

# Rejection of Phenolic Derivatives in Aqueous Solution by an Interpolymer Anionic Composite Reverse Osmosis Membrane

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## Synopsis

Reverse osmosis separation for 23 phenolic derivatives was examined by an anionic charged composite membrane. The solute permeation was carried out in single-solute aqueous solution (200 mg/L) under applied pressure of 3.92–7.85 MPa at 25°C. The correlation between the solute rejection and polar parameters for phenolic derivatives has been investigated. For *p*-alkylphenols, the solute rejection increased with molecular weight and/or molecular branching. In undissociated state, the rejection of phenolic derivatives was closely related with the Taft's number and the Hammett's number of substituents. Also rejections of phenolic derivatives depended upon the pH value of feed solution and the polar effect of substituted groups. For example, rejections of aminophenols showed the minimum value at a certain pH value and on either side of the minimum point, the rejection of aminophenol increased. From these facts, the main factors in reverse osmosis separation by an anionic composite membrane were discussed.

## INTRODUCTION

Cellulose acetate membrane has been widely used for reverse osmosis separation. However, Matsuura and Sourirajan<sup>1</sup> reported that cellulose acetate membrane showed lower or negative rejection for phenol in undissociated state.

In previous papers,<sup>2,3</sup> the authors have reported the correlation between the separation and polar parameters for various organic solutes in reverse osmosis by an anionic and a cationic charged composite membranes. It may be expected that the solute separation by ionic charged membranes are different from that of noncharged membranes. Particularly, it was found that an anionic composite membrane (with sulfonic acid groups) showed higher rejection for phenol in an undissociated state in comparison to the other types of reverse osmosis membranes.

In this article, we deal with the reverse osmosis separation of more than 20 different phenolic derivatives by an interpolymer anionic composite membrane with sulfonic acid groups.

## EXPERIMENTAL

An interpolymer anionic composite membrane was prepared from poly (vinyl alcohol) and poly (styrene sulfonic acid) by the method used in a previously reported article.<sup>4</sup> The composite membrane was formed by casting the polymer solution composed of two polymers and water–ethyl alcohol

TABLE I  
Reverse Osmosis Performance of Anionic Membranes Used<sup>a</sup>

Membrane No.	Rejection (%)	Flux (L/m <sup>2</sup> · h)
1	95.4	21.5
2	88.8	20.4
3	96.2	22.6
4	88.2	39.7
5	97.9	10.5
6	93.7	21.7
7	87.8	45.4
8	98.9	6.1
9	95.0	16.9
10	97.1	12.7
11	93.3	33.6
12	91.4	35.6
13	92.8	20.8
14	90.9	34.3

<sup>a</sup> Feed concentration: 0.5% NaCl aqueous solution. Measured under applied pressure of 7.85 MPa at 25°C.

mixture (12/7, wt %) in a thin film on a microporous polypropylene supporter, evaporating the solvent at 30°C, and then heat curing at 120°C for 2.5 h. Water flux and salt rejection of the membrane were measured under applied pressure of 7.85 MPa with 0.5% NaCl aqueous solution at 25°C, and these data are shown in Table I.

Water flux and solute rejection of the membrane were measured by the recirculating-type reverse osmosis cells described in an earlier paper.<sup>5</sup> The effective membrane area was 12.5 cm<sup>2</sup> in all cases.

Guaranteed reagent-grade phenolic derivatives shown in Table II were used for experiments without further purification.

The solute permeation was carried out with single-solute aqueous solution (200 mg/L) under applied pressure of 3.92–7.85 MPa at 25°C. A solute concentration in the feed solution and permeate were determined with the total organic carbon analyzer (Yanagimoto Co., Ltd., Model TOC-1LW).

## RESULTS AND DISCUSSION

### Rejection of *p*-Alkylphenols

The rejection of *p*-alkylphenols was examined. The correlation between the rejection and molecular weight of *p*-alkylphenols is shown in Figure 1. The rejection of *p*-alkylphenols increased with molecular weight. It may be considered that diffusion constants of *p*-alkylphenols within the membrane matrix decrease with increase in molecular weight.

This membrane (an anionic composite membrane with sulfonic acid groups) showed higher rejection (80%) for phenol in undissociated state at a 98% rejection level of NaCl. On the other hand, there was no correlation between molecular weight and the rejection of other phenolic derivatives.

