Removal of Alcohols, Amines, and Aliphatic Acids in Aqueous Solution by NS-100 Membrane

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Synopsis

Removal of alcohols, amines, and aliphatic acids in single-solute aqueous solution in the concentration range from 0.001 to 0.01M have been studied using the NS-100 membrane. All the tests were conducted at 600 psig, 25°C, and a flow rate of 0.30 gpm. The mechanism of solute separation by the NS-100 membrane differs from that of the cellulose acetate membrane. There was no significant correlation between the removal and the hydrogen bonding ability of the organic solute. Instead, for a given organic solute, its removal increases with the increase in the degree of crosslinkage of the skin layer of NS-100 membrane, and is proportional to its degree of ionization (or degree of dissociation). For organic compounds having a same functional group, the removal of a compound increases with the increase in molecular weight and/or molecular branching. All of these are attributable to the relative nonpolarity and the anion exchanger characteristics of the membrane as well as to the steric resistance for the solute to permeate through the membrane.

INTRODUCTION

Since Breton and Reid[1,2] and, independently, Loeb and Sourirajan[3,4] discovered the cellulose acetate membrane, reverse osmosis has become one of the major separation processes in the last decade. This process physically removes solutes from the water by circulating the solution at high pressure over the surface of a semipermeable membrane. Although it was first developed for the desalination of brackish and sea waters, reverse osmosis has gradually found its application in a great number of wastewater treatments. This is especially true with the development of new membrane materials, such as aromatic polyamides and crosslinked polyethylenimine, commonly known as NS-100.[5,6]

The NS-100 membrane essentially consists of a microporous polysulfone support coated with polyethylenimine which is crosslinked with m-tolylene 2,4-diisocyanate. When tested with 5000 parts per million (ppm) of sodium chloride solution at 600 pounds per square inch (psig) and 25°C, the NS-100 membrane yielded a permeate flux of 10–12 gallons per square foot per day (gfd) at 99% removal of salt. Also, it removes an average of 70%, as compared to 20% by cellulose acetate membrane, of the low molecular weight polar organic compounds such as alcohols, phenols, acids, ketones, etc.[5,6] Furthermore, this membrane is reported to be stable in both acidic and basic solutions. Its stable operational range is from pH 2 to pH 12.[6] Recent studies have also shown that using NS-100 membrane reverse osmosis is an effective means for the removal of

pesticides and other toxic compounds in water.[7,8] All of this evidence indicates that the NS-100 membrane appears to be the most promising reverse osmosis membrane in the near future.

Removal of organic solutes in aqueous solutions using reverse osmosis membranes is of great interest from the viewpoint of both the mechanism of the separation process as well as the application for various water and wastewater treatments. Duvel et al.[9,10] and Matsuura and Sourirajan[11-14] have studied in detail the performance of cellulose acetate membranes. They found that the removal of a polar organic solute by cellulose acetate membranes is dependent upon the size and steric configuration of the solute as well as its ability to form hydrogen bonds with the membrane.

The object of this study is to establish the physicochemical criteria for the removal of polar organic compounds by NS-100 membranes with particular emphasis on the removal of alcohols, amines, and aliphatic acids, which are poorly removed by cellulose acetate membranes.

EXPERIMENTAL

Fabrication of NS-100 Membrane

NS-100 is a membrane made from polyethylenimine coated on a microporous polysulfone support and crosslinked with m-tolylene 2,4-diisocyanate. There are four steps involved in its fabrication: (1) casting of the polysulfone support; (2) coating of polyethylenimine; (3) reaction with m-tolylene 2,4-diisocyanate; and (4) heat curing of the membrane.

