

The Rejection of Polar Organic Solutes in Aqueous Solution by an Interpolymer Anionic Composite Reverse Osmosis Membrane

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Synopsis

Reverse osmosis separation for many kinds of polar organic solutes (alcohols, phenols, monocarboxylic acids, amines, and ketones) 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 7.88 MPa at 25°C. The correlation between the solute rejection and polar parameters for these organic solutes have been investigated. For *n*-alkyl alcohols, monocarboxylic acids, and ketones, the solute rejection increases with molecular weight and/or molecular branching. For undissociable polar organic solutes such as alcohols and ketones, solute rejections are closely related with the Taft's number. For dissociable polar organic solutes, solute rejections depend greatly upon the dissociation constant and the degree of dissociation of solute. This membrane showed higher rejection (80%) for phenol in an undissociated state at a 98% rejection level of NaCl. Also, rejections of phenolic derivatives depend upon the pH value of the feed solution and the polar effect of substituted groups. For acetic acid and methylamine, the solute rejection increases proportionally to the degree of dissociation of solute. From these facts, the main factors in reverse-osmosis separation by an anionic composite membrane are discussed.

INTRODUCTION

Systematic and detailed work on reverse-osmosis separation of organic solutes by noncharged membranes, such as cellulose acetate and aromatic polyamide, has been done by Matsuura and Sourirajan and co-workers.¹⁻⁶ For many organic solutes, the correlation between their separation and physicochemical parameters of solutes such as the Taft's number, the dissociation constant, and the molar attraction constant have been elucidated.

Recently, much interest is focused on reverse-osmosis separation by charged membranes.⁷ It may be expected that the solute separation by charged membranes (with fixed ionic groups) are different from that of noncharged membranes.

Fang and Chian⁸ have reported on the physicochemical criteria for the separation of polar organic compounds using NS-100 membrane. In a previous paper,⁹ the authors have reported the correlation between the solute separation and polar parameters for some organic solutes by a cationic composite membrane with quarternary ammonium groups.

In this paper, we deal with the reverse-osmosis separation of polar organic compounds, such as alcohols, phenols, monocarboxylic acids, aliphatic amine, aniline derivatives, and ketones, by an interpolymer anionic composite membrane with sulfonic acid groups.

TABLE I
Performance of Anionic Membranes Used^a

Membrane no.	Rejection (%)	Flux (L/m ² ·h)
1	92.3	15.5
2	93.1	19.8
3	92.7	23.2
4	92.6	21.8
5	93.7	16.0
6	93.9	14.5
7	88.9	44.1
8	91.9	15.5
9	88.1	34.8
10	91.8	20.3
11	93.4	16.5
12	97.9	6.5
13	92.2	12.0
14	98.0	6.7
15	92.8	20.8
16	90.9	34.3

^a Feed concentration: 0.5% NaCl aqueous solution. Measured under applied pressure of 7.88 MPa at 25°C.

EXPERIMENTAL

An interpolymer anionic composite membrane was prepared from poly(vinyl alcohol) and poly(styrene sulfonic acid) by the method used in a previous paper.¹⁰ The composite membrane was formed by casting from water and ethyl alcohol mixture (12/7, wt%) both polymers in a thin film on a polypropylene microporous supporter, evaporating the solvent at 30°C, and then heat-curing at 120°C for 2 h. Water flux and salt rejection of membranes were measured under applied pressure of 7.88 MPa with 0.5% NaCl aqueous solution at 25°C, and these data are shown in Table I.

TABLE II
Solute No. and Solute Name

No.	Solute	No.	Solute
	<i>Alcohols</i>	16	Resorcinol
1	Methyl alcohol	17	<i>p</i> -Chlorophenol
2	Ethyl alcohol	18	<i>o</i> -Nitrophenol
3	<i>n</i> -Propyl alcohol	19	<i>p</i> -Nitrophenol
4	<i>n</i> -Butyl alcohol	20	<i>o</i> -Aminophenol
5	<i>Iso</i> -butyl alcohol	21	<i>m</i> -Aminophenol
6	<i>Sec</i> -butyl alcohol	22	<i>p</i> -Aminophenol
7	<i>Tert</i> -butyl alcohol		<i>Amines</i>
8	<i>n</i> -Amyl alcohol	23	Methylamine
9	<i>Iso</i> -amyl alcohol	24	Aniline
10	Benzyl alcohol	25	<i>m</i> -Methylaniline
11	β -Phenethyl alcohol	26	<i>p</i> -Nitroaniline
	<i>Monocarboxylic acids</i>	27	<i>p</i> -Chloroaniline
12	Formic acid		<i>Ketones</i>
13	Acetic acid	28	Acetone
14	Propionic acid	29	Methylethyl ketone
	<i>Phenols</i>	30	Di- <i>iso</i> -propyl ketone
15	Phenol		