TABLE II  
 Phenolic Derivatives Used in Experiments

No.	Solute	No.	Solute
1	<i>o</i> -Aminophenol	13	Pyrocatechol
2	<i>m</i> -Aminophenol	14	Resorcinol
3	<i>p</i> -Aminophenol	15	Hydroquinone
4	<i>o</i> -Cresol	16	Pyrogallol
5	<i>m</i> -Cresol	17	<i>o</i> -Methoxyphenol
6	<i>p</i> -Cresol	18	<i>m</i> -Methoxyphenol
7	<i>o</i> -Chlorophenol	19	<i>p</i> -Methoxyphenol
8	<i>m</i> -Chlorophenol	20	<i>p-tert</i> -Butycatechol
9	<i>p</i> -Chlorophenol	21	<i>p-tert</i> -Butylphenol
10	<i>o</i> -Nitrophenol	22	<i>p</i> -Ethylphenol
11	<i>m</i> -Nitrophenol	23	Phenol
12	<i>p</i> -Nitrophenol		

### Rejection of Phenolic Derivatives

The correlation between the rejection and acidity function ( $\Delta\nu_s$ )<sup>6</sup> of phenolic derivatives was shown in Figure 2. The solute rejection decreased with increase in the acidity of the solute molecule ( $\Delta\nu_s$ ).

$\Delta\nu_s$  represents the total polar effect of the molecule and Taft's number ( $\sigma^*$ )<sup>1</sup> and Hammett's number ( $\sigma$ )<sup>1</sup> represent the contribution of substituent group to this total effect. Matsuura and Sourirajan<sup>6</sup> have reported the correlation between  $\Delta\nu_s$  and  $\sigma^*$  or  $\sigma$  for functional groups in reverse osmosis separation.

The correlation between the rejection and  $\sigma^*$  or  $\sigma$  of phenolic derivatives is shown in Figure 3. The rejection of monosubstituted phenols decreases with increase in  $\sigma^*$  or  $\sigma$ . Phenol would be rejected by the electrostatic effect between fixed anionic groups in membrane matrix and hydroxyl groups of phenol. The rejection of monosubstituted phenols depends deeply upon electron density in the neighborhood of the hydroxyl groups.

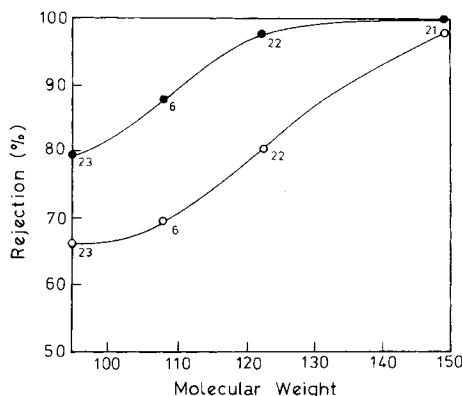


Fig. 1. The correlation between molecular weight and the rejection of *p*-alkylphenols in aqueous solution: membrane Nos. 8 (●) and 9 (○), applied pressure 7.85 MPa.

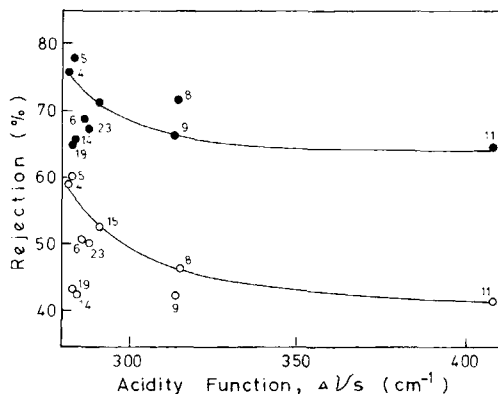


Fig. 2. The rejection of phenolic derivatives in aqueous solution as an acidity function ( $\Delta\nu_s$ ): membrane Nos. 1 (●) and 4 (○), applied pressure 7.85 MPa.

For phenolic derivatives with higher electron-withdrawing substituents, the electron density of the hydroxyl groups gets lower. Thus, the electrostatic repulsion between fixed charges in membrane matrix ( $-\text{SO}_3^-$ ) and solute gets weaker, and the solute rejection would decrease.

*o*-Hydroxyl phenol showed relatively higher rejection in comparison to *m*- and *p*-hydroxyl phenols. In *o*-hydroxyl phenol, the negativity of phenolic hydroxyl group increased by intramolecular hydrogen bonding ability between substituted hydroxyl group and phenolic hydroxyl group.