A polysulfone supporting film of 7 mils in thickness was first cast from a 15% solution of polysulfone in dimethylformamide. The film was drawn out on a glass plate and gelled by immersion in deionized water for 60 min. The film was coated by a 0.67% polyethylenimine aqueous solution. After 60 sec of soaking, the film was held in a vertical position to drain the excess solution from the surface. Then, a 0.5% solution of m-tolylene 2,4-diisocyanate in hexane was allowed to react with the coated surface. During the reaction, an amide linkage was formed between the polyethylenimine and the m-tolylene 2,4-diisocyanate. After 60 sec, the film was again held in a vertical position to drain the excess hexane solution from the surface. The coated film was afterward cured in an oven at 110–115°C for 10 min. Polyethylenimine crosslinked with the neighboring chains during the curing process. The ideal structure of the ultrathin skin layer of crosslinked polyethylenimine on NS-100 membrane is shown in Figure 1.[15]

Reverse Osmosis Experiments

Three stainless steel 316 test cells based upon Manjikian's design[16] were used for the reverse osmosis experiments. The effective diameter of each circular membrane was 2 in. All tests were conducted at 600 psig, 25°C, and a flow rate of 0.30 gallons per minute (gpm). Prior to testing the organic solutes, each membrane was subjected to a test of 5000 ppm of sodium chloride solution for 2 hr. The performance of each membrane used in this study is shown in Table I. The per cent solute removal is defined as follows:

$$\text{solute removal} = \frac{\text{solute in feed (ppm)} - \text{solute in permeate (ppm)}}{\text{solute in feed (ppm)}} \times 100\%.$$

TABLE I
Performance of NS-100 Membranes When Tested With 5000 ppm Sodium Chlorides
Solution at 600 psig and 25°C

Membrane	Permeate flux gfd	Solute removal, %
0316A	7.15	98.20
0316B	16.00	97.62
0906A	11.0	98.98
0906B	8.11	99.08
0710A	13.50	98.40
0710B	22.68	97.80
0514C	12.19	99.17
0514D	24.89	97.73
0425A	9.85	98.39
0425B	9.57	96.27
0517A	10.13	98.41
0517B	21.17	97.56
0517C	11.52	98.32
1008A	30.22	96.28
1008B	33.42	97.36
1008C	27.85	98.12
0508A	26.78	98.46
0508B	9.45	99.29

CROSSLINKED POLYTHYLENIMINE

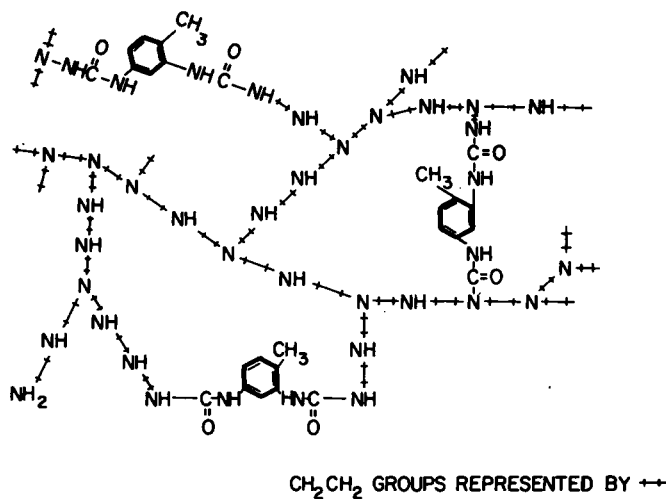CH$_2$CH$_2$ GROUPS REPRESENTED BY ⤙

Fig. 1. Ideal structure of the skin layer of the NS-100 membrane.

All membranes were tested with single-solute solutions. The concentration of each organic solute in test solution ranged from 0.01 to 0.001M. Each test solution was circulated on the membrane surface under testing conditions for 1 hr prior to collecting the permeate samples.

Analysis

A Yellow Springs Conductivity Bridge, Model 1485, was used to measure the concentration of sodium chloride. With dilute concentration (<100 ppm), the

conductivity is proportional to the concentration of the salt solution.   Therefore, by comparing the relative conductivity of the permeate and the diluted feed solutions, the salt removal of each membrane could be determined.