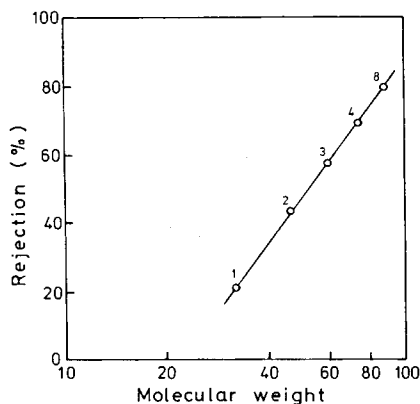


Fig. 1. The correlation between molecular weight and the rejection of *n*-alkyl alcohols in aqueous solution: membrane no. 1.

Water flux and solute rejection of membrane were measured by the recirculating-type reverse-osmosis cells described in an earlier paper.¹¹ The effective membrane area was 12.5 cm² in all cases.

Guaranteed reagent-grade organic chemicals shown in Table II were used without further purification.

The organic solute permeation was carried out with single-solute aqueous solution (200 mg/L) under applied pressure of 7.88 MPa at 25°C. An organic 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

Alcohols

The rejection of *n*-alkyl alcohols (from C₁ to C₅), their isomers, and aromatic alcohols (benzyl and phenethyl alcohol) were examined.

The correlation between the rejection and molecular weight of *n*-alkyl alcohols

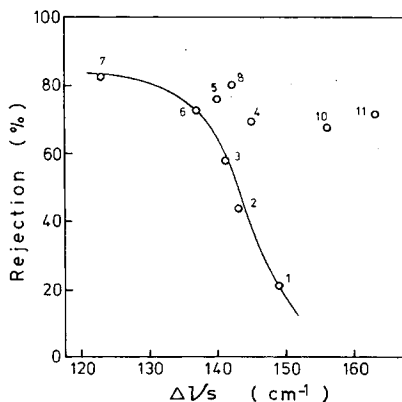


Fig. 2. The rejection of alcohols in aqueous solution as a function of acidity ($\Delta\nu_s$): membrane nos. 1, 2, and 3.

TABLE III
Rejection for Isomeric Butyl Alcohols^a

Isomer	Rejection ^b (%)	Rejection ^c (%)
<i>n</i> -C ₄ H ₉ OH	69.2	68.8
<i>Sec</i> -C ₄ H ₉ OH	72.5	71.6
<i>Iso</i> -C ₄ H ₉ OH	75.8	74.4
<i>Tert</i> -C ₄ H ₉ OH	82.5	80.9

^a Feed concentration: 200 mg/L. Measured under applied pressure of 7.88 MPa at 25°C.

^b Membrane no. 2.

^c Membrane no. 10.

is shown in Figure 1. The rejection of *n*-alkyl alcohols increases with molecular weight. The rejection is proportional to the logarithm of molecular weight of alcohols. On the other hand, there was no linear correlation between molecular weight and the rejection of alcohols by cellulose acetate membranes.¹

The correlation between the rejection and acidity function ($\Delta\nu_s$)¹ of alcohols

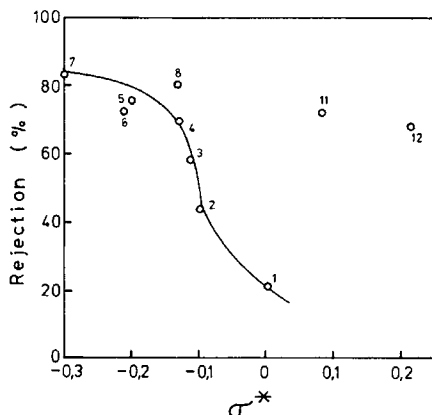


Fig. 3. The rejection of alcohols in aqueous solution vs. the Taft's number (σ^*): membrane nos. 1, 2, and 3.

