酢酸セルロース誘導体逆浸透膜による低分子量有機物 水溶液の分離特性の研究

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Studies on Reverse Osmosis Separation of Aqueous Solutions of Low Molecular Weight Organics by Cellulose Acetate Derivative Membranes

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Membranes of cellulose acetate derivatives-cyanoethyl cellulose acetate (CACN), hydroxypropyl cellulose acetate (CAHP) and cellulose acetate (CA) have been prepared. The reverse osmosis separation of aliphatic acids, alcohols and amines have been made. It was found that for *n*-alkyl organics, the solute rejections (R_a) firstly increased with the increase of carbon numbers of *n*-alkyl organics and reached a maximum when the organic molecule contained about three carbon atoms, and then decreased or kept stable. The order of solute rejections for organics with different structures was *n*-<iso-<sec-<tert- because of the steric hindrance. The effect of operating pressure on the properties of reverse osmosis have also been investigated and it was found that the solute rejections and the fluxes of solution increased with the increase of the operating pressure in the experimental extent. An analysis of experimental data with Spiegler-Kedem's transport model has been carried out and the membrane constants such as reflection coefficient σ , solute and hydraulic permeabilities ω and L_p for several organic solutes have been obtained.

Key words : Reverse osmosis, Low molecular weight organics, Cellulose acetate, Cyanoethyl cellulose acetate, Hydroxypropyl cellulose acetate

1. INTRODUCTION

Reverse osmosis separation of organic solutes in aqueous solution are of interest from the point of view of both the mechanism of the process as well

as its application for waste water treatment and water pollution control. Matsuura and Sourirajan^{1) ~ 5)} used the porous cellulose acetate membranes to study such separations with respect to alcohols, phenols, organic acids, hydrocarbons,

Table 1 Membrane Characteristics

membrane	before testing with organics		after testing with organics	
	salt rejection (%)	flux (mol/m ² ·s)	salt rejection (%)	flux (mol/m ² ·s)
CACN	95.50	0.1610	97.04	0.1258
CAHP	95.65	0.1941	96.30	0.1759
CA	96.10	0.3048	97.09	0.2780

test conditions : 25±0.5°C, 2.0 MPa, NaCl : 3500 ppm

aldehydes, ethers etc. And the experimental results have been interpreted using "Preferential Sorption Capillary Flow" model. They concluded that solute separation of organics in reverse osmosis was governed by the hydrogen bonding ability of the organic molecule when it was essentially undissociated and by electrostatic repulsion of ions when the molecule was partially or completely dissociated. They also provided some physicochemical criteria for RO separation of organics such as $\Delta\nu$, (shift in the OH band maximum in the IR spectra) as well as the Taft number and Hammett number for alcohols and phenols¹⁾, K_a (dissociation constant) and the degree of dissociation of the molecule for organic acids³⁾, the Small's number for hydrocarbons⁴⁾.

The distribution properties and separation properties for alcohols have been investigated using liquid chromatography and reverse osmosis before⁶⁾. The results have been discussed according to the polarity, non-polarity, and steric effect of organic molecule. It was shown that the main factors, coming from the chemical nature of organics, governing the properties of distribution and separation were different because of the differences in the performance of solute between liquid chromatography and reverse osmosis processes⁶⁾.

Some modified CA membrane materials such as CACN⁷⁾, CAHP⁸⁾, titanium cellulose acetate (TiCA)⁹⁾, etc. have been synthesized with regard to CA because of its weakness and studied before. The resistance to microbial decomposition¹⁰⁾, thermal stability^{8, 9)}, and antipollution ability¹¹⁾ have

been improved as compared with CA.

In this work the reverse osmosis separation of *n*-alkyl aliphatic alcohols, acids, amines and these organics with different structures in aqueous solutions have been studied using the cellulose acetate derivatives—CACN, CAHP and CA membranes. The effect of operating pressure on the reverse osmosis properties has been investigated. An analysis of experimental data with Spiegler-Kedem's transport model has also been carried out to obtain the membrane constants such as reflection coefficient σ , solute and hydraulic permeabilities ω and L_p .