A Beckman Total Carbon Analyzer, Model 915, was used to measure the concentration of organic solute in both permeate and feed solutions.   In this apparatus, the solution sample was injected and swept by an air stream into a high-temperature (950°C) catalytic combustion tube where the total carbon in the sample was oxidized to carbon dioxide which was then analyzed by a Beckman nondispersive infrared analyzer, Model IR-215B.   A sample size of 20 microliters and an air flow rate of 150 cc/min were used for the analysis.   The carbon content of a dilute solution (total carbon <100 ppm) was proportional to the peak height shown in the recorder.   Three to five injections were made for each sample in order to confirm the reproducibility of the analysis.   The accuracy of the analysis was ±1 ppm in terms of carbon content.

RESULTS AND DISCUSSION

Removal of Alcohols

Two NS-100 membranes, 0316A and 0316B, were used to test the aqueous solutions containing single alcohol in a concentration of 100 ppm.   Normal alkyl alcohols (from C_1 to C_6) and their isomers were tested.   The dissociation constants of alcohols are extremely small; consequently, the alcohols exist as molecules in test solution.   Figure 2 illustrates the correlations between the removal and the number of carbon atoms of n-alkyl alcohols.   It clearly indicates that the removal of n-alkyl alcohols increases with the number of carbon atoms or, in other words, with the molecular weight of the alcohol.

Chian and Fang[6] and Matsuura and Sourirajan,[11] however, found that there was no necessary correlation between the molecular weight and the removal of n-alkyl alcohols by cellulose acetate membrane.   Chian and Fang[6] found that the
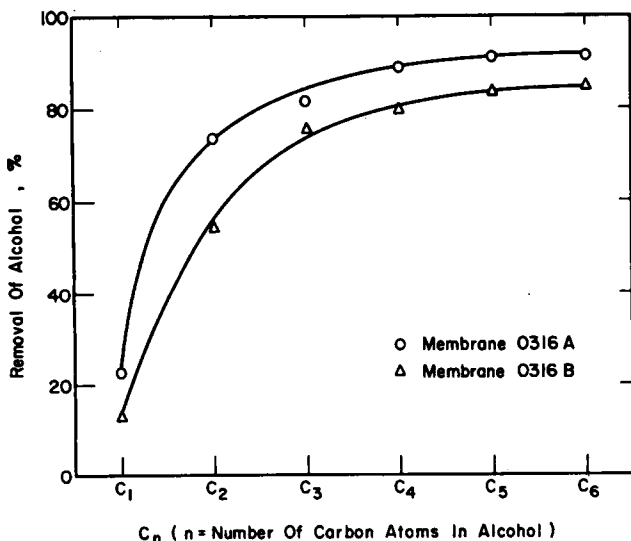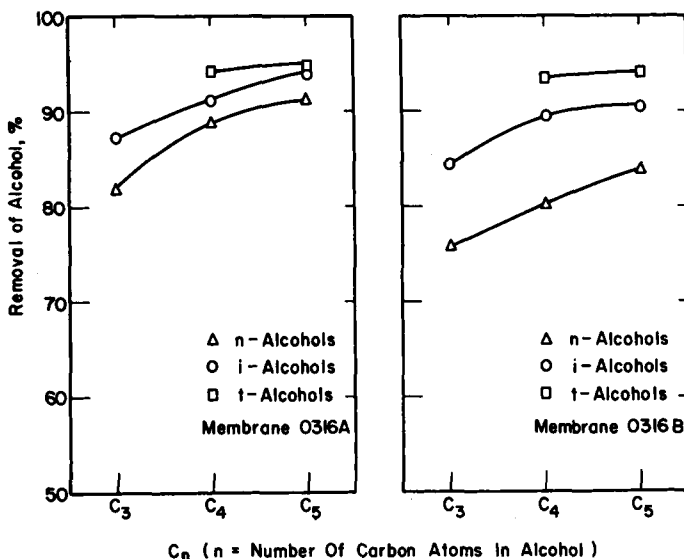

Fig. 2. Removal of n-alkyl alcohols.