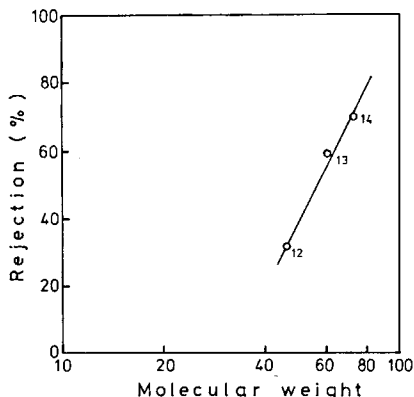


Fig. 4. The rejection of monocarboxylic acids in aqueous solution vs. molecular weight: membrane no. 4.

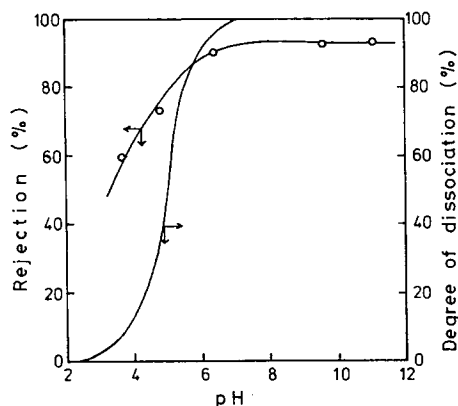


Fig. 5. The degree of dissociation and the rejection curves of acetic acid in aqueous solution: membrane no. 4.

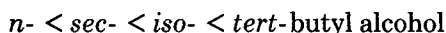
is shown in Figure 2. Matsuura and Sourirajan¹⁻⁴ have concluded that the rejection of an organic solute by cellulose acetate membrane strongly depends upon its hydrogen bonding ability.

It may be considered that the hydrogen bonding effect is less effective in an anionic composite membrane in comparison to cellulose acetate membranes, and the diffusivity of alcohols within the membrane is a more important factor for the solute rejection. Diffusion constants of alcohols in the membrane matrix decrease with increase in molecular weight of alcohols.

An anionic composite membrane has a higher rejection for *n*-alkyl alcohols with low molecular weight than that of cellulose acetate. The rejection of alcohols tend to decrease at higher value of $\Delta\nu_s$, a parameter of proton donor.

Aromatic alcohols have a large value of $\Delta\nu_s$. Also, an anionic charged membrane has a high affinity with aromatic alcohols, due to the presence of an aromatic ring in the membrane. From these facts, the rejection of aromatic alcohols would be relatively low.

The rejection of the isomeric butyl alcohols is summarized in Table III. The rejection of butyl alcohol isomers by an anionic composite membrane are in this order:



In other words, the rejection of butyl alcohol isomers increases with chain-branching degree, due to the factor of a steric effect.

The correlation between the rejection and the Taft's number (σ^*)¹ of alcohols are shown in Figure 3. The rejection of alcohols decreases with increase in the Taft's number, which parallels that of $\Delta\nu_s$.

Monocarboxylic Acids

Monocarboxylic acids such as formic acid, acetic acid, and propionic acid were tested. These acids are weak acids with pKa values of 3.75–4.90.¹² These acids dissociate into ions in aqueous solution at pH above 5. Hence, the electrostatic effect between fixed ionic groups in membrane and solute ion is a main factor for the rejection of monocarboxylic acids.

The rejection of acetic acid in aqueous solution was measured at various degrees of dissociation. The degree of dissociation of acetic acid was calculated from pKa and pH value of the feed solution with the method reported by Fang and Chiang.⁸

The correlation between the rejection and molecular weight of undissociated monocarboxylic acids is shown in Figure 4.

The rejection is proportional to the logarithm of molecular weight of monocarboxylic acids, which is the same as in case of alcohols.

The correlation between the rejection of acetic acid and pH values of the feed solution is shown in Figure 5. The rejection of acetic acid increases with pH value of the feed solution, and is almost constant at pH above 7. In other words, the rejection of acetic acid is parallel to the degree of dissociation curve.

Figure 6 indicates that the rejection of acetic acid is proportional to the degree of dissociation.

It may be suggested that the electrostatic effect between fixed ionic groups in membrane and solute ion is a main factor for the solute rejection.

Phenols

The reverse-osmosis separation for phenol and monosubstituted phenols are summarized in Table IV. Most of the phenolic molecules are in the undissociated state at the feed solution (pH 6.3). However, an anionic charged membrane showed higher rejection (80%) for phenol in comparison to the other type of reverse osmosis membranes.