2. EXPERIMENTAL

2.1 Materials

Cyanoethyl cellulose acetate (CACN), hydroxypropyl cellulose acetate (CAHP) and cellulose acetate were the same as reported previously⁶⁾.

2.2 Membrane Preparation

The compositions of membrane casting solutions, the conditions and the procedures for membrane casting were all the same as reported earlier⁶⁾. All membranes were subjected to an initial permeation of pure water under pressure of 2.5 MPa for 2 hours, prior to their subsequent use in RO experiments.

2.3 Reverse Osmosis (RO) Experiments

The experimental apparatus and the procedure for RO experiments were as described in a previ-

Fig. 1 The separation properties for *n*-alkyl aliphatic acids

Fig. 3 The separation properties for *n*-alkyl aliphatic alcohols

ous paper⁶⁾. Both before and after testing with organic solutes the membranes were subjected to a test solution of sodium chloride 3500 ppm to re-evaluate their properties of the membranes and their constancy. The results were shown in Table 1. All membranes were tested with single-solute solution of 500 ± 50 ppm. Each test solution was circulated over membrane surface under test conditions for 2 hours prior to collecting the permeate samples.

A Shimadzu total carbon analyzer, Model TOC-500, equipped with an automatic sample injector, ASI-502, was used to measure the concentration of

Fig. 2 The separation properties for *n*-alkyl aliphatic amines

Fig. 4 The separation properties for *n*-alkyl dicarboxylic acids

organics in both permeate and feed solutions.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

3.1. The Separation Properties for *n*-alkyl Organics

The separation properties of CACN, CAHP and CA membranes for *n*-alkyl aliphatic acids, amines and alcohols were shown in Fig. 1, 2, 3, respectively. It was found that at first the solute rejections increased with the carbon numbers of organics and reached a maximum when the organic molecule contained about three carbon atoms, and then

Fig. 5 The separation properties for valeric acids with different structures

Fig. 6 The separation properties for butylamine with different structures

Fig. 7 The separation properties for butyl alcohols with different structures

kept constant for *n*-aliphatic acids or decreased for *n*-aliphatic amines and alcohols. This was mainly due to the increase of the distribution of solute with longer carbon chains into membrane as discussed in a previous paper for alcohols⁶⁾. The separation properties for *n*-alkyl dicarboxylic acids were also shown in Fig. 4. It could be seen that the solute rejections for dicarboxylic acids were larger than those for monocarboxylic acids, especially for oxalic acid because of the dissociation degrees.

Fig. 8 The effect of operating pressure on the RO properties of CACN membrane

3. 2 The Separation Properties for Organics with Different Structures

The separation properties of CACN, CAHP and CA membranes for valeric acids, butylamines and butyl alcohols with different structures were

Fig. 9 The effect of operating pressure on the RO properties of CAHP membrane

shown in Fig. 5, 6, 7, separately. It could be seen that the solute rejections for these organics with different structures all followed the order of n -<iso-<sec-<tert-. Obviously this was mainly due to the effect of steric hindrance.

3.3 The Effect of Operating Pressure

The effect of operating pressure on the RO properties of CACN, CAHP and CA membranes were shown in Fig. 8, 9, 10, respectively as the examples for n -butylric acid, n -propylamine and ethyl alcohol. It was found that both the solute rejections and the fluxes of solutions increased with the increase of the operating pressure in the experimental extent.

Fig. 10 The effect of operating pressure on the RO properties of CA membrane

4. ANALYSIS OF EXPERIMENTAL DATA

4.1. Transport Equation

The relation between concentration of solute at the membrane surface (C_2) and concentration in the bulk solution (C_1) can be expressed by Eq. (1) as follows^{1,2)}.

$$(C_2 - C_3)/(C_1 - C_3) = \exp(J_v/k) \quad (1)$$

Where C_3 is the concentration of solute in the permeate solution, k is the mass transfer coefficient at membrane surface. In this RO system and cells used, k can be obtained by the following equation as reported earlier^{1,3)}

$$Sh = 1.77 Re^{0.734} Sc^{0.33} \quad (2)$$

Where $Sh = kd/D$, $Sc = \nu/D$, $Re = Ud/\nu$. The concentration of solute at the membrane surface (C_2) can be obtained from Eq. (1).