Fig. 3. Steric effect on the removal of isomers of propanol, butanol, and pentanol.

removal of n-hexanol by cellulose acetate membrane was -8.2% as compared to 9.2% for n-pentanol, 19.8% for n-butanol, and 30.5% for n-propanol. According to their study on the removal of numerous organic compounds, Matsuura and Sourirajan[11-14] have concluded that cellulose acetate has the characteristics of a proton acceptor. As a consequence, the removal of an organic solute is strongly dependent on its hydrogen bonding ability. For an alcohol, the hydrogen bonding ability can be expressed as the $\Delta\nu_s$ (acidity), which represents the shift in the OH band maximum in the infrared spectra. An alcohol with a higher $\Delta\nu_s$ (acidity) forms a stronger hydrogen bond with the membrane; thus, as a result, it is poorly removed by the cellulose acetate membrane.

The data of NS-100 membranes indicate no such correlation between the removal and the $\Delta\nu_s$ (acidity) of alcohols. This is partially attributed to the apolar characteristics of the NS-100 membranes. These characteristics have also been observed in the study of pesticidal removal. Chian, Bruce, and Fang[7] have reported that nonpolar pesticides, such as most chlorinated pesticides, were strongly adsorbed on the skin layer of NS-100 membranes. The adsorption resulted from the London–van der Waals interaction between the membrane and the solute molecule.

Figure 3 illustrates the removal of isomeric alcohols by membranes 0316A and 0316B. With no exception, a *tert*-alcohol was removed better than its iso isomer, which was removed better than its normal isomer. In other words, the removal increases with increased isomer branching. This agrees with the results observed in the alcohol removal by cellulose acetate membranes.[9,11]

An alcohol molecule enters the NS-100 membrane by passing into a gap between polymer segments which is large enough to accommodate the molecule. Once in the membrane, the molecule then diffuses through the membrane under the influence of concentration gradient. The diffusivity of the molecule in the membrane decreases with the increase in molecular size (molecular weight) and cross-sectional area (molecular branching). Consequently, alcohols with high

molecular weight and/or large branching are removed effectively by NS-100 membranes.

Removal of Amines

Amines are weak bases; their basicity can be expressed by the pK_a values, which are defined as follows:

$$K_a = \frac{[NR_3][H^+]}{[R_3NH^+]} \tag{1}$$

$$pK_a = -\log K_a \tag{2}$$

where R can be a hydrogen atom, alkyl, or aryl group attached to the N atom. The pK_a of aliphatic amines ranges from 10 to 11.[17]   As a result, aliphatic amines exist as ions in ordinary solutions (pH < 10).   On the other hand, the skin layer of NS-100 membranes consists of primary, secondary, and tertiary amines as shown in Figure 1.   Therefore, it also possesses the characteristics of a weak anion exchanger.   An anion exchanger with amines and imines as ionogenic groups has an apparent pK_a value of 7–9.[18]   In other words, the skin layer of NS-100 membranes carries positive charges in solutions at pH <7.   Since both the skin layer and the solute amines carry positive charges at pH <7, the electrostatic repulsion force acts between them and becomes a predominant factor in solute removal.

A series of experiments were conducted to study the removal of methylamine at various degrees of ionization with membranes 0906A and 0906B.   The concentration of methylamine was 0.01M for each test.   The pH value of the test solutions was adjusted from 2.5 to 12.0 by adding hydrochloric acid.   The degree of ionization of methylamine was calculated from the pK_a (10.66) and pH of the solution:

$$\alpha = \frac{[CH_3NH_3^+]}{[CH_3NH_2] + [CH_3NH_3^+]} \times 100\%. \tag{3}$$