Phenol would be rejected by the electrostatic effect between fixed anionic groups and hydroxyl groups of phenols. While the rejection of monosubstituted phenols decreases with increase in Hammett's number (σ)¹ as shown in Table IV, except for aminophenol. The rejection of monosubstituted phenols depend deeply upon electron density in the neighborhood of the hydroxyl groups.

For phenolic derivatives with higher electron-withdrawing substituents, the electron density of the hydroxyl groups is lower.

Thus, the electrostatic repulsion between fixed charged groups ($-\text{SO}_3^-$) and solute gets weaker, and the solute rejection would be decreased.

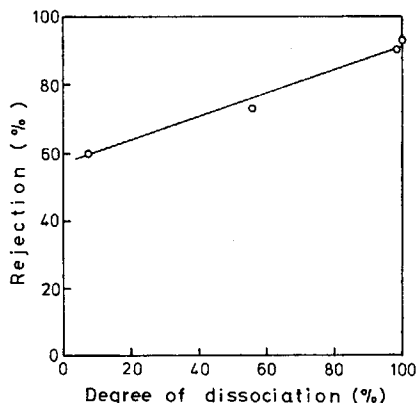


Fig. 6. The correlation between the rejection and the degree of dissociation of acetic acid in aqueous solution: membrane no. 4.

TABLE IV
Rejection for Phenol and Monosubstituted Phenols^a

Solute	pH	Rejection ^b (%)	Rejection ^c (%)	Hammett's no.
<i>m</i> -OH—C ₆ H ₄ OH	5.98	73.9	84.4	-0.002
<i>p</i> -Cl—C ₆ H ₄ OH	5.45	68.9	78.6	0.227
<i>o</i> -NO ₂ —C ₆ H ₄ OH	5.67	74.6	78.5	—
<i>p</i> -NO ₂ —C ₆ H ₄ OH	5.41	67.2	74.0	0.778
<i>o</i> -NH ₂ —C ₆ H ₄ OH	6.55	34.4	41.2	—
<i>m</i> -NH ₂ —C ₆ H ₄ OH	6.50	37.1	44.2	—
<i>p</i> -NH ₂ —C ₆ H ₄ OH	6.92	54.1	55.0	—
C ₆ H ₅ OH	6.30	66.9 ^d	84.5 ^e	0

^a Feed concentration: 200 mg/L. Measured under applied pressure of 7.88 MPa at 25°C.

^b Membrane no. 13.

^c Membrane no. 14.

^d Membrane no. 11.

^e Membrane no. 12.

The variation in the rejection of phenol and *p*-aminophenol at various pH values of the feed solution are given in Figures 7 and 8, respectively.

The rejection of phenol increases with pH value of the feed solution. The rejection of *p*-aminophenol is at minimum at pH 7, and the rejection of non-charged *p*-aminophenol is poor. The rejection of aminophenol with amphoteric character depends upon the effect of both acidity and basicity of the polar groups and is complicated. On both sides of the isoelectric point, the rejection of *p*-aminophenol increases. It may be considered that the rejection of phenol and *p*-aminophenol increases due to the electrostatic effect between fixed charged groups and solute ion.

Amines

Methylamine and aniline derivatives were selected. The rejection of methylamine in aqueous solution was examined at various degree of dissociation. The pH value of the feed solution was adjusted by addition of HCl. The degree

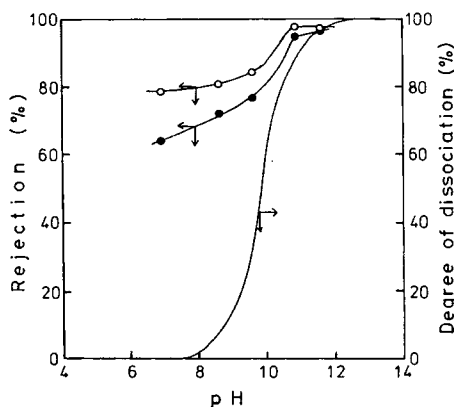


Fig. 7. The degree of dissociation and the rejection curves of phenol in aqueous solution: membrane nos. 13 (●) and 14 (○).