### Rejection of Phenol—Effect of pH of Feed Solution

The rejection of phenol in aqueous solution was examined at various degrees of dissociation. The pH value of the feed solution was adjusted by addition of HCl or NaOH. Reverse osmosis experiments were then carried out in the pH range 2–12 at 3.92 and 7.85 MPa. The results for two membranes with different NaCl rejection level are given in Figure 4. Within the pH range 2–7, phenol is less dissociated in the feed solution and the rejection of phenol is almost invariable.

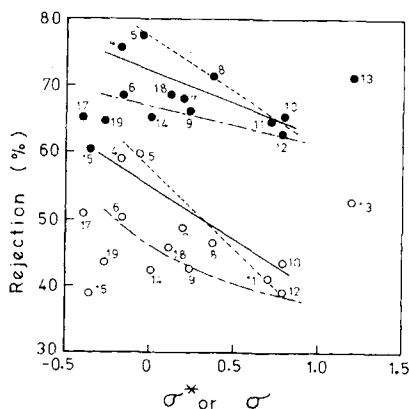


Fig. 3. The rejection of phenolic derivatives in aqueous solution vs. the Taft's number ( $\sigma^*$ ) or the Hammett's number ( $\sigma$ ): membrane Nos. 3 (●) and 4 (○), *o*- (—), *m*- (---), and *p*- (—), applied pressure 7.85 MPa.

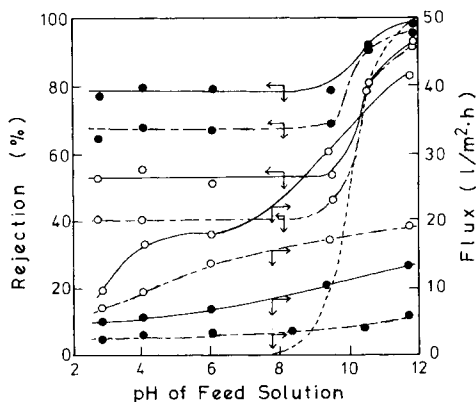


Fig. 4. Effect of pH of feed solution on the rejection of phenol: membrane Nos. 5 (●) and 7 (○), applied pressure 3.92 MPa (---) and 7.85 MPa (—).

It may be considered that an anionic membrane has less affinity for phenol at undissociated state, and the chemical affinity of phenol with the membrane is one of the most important factors for the solute rejection at undissociated state.

At the pH range 8.36–11.83, the degree of dissociation of phenol increases from 2.3% to 100% in aqueous solution. The pH vs. degree of dissociation correlation is given with the dotted line in Figure 4. With respect to each membrane, the pH vs. solute rejection correlation curve showed a similar tendency with the pH vs. degree of dissociation correlation one.

In dissociated state, it may be suggested that the electrostatic repulsion between fixed charges in membrane matrix and solute co-ions is the prominent factor for solute rejection. Water flux increases due to the fact that water would be adsorbed selectively in the membrane interface.

#### Rejection of Phenol—Effect of Applied Pressure

The effect of applied pressure on the rejection of undissociated phenol and water flux in aqueous solution are shown in Figure 5. The experiments were carried out under applied pressure of 3.93–7.85 MPa. As shown in Figure 5, water flux and solute rejection increase with applied pressure. Water flux is proportional to applied pressure. The membrane would undergo a slight compaction under the influence of applied pressure, and, subsequently, the interstitial ionic concentration in the membrane will be increased. Thus, solute rejection increases slightly with applied pressure.

#### Rejection of Aminophenols

The variation in the rejection of aminophenols (*o*-, *m*-, and *p*-isomers) with pH of the feed solution is given in Figure 6. The rejection of *o*-, *m*-, and *p*-aminophenols are at minimum in pH 5.5, 4.5, and 7.0, respectively. For each solute, the pH value at minimum rejection was the same, even though the anionic membranes with different rejection level of NaCl were used, as shown in Tables III and IV.

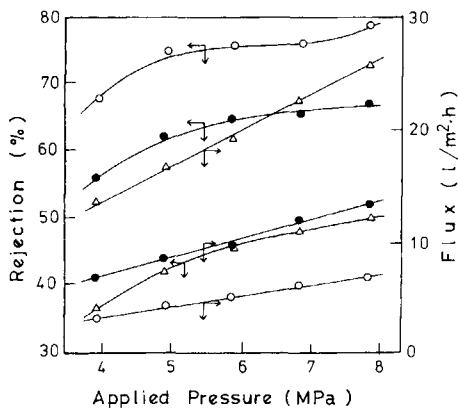


Fig. 5. Effect of applied pressure on the rejection of phenol: membrane Nos. 5 (○), 6 (●), and 7 (△).