From the definition of K_a as shown in eq. (1),

$$\alpha = \frac{[H^+]}{K_a + [H^+]} \times 100\% \tag{4}$$

$$= \frac{10^{-pH}}{10^{-pK_a} + 10^{-pH}} \times 100\%. \tag{5}$$

Figure 4 illustrates the correlation between the removal of methylamine and its degree of ionization.   In acidic solution, methylamine existed as ion and hence was removed effectively, i.e., 98% by both membranes.   On the other hand, in basic solution at pH 12, 96% of methylamine existed as molecules; hence it was removed less effectively, i.e., 50%, because of the drastic decrease in electrostatic repulsion between the solute and the skin layer of the membrane.   When the solute was partially ionized, the removal of the solute was proportional to its degree of ionization as shown in Figure 4.

Figure 5 illustrates the removal of primary and secondary amines by membranes 0710A and 0710B.   Since the pK_a values of the test amines were within a narrow range, i.e., 10.50–11.00, there was no significant difference in the degree of
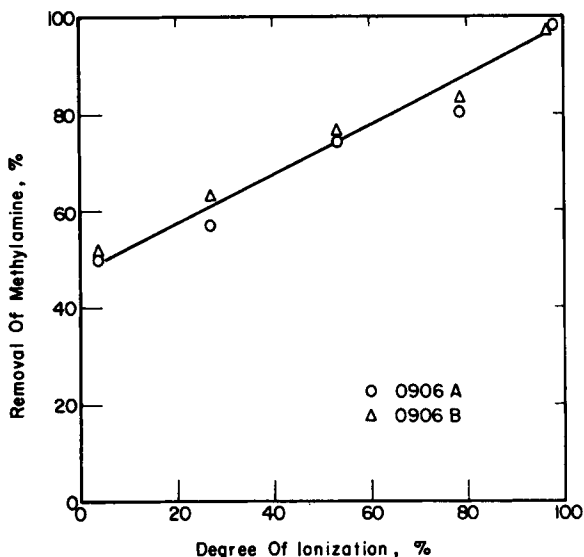
Fig. 4. Removal of methylamine at various degrees of ionization.

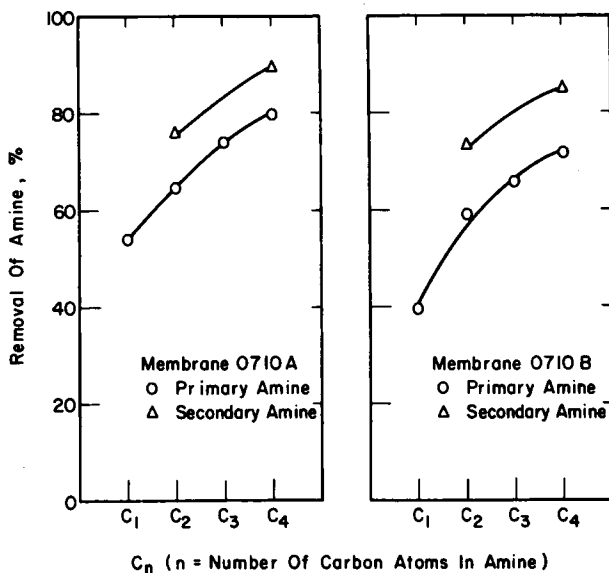C_n (n = Number Of Carbon Atoms In Amine)

Fig. 5. Comparison of the removal of primary and secondary amines.

ionization among the test amines. Figure 5 illustrates that the removal of an amine depends upon its molecular weight and classification. Similar to the alcohols, the removal increases with increase in molecular size (molecular weight). On the other hand, secondary amines were removed better than the primary amines. This is attributed to the spatial configuration of the amines; primary amines consist of a straight chain, while secondary amines have a branch on the chain. A test of a tertiary amine, such as tripropylamine, indicated 98.3% and 99.2% removal by membranes 0710A and 0710B, respectively. Such a high degree of removal is obviously due to its high molecular weight and its degree of branching.