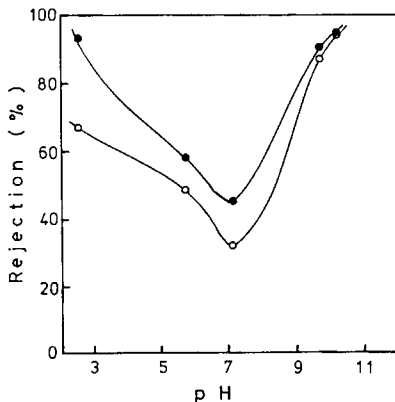


Fig. 8. The correlation between the rejection of *p*-aminophenol and pH value of the feed solution: membrane nos. 15 (●) and 16 (○).

of dissociation of methylamine was calculated from pK_a (10.624¹²) and pH of the feed solution.

The plot of the rejection versus pH of the feed solution is shown in Figure 9, and the correlation between the rejection of methylamine and its degree of dissociation is given in Figure 10.

The rejection of methylamine increases proportionally to the degree of dissociation. Most of the methylamine molecules dissociate into $CH_3NH_3^+$ ion in aqueous solution at a pH value lower than 8, and the rejection level is at more than 90%. On the other hand, the rejection of partially ionized methylamine was 37%.

It may be considered that the rejection of methylamine increases by the electrostatic effect between fixed charged groups and Cl^- , co-ion of $CH_3NH_3^+$.

The rejection of aniline derivatives were given in Table V. In general, the rejection level of aniline derivatives is very low at the range of -5.29-45.5%.

The correlation between the rejection and pK_a of aniline derivatives is shown in Figure 11. The rejection of aniline derivatives decreases linearly with increase in pK_a .

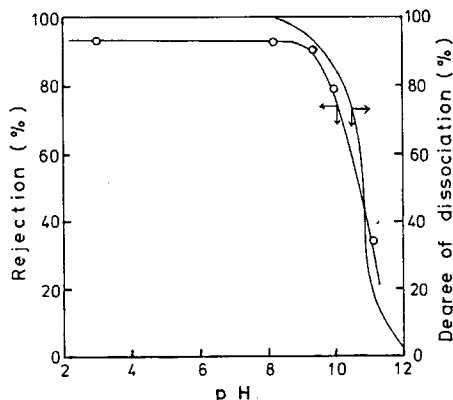


Fig. 9. The degree of dissociation and the rejection curves of methyl amine in aqueous solution: membrane no. 5.

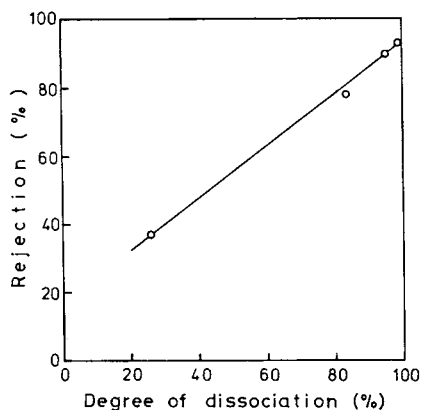


Fig. 10. The rejection of methyl amine in aqueous solution vs. the degree of dissociation: membrane no. 5.

It may be considered that an anionic membrane with acidic groups ($-\text{SO}_3\text{H}$) has a higher affinity for aniline derivatives with basic- NH_2 groups and shows a negative or little rejection.

The rejection of aniline derivatives is getting lower with higher basicity of NH_2 groups (increase in pK_a), because the chemical affinity between an anionic membrane and solute would be increased. Thus, the rejection by an anionic membrane decreases in the order of decreasing acidity (or increasing basicity) of solutes.

Ketones

Acetone, methylethyl ketone, and di-*iso*-propyl ketone were examined.

The correlation between the rejection and molecular weight of ketones is shown in Figure 12. The rejection increases with molecular weight.

The correlation between the rejection and the Taft's number ($\Sigma\sigma^*$)¹ of ketones is shown in Figure 13.

The rejection increases with decrease in $\Sigma\sigma^*$, which is parallel to that of alcohols.

Ketones are undissociable polar solutes. The Taft's number is a parameter of the electron-withdrawing power by substituent groups in a molecule.

