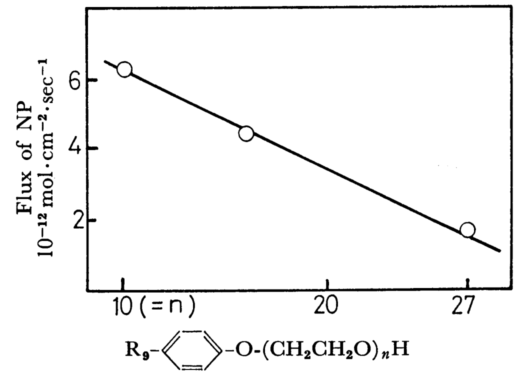
CMC; ABS: 1.40×10^{-3} mol/l, TDBNC: 4.20×10^{-3} mol/l

TABLE 1-2 RESULTS OF REVERSE OSMOSIS EXPERIMENTS

Solute	Membrane	Concn of feed 10^{-5} mol/l	Water flux 10^{-3} g/cm²·sec	Solute flux 10^{-10} mol/cm²·sec	Rejection %
NP-10	60—3	2.54	1.40	3.42	5.0
	60—4	2.54	1.82	4.42	5.0
	70—4	2.54	1.43	2.87	21.4
	75—3	2.54	1.10	1.62	42.1
NP-10	60—2	7.85	1.41	6.97	37.3
	60—3	7.85	1.89	10.1	31.3
	70—2	7.85	1.52	4.33	63.6
	70—5	7.85	1.38	3.93	63.6
	75—3	7.85	1.23	1.57	83.9
	75—6	7.85	1.48	2.20	80.9
NP-16	60—3	3.75	1.40	4.98	5.4
	60—4	3.75	1.82	6.37	5.4
	70—4	3.75	1.43	4.07	24.3
	75—3	3.75	1.10	1.68	59.5
NP-16	60—4	10.8	2.33	14.2	33.0
	70—4	10.8	1.92	6.17	70.0
	75—3	10.8	1.47	1.56	90.1
	80—1	10.8	0.47	0.22	96.0
NP-27	60—5	5.08	1.93	6.38	26.0
	70—4	5.08	1.56	3.33	54.8
	75—3	5.08	1.26	1.08	83.1
	80—1	5.08	0.36	0.27	86.0
NP-27	60—5	16.9	1.74	13.24	55.0
	70—4	16.9	1.40	6.19	73.9
	75—3	16.9	1.15	1.52	92.0

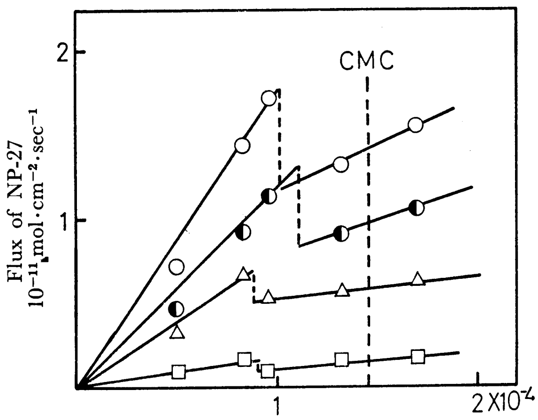
CMC; NP-10: 5.27×10^{-5} mol/l, NP-16: 6.80×10^{-5} mol/l, NP-27: 1.44×10^{-4} mol/l.

that of NP–27 is approximately one–third of that of NP–10 (Fig. 3). The concentration of feed solution is below CMC; in the solution above CMC, the tendency is almost the same (Fig. 2).



Concentration of feed 1.0×10^{-5} M

Fig. 2. Effect of molecular weight on the permeation of NP.



Concentration of the feed (M)

Fig. 3. Effect of CMC on the permeation of NP-27.
○: Membrane annealed at 60°C.
◐: Membrane annealed at 60°C.
△: Membrane annealed at 70°C.
□: Membrane annealed at 75°C.

Discussion

Rejections of Surfactants. The rejection of ABS and TDBNC is approximately the same and greater than that of NP–27 (Fig. 1). It was observed that the dissociated species can hardly pass through the membrane.[4] The present results seem to support this. The size of the molecule should be closely related to its permeability, but to explain molecular permeability through the membrane by ascribing it mainly to the molecule is not satisfactory since the molecular weights of ABS, TDBNC, and NP–27 are 348, 327, and 1408, respectively.

Effect of Molecular Weight. The permeation of NP changes with its molecular weight, but it cannot be said whether this is due to the molecular size or to hydrophilic property by increasing ethylene oxide units. No difference was found between the decreasing tendencies of NP flux with increasing molecular weight below and above CMC. Most of the permeated NP is supposed to be a monomer in equilibrium with micelle. According to Kesting *et al.*,[5] water flux increases with the increase of hydrophilic property of the surfactant, but in the present work, the change of water flux with chemical property of surfactant was within experimental error.

Effect of CMC. It is generally recognized that in the case of inorganic salts, their fluxes are in linear proportion to the concentrations of the feed solution.[6,7] In the case of NP the rejection of the solute below CMC differs remarkably from that above CMC for each membrane (Table 1–2). In other words the solute fluxes are not in proportion to the feed concentration for a determined membrane. To make this effect clearer, the relation between concentration of the feed and the solute flux was investigated in detail with NP–27. The fluxes of NP–27 were in linear proportion to the concentration of the feed before it reached a certain concentration, at which an abrupt decrease occurred (Fig. 3). It might be considered that the concentration of NP–27 at the surface of the membrane reached CMC. The concentration polarization can be given by[8])

$$\frac{C_2-C_3}{C_1-C_3} = e^{J_v/K}$$

where C_1, C_2, and C_3 are the bulk concentration of the feed, the concentration at the membrane surface and the concentration of the product, respectively. J_v is water flux (cm/sec), and K is mass-transfer coefficient (cm/sec). If we know the critical feed concentration which would cause the concentration at the membrane surface to amount to CMC, the ratio of the concentration at bulk solution to that at boundary layer ($=C_2/C_1$) could be estimated.

Under the assumption that the value of K remains constant below and above CMC, the value of K was calculated by the above equation with the values of C_2 ($=1.45\times10^{-4}$ mol/l=CMC), C_3 ($=0.30\times10^{-4}$ mol/l), and J_v ($=1.62\times10^{-3}$ cm/sec), the data for the membrane annealed at 70°C. The value of C_1 was assumed to be the average 0.89×10^{-4} mol/l of the concentrations which lie on both sides of inflection (see Fig. 3). The critical values ($=C_1$) for the other membranes were then calculated with $K(=2.40\times10^{-3}$ cm/sec) estimated above. The concentrations shown by dotted lines indicate calculated values (Fig. 3). A micelle is supposed to be composed of 20—30 monomers, making it large enough to be rejected by the membrane.

From the results (Fig. 3) the ratio of the concentration at bulk solution to that at boundary layer ($=C_2/C_1$) is found to be between 1.32—1.61 depending on the membrane under conditions described in the experimental section.

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