TABLE II
Removal of Isomers of Butylamine by NS-100 Membranes

Butylamine	0710A Removal, %	0710B Removal, %
Normal	80.1	71.8
sec-	85.3	78.8
iso-	91.6	87.0
tert-	93.9	88.3

Table II shows the removal of four isomers of primary butylamine. The spatial configuration was the sole factor for the differences among the removal of these amines. Table II indicates that the removal of butylamine follows the order: tert- > iso- > sec- > normal. Again, it shows that the amine with more branching was better removed. This agrees with the conclusions drawn from the study of alcohol removal.

Removal of Aliphatic Acids

Aliphatic acids are weak acids, with pK_a ranging from 3.75 to 4.90. They carry negative charges in aqueous solution at pH > 5. Hence, the electrostatic interaction between the anion and the skin layer of the NS-100 membrane is the predominant factor in the removal of aliphatic acids. Aqueous solutions containing $0.01M$ acetic and formic acids, respectively, were tested at various degrees of dissociation by NS-100 membranes. The degree of dissociation of an acid was determined by its pK_a and the pH of the test solutions. The pK_a is defined in eq. (2) where the dissociation constant, K_a, of an acid, say, acetic acid, is defined as

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}. \tag{6}$$

The degree of dissociation, α', is defined as

$$\alpha' = \frac{[CH_3COO^-]}{[CH_3COOH] + [CH_3COO^-]} \times 100\% \tag{7}$$

Hence, by combining eqs. (6) and (7),

$$\alpha' = \frac{K_a}{K_a + [H^+]} \times 100\% \tag{8}$$

$$= \frac{10^{-pK_a}}{10^{-pK_a} + 10^{-pH}} \times 100\%. \tag{9}$$

Figures 6 and 7 illustrate that the removal of both acetic and formic acids is proportional to their degree of dissociation. This is consistent with the observation of methylamine as shown in Figure 4, although the acids and methylamine carry opposite charges.

Single-solute aqueous solutions containing alkyl acids at a concentration of 200 ppm were tested by membranes 0517A, 0517B, and 0517C. In order to ensure that the acids existed as molecules, the pH of each test solution was adjusted to pH 2 by adding hydrochloric acid. Figure 8 illustrates that the removal of undissociated n-alkyl acids increases with an increase in molecular weight. On the
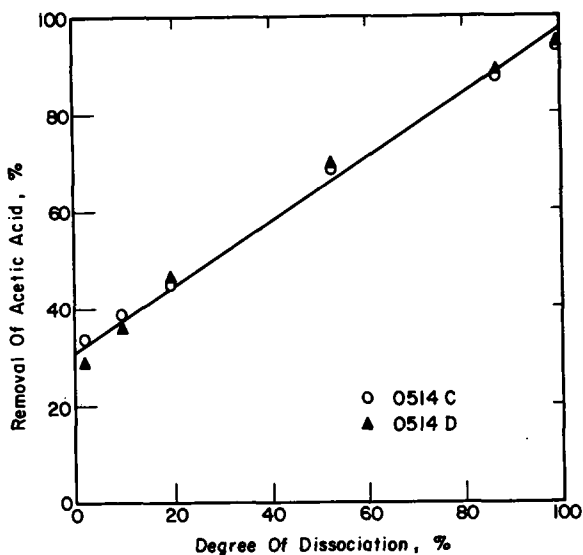
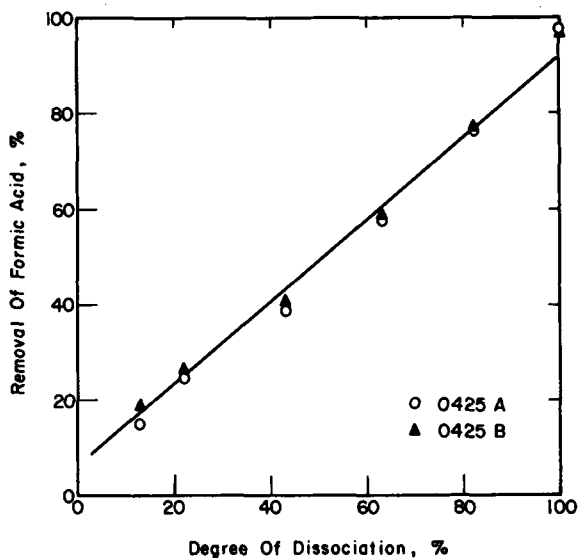Fig. 6. Removal of acetic acid at various degrees of dissociation.