TABLE V
Correlation between pK_a and Rejection of Aniline Derivatives in Aqueous Solution^a

Solute	pH	pK_a	Degree of dissociation (%)	Rejection ^b (%)	Rejection ^c (%)
$\text{C}_6\text{H}_5-\text{NH}_2$	6.62	4.596	0.94	-0.01	-0.07
<i>m</i> - $\text{CH}_3-\text{C}_6\text{H}_4-\text{NH}_2$	6.78	4.683	0.79	4.28	-5.92
<i>p</i> - $\text{NO}_2-\text{C}_6\text{H}_4-\text{NH}_2$	5.62	0.991	0.00	45.5	32.9
<i>p</i> - $\text{Cl}-\text{C}_6\text{H}_4-\text{NH}_2$	5.98	3.99	1.01	15.0	-5.73

^a Feed concentration: 200 mg/L. Measured under applied pressure of 7.88 MPa at 25°C.

^b Membrane no. 6.

^c Membrane no. 7.

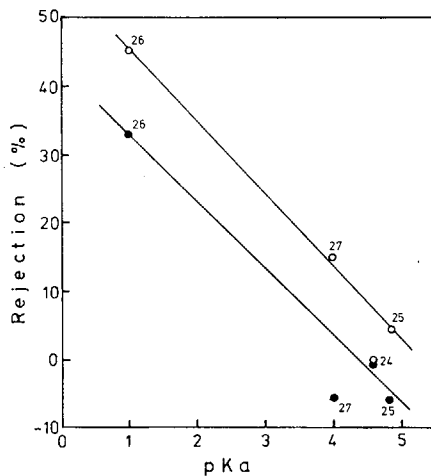


Fig. 11. The correlation between pKa and the rejection of aniline derivatives in aqueous solution: membrane nos. 6 (●) and 7 (○).

In the case of the presence of the electron-releasing substituent groups, electron density surrounding carbonyl groups in ketones grows larger.

It may be considered that the rejection of ketones with the electron-releasing groups increases due to the strong electrostatic repulsion effect between fixed charged groups in the membrane and solutes.

CONCLUSIONS

The correlation between the solute rejection and polar parameters for these organic solutes have been investigated.

The solute rejection for undissociable organic solutes such as alcohols and ketones are closely related to the Taft's number. The solute rejection decreases with increase in the Taft's number. For alkylalcohols, undissociated monocarboxylic acids, and ketones, the solute rejection increases with molecular weight and/or chain-branching degree. For dissociable organic solutes such as phenols,

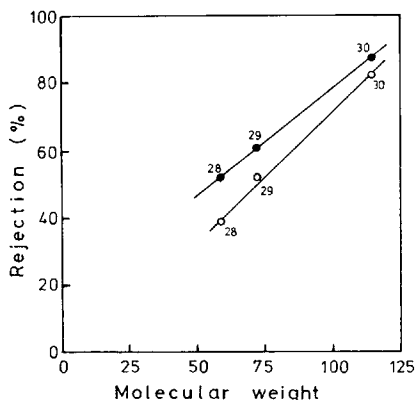


Fig. 12. The correlation between molecular weight and the rejection of ketones in aqueous solution: membrane nos. 8 (●) and 9 (○).

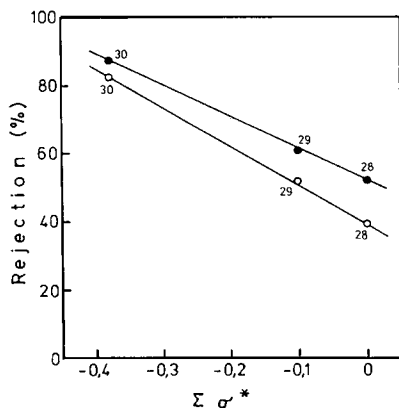


Fig. 13. The rejection of ketones in aqueous solution vs. the Taft's number ($\Sigma\sigma^*$): membrane nos. 8 (●) and 9 (○).

monocarboxylic acids, and amines, the solute rejections depend upon the dissociation constant and the degree of dissociation of solutes. The solute rejection increases proportionally to the degree of dissociation of solute, and decreases with increase in the dissociation constant. Also, an anionic charged composite membrane showed higher rejection (80%) for undissociated phenol in comparison to the other type of reverse-osmosis membranes.

These results suggest that an organic solute rejection of an anionic charged composite reverse-osmosis membrane are governed by the following factors: electrostatic effects between fixed charged groups in membrane and ionic solute, the steric effects of solutes, and the diffusivity and chemical affinity between solute and membrane.

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