If the solute rejection were only dependent upon electrostatic effects between fixed charges in membrane matrix and solute ion, the solute rejection would be the least at the isoelectric point.

The isoelectric points of three isomers (*o*-, *m*-, and *p*-) were measured by potentiometric titration method, and the values were 7.35, 8.02, and 7.22, respectively.

However, the pH value at minimum rejection level does not always agree with the isoelectric point, except for *p*-aminophenol.

On acid side, most of amino group in solute dissociates into ammonium ion, and solute rejection increases by the electrostatic repulsion between fixed charges and Cl<sup>-</sup> co-ion of solute. As the pH value approaches from acid side into neutral area, the dissociation of amino groups are depressed, and the electrostatic repulsion between membrane and solute is getting weaker. Also, the chemical affinity between membrane and solute increases. Therefore, the rejection of solute decreases abruptly.

On alkali side, most of the hydroxyl group in solute dissociates into phenolate ion, and the electrostatic repulsion between fixed charges in mem-

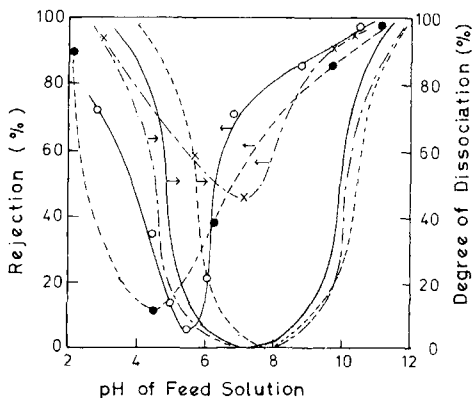


Fig. 6. Effect of pH of feed solution on the rejection of aminophenols: membrane Nos. 10 and 13, *o*- (○), *m*- (●), and *p*- (χ), applied pressure 7.85 MPa.

TABLE III  
Rejection of *o*- and *m*-Aminophenol<sup>a</sup>

pH of feed solution	Rejection <sup>b</sup> (%)	Rejection <sup>c</sup> (%)	Rejection <sup>d</sup> (%)
<i>o</i> -Aminophenol			
2.86	72.6	72.1	79.1
4.48	35.2	14.5	21.0
5.02	14.1	-14.7	-13.3
5.48	6.0	-36.7	-32.9
6.05	21.0	-18.8	-21.6
6.83	71.1	55.2	50.7
8.86	85.3	78.3	73.6
10.48	96.4	92.9	92.3
<i>m</i> -Aminophenol			
2.08	89.4	82.5	80.0
4.50	11.1	-19.5	-14.9
6.15	38.0	11.5	4.2
9.68	85.1	80.2	75.4
11.11	97.4	94.3	92.7

<sup>a</sup> Measured under applied pressure of 7.85 MPa at 25°C.

<sup>b</sup> Membrane No. 10.

<sup>c</sup> Membrane No. 11.

<sup>d</sup> Membrane No. 12.

brane and phenolate ion is a prominent factor for solute rejection. For *o*- and *m*-isomers, it may be considered that the interaction between incompatible acid and base characters is more complicated, and the pH value at minimum rejection is not the same as the isoelectric point.

### CONCLUSION

The correlation between the solute rejection and polar parameters for phenolic derivatives has been investigated.

The solute rejection for phenolic derivatives in undissociated state is closely related to Taft's number or Hammett's number. For *p*-alkylphenols in undissociated state, the solute rejection increases with molecular weight and/or chain branching degree. For phenol, the solute rejection depends on the degree of dissociation of solute. The solute rejection increases with

TABLE IV  
Rejection of *p*-Aminophenol<sup>a</sup>

pH of feed solution	Rejection <sup>b</sup> (%)	Rejection <sup>c</sup> (%)
3.00	93.8	66.9
5.70	58.7	48.9
7.10	45.5	31.8
9.70	90.4	87.4
10.23	94.2	94.3

<sup>a</sup> Measured under applied pressure of 7.85 MPa at 25°C.

<sup>b</sup> Membrane No. 13.

<sup>c</sup> Membrane No. 14.

the degree of dissociation of solute. The water flux and solute rejection increase with increase in applied pressure. For aminophenols, the rejection of *o*-, *m*-, and *p*-aminophenols are minimum at pH 5.5, 4.5, and 7.0, respectively. On either side of minimum point, the rejection of aminophenol increases.

The results suggest that the solute rejection is influenced by the following factors: electrostatic effects between fixed charges in membrane matrix and ionic solute, the steric effects of solutes, and the diffusivity and chemical affinity between solute and membrane.

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