Fig. 7. Removal of formic acid at various degrees of dissociation.

other hand, Figure 9 illustrates the comparison between the removal of isomers of butyric and valeric acids. The iso isomers were removed consistently better than normal isomers. Both of these observations are congruent with those observations from the study of alcohol and amine removal.

Crosslinkage of Skin Layer

Figures 2, 5, and 8 show a general trend, i.e., the membrane exhibiting better salt removal also removed a higher percentage of organic solute. For instance, membrane 0316A removed n-alkyl alcohols 10% better than membrane 0316B, as
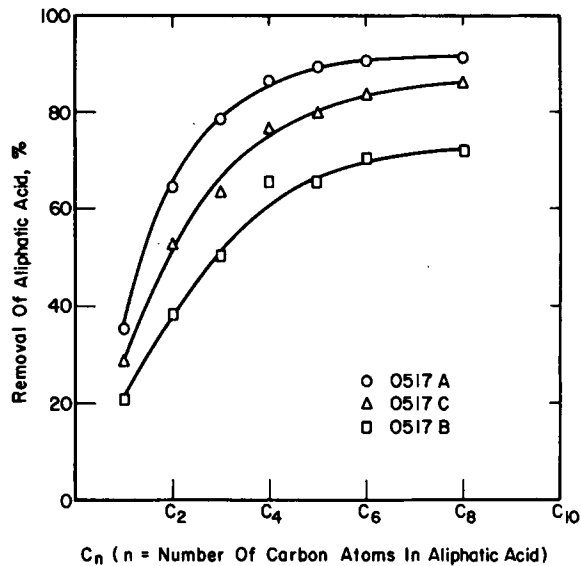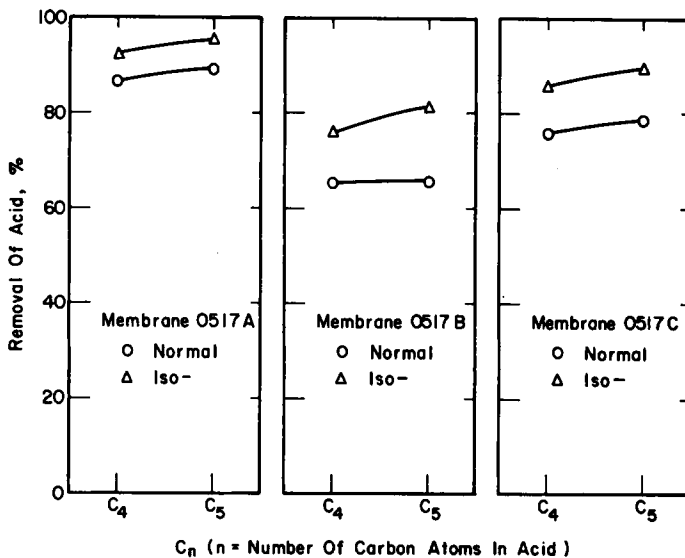
Fig. 8. Removal of n-alkyl acids.

Fig. 9. Steric effect on the removal of isomers of butyric and valeric acids.

shown in Figure 2; the former exhibited 98.20% salt removal as compared to 97.62% by the latter. The existence of this trend is further illustrated in the following series of experiments.