The process of permeation of any binary solu-

Table 2 Membrane Constants of CACN for Several Organic Solutes

solutes	σ [—]	$L_p \times 10^{12}$ [m ³ /m ² · Pa · s]	$\omega \times 10^9$ [mol/m ² · Pa · s]
Methanol	0.09246	2.7800	4.9889
Ethanol	0.3398	2.6599	3.7758
<i>n</i> -propyl alcohol	0.4600	2.7275	3.6201
<i>n</i> -butyl alcohol	0.2354	2.7713	1.3833
<i>n</i> -amyl alcohol	0.1418	2.5912	1.2813
Formic acid	0.1752	2.5924	3.8880
Acetic acid	0.3386	2.5682	3.1481
<i>n</i> -propionic acid	0.3624	2.6445	2.9021
<i>n</i> -butyric acid	0.3931	2.5324	2.2520
<i>n</i> -valeric acid	0.2456	2.5825	1.9410
Methylamine	0.6935	3.0701	4.9407
Ethylamine	0.7243	3.1559	2.2213
<i>n</i> -propylamine	0.7552	2.9891	2.3368
<i>n</i> -butylamine	0.5162	2.9857	1.4842

Table 3 Membrane constants of CAHP for Several Organic Solutes

solutes	σ [—]	$L_p \times 10^{12}$ [m ³ /m ² · Pa · s]	$\omega \times 10^9$ [mol/m ² · Pa · s]
Methanol	0.0980	2.1902	3.0251
Ethanol	0.3431	2.0729	2.5670
<i>n</i> -propyl alcohol	0.3599	2.1396	1.3593
<i>n</i> -butyl alcohol	0.3029	2.1541	1.2952
<i>n</i> -amyl alcohol	0.2128	1.9918	1.7618
Formic acid	0.2100	1.9750	3.7123
Acetic acid	0.4060	1.9660	2.6290
<i>n</i> -propionic acid	0.3305	2.0320	1.6412
<i>n</i> -butyric acid	0.4095	1.9301	1.5576
<i>n</i> -valeric acid	0.2958	1.9754	1.2730
Methylamine	0.6838	1.7968	4.2512
Ethylamine	0.6149	1.8062	2.4563
<i>n</i> -propylamine	0.5887	1.9761	1.7240
<i>n</i> -butylamine	0.3142	2.3796	1.0353

tion through a membrane is described by the following Spiegler-Kedem's transport equation¹⁵⁾

$$J_v = L_p (\Delta P - \sigma \Delta \pi) \quad (3)$$

$$J_s = \omega \Delta \pi + (1 - \sigma) J_v \bar{C}_s \quad (4)$$

Spiegler and Kedem¹⁵⁾ divided the membrane into differential element in the direction of its thickness and applied Eq.(3) in it in the form of a dif-

Table 4 Membrane Constants of CA for Several Organic Solutes

solutes	σ [-]	$Lp \times 10^9$ [m ³ /m ² ·Pa·s]	$\omega \times 10^9$ [mol/m ² ·Pa·s]
Menthanol	0.0800	2.2700	3.1256
Ethanol	0.3223	2.1852	2.1643
<i>n</i> -propyl alcohol	0.3146	2.3235	0.8212
<i>n</i> -butyl alcohol	0.3178	2.3330	1.1084
<i>n</i> -amyl alcohol	0.2258	2.1995	1.2332
Formic acid	0.2387	2.2354	5.4066
Acetic acid	0.4212	2.1816	3.0665
<i>n</i> -propionic acid	0.4193	2.2264	2.5862
<i>n</i> -butyric acid	0.3111	2.0829	1.0885
<i>n</i> -valeric acid	0.3111	2.3227	1.2796
Methylamine	0.5971	2.3738	5.2272
Ethylamine	0.6146	3.0581	3.4639
<i>n</i> -propylamine	0.5254	3.4279	3.0717
<i>n</i> -butylamine	0.2054	3.8970	1.4975

ferential equation, integrating the equation to give the following intrinsic rejection ($R_{i_{nt}}$).

$$R_{i_{nt}} = 1 - SP = (C_2 - C_3) / C_2 = \sigma(1 - F) / (1 - \sigma F) \quad (5)$$

where

$$F = \exp[-(1 - \sigma)Jv / (\omega RT)] \quad (6)$$

By extrapolating Jv to infinite value, the value of $R_{i_{nt}}$ in Eq.(5) approaches reflection coefficient σ as the value of F approaches zero.

4.2 Estimation of σ , Lp and ω

As mentioned above, the reflection coefficient σ can be obtained by extrapolating the intrinsic rejection $R_{i_{nt}}$ to infinite flux Jv or zero of $1/Jv$ on the ordinate axis. Therefore, we can plot $R_{i_{nt}}$ v. s. $1/Jv$ and get the reflection coefficient σ by extrapolating $R_{i_{nt}}$ to zero of $1/Jv$ as described earlier¹⁵⁾.

By using σ estimated as above, the hydraulic and solute permeabilities Lp, ω can be obtained from Eq.(3) and (4) where $\bar{C}_s$ is the logarithmic averaged molar concentration of C_2 and C_3 , and $\Delta\pi$,

the osmotic pressure was estimated using the van't Hoff equation as follows

$$\Delta\pi = RT\Delta C \quad (7)$$

4.3. Analysis Results and Discussions

The values of σ , Lp , and ω obtained by the method as mentioned above, for several organic solutes were shown in Table 2, 3, and 4, for CACN, CAHP and CA membranes respectively. It could be seen that the hydraulic permeability almost unchanged with the carbon number of organic molecules having the same functional group, while the solute permeability decreased with the increase of the carbon numbers because of the steric hindrance.

5. CONCLUSIONS

1. Cellulose acetate derivatives-cyanoethyl cellulose acetate, hydroxypropyl cellulose acetate and cellulose acetate membranes have been prepared and the reverse osmosis separation of low molecular weight organics have been investigated. It was found that the solute rejections of *n*-alkyl aliphatic

Nomenclatures

Symbols

C	: molar concentration	[mol/m ³]
$\bar{C}_s$	: logarithmic averaged molar concentration	[mol/m ³]
D	: diffusivity	[m ² /s]
F	: quantity defined by Eq. (5)	[-]
J _v	: volume flux of solution	[m ³ /m ² ·s]
J _s	: molar flux of solute	[mol/m ² ·s]
k	: mass transfer coefficient	[m/s]
L _p	: hydraulic permeability	[m ³ /m ² ·Pa·s]
P	: pressure	[Pa]
R	: gas constant	[J/mol·K]
R _a	: apparent solute rejection (C ₁ -C ₃)/C ₁	[-]
R _i	: intrinsic solute rejection (C ₂ -C ₃)/C ₂	[-]
Re	: Reynolds number	[-]
Sc	: Schmidt number	[-]
Sh	: Sherwood number	[-]
SP	: solute passage C ₃ -C ₂	[-]
T	: temperature	[K]
Greek letters		
Δ	: difference	
π	: osmotic pressure	[Pa]
σ	: reflection coefficient	[-]
ω	: solute permeability	[mol/m ² ·Pa·s]
subscripts		
1	: bulk solution	
2	: membrane-solution interface	
3	: permeate solution	

ic acids, amines, and alcohols at first increased with the increase of carbon numbers and reached a maximum when the organic molecule contained about three carbon atoms, and then kept constant or decreased. The order of solute rejections for organics with different structures was *n*-<iso-~sec-<tert- because of the steric hindrance.

2. Both the solute rejections and the solution fluxes increased with the increase of operating pressure.

3. An analysis of experimental data with Spiegler-Kedem's transport model has been carried

out and some membrane constants such as reflection coefficient σ , solute and hydraulic permeabilities ω and L_p have been obtained for several organic solutes. It was found that the hydraulic permeability L_p almost unchanged with the carbon numbers of the organics having the same functional group, while the solute permeability ω decreased with the increase of the carbon numbers because of the steric effects coming from the molecular size.

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