By adjusting the polyethylenimine concentration in aqueous solution, five membranes, 1008A, 1008B, 1008C, 0508A, and 0508B, were fabricated at various degrees of crosslinkage. Their removal of salt varied from 96.28% with 1008A to 99.29% with 0508B. Thirteen model organic compounds[5] were tested individually by these membranes. They were methanol, ethanol, isopropanol, acetic acid, formaldehyde, acetone, ethyl ether, glycerol, hydroquinone, phenol,
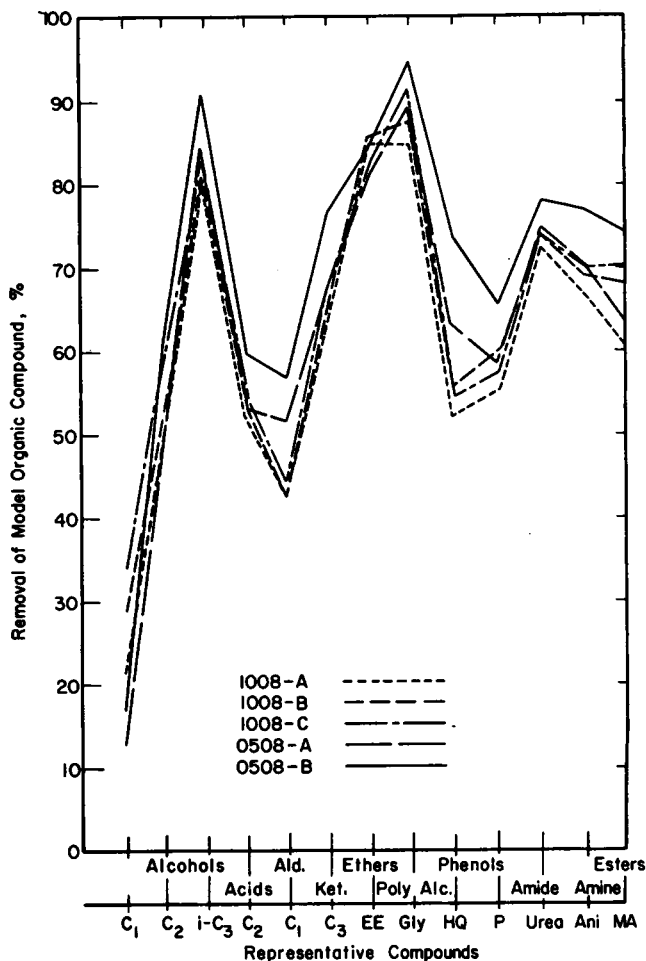
Fig. 10. Removal of organic model compounds.

urea, aniline, and methyl acetate. The removal of each model compound is illustrated in Figure 10.

With few exceptions, a general trend also suggests that for a given membrane material, a membrane with a higher salt removal capacity also removes a greater percentage of organic compounds. This trend is independent of the characteristics of solutes, e.g., salt or molecule, organic or inorganic, basic or acidic, and polar or nonpolar solute. For NS-100 membranes, the salt removal is a measure of the degree of crosslinkage of the skin layer. As a consequence, it is reasonable to characterize the membrane performance for a given membrane material with a simple test using sodium chloride solution. This has indeed been conducted in the study on the optimization of membrane performance.[19]

CONCLUSIONS

The NS-100 membrane has demonstrated itself as an effective membrane for the removal of organic compounds from water. For a given organic compound, its removal increases with the increase in the degree of crosslinkage of the skin

layer. On the other hand, the removal of a given organic compound also increases with the increase of its degree of ionization (or degree of dissociation). This is attributed to the anion exchanger characteristics of the NS-100 membrane. For organic compounds having the same functional group, the removal of a compound increases with the increase in molecular weight and/or molecular branching. This is due to the steric resistance for the molecule to diffuse through the polymeric matrix of the membrane. There is no significant correlation between the removal of a solute and its hydrogen bonding ability because of the relative nonpolarity of the skin layer of NS-100 membranes. Consequently, the mechanism of solute removal differs from that of cellulose acetate as reported by Matsuura and Sourirajan.[11]

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