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Studies on a Novel Approach for the Separation of L-Phenylalanine Amino Acid from Fermentation Broth Using a Newly Developed Charged Ultrafiltration Membrane. I. Single Solute System

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ABSTRACT

A newly developed thin-film composite (TFC) ultrafiltration membrane made of sulfonated poly(phenylene oxide) (SPPO) was used to establish the feasibility of separating L-phenylalanine from the fermentation broth containing a number of dissolved inorganic and organic solutes as an alternative approach to the currently used complex and uneconomical conventional ion-exchange schemes. It was found that the rejection of inorganic salts in a single component system was highly dependent on the feed solution concentration and varied inversely with it. The pH of the feed solution was found to have a strong effect on the rejection of L-phenylalanine, changing it from −10 to 90%. This rejection behavior was identical for the two TFC-SPPO membrane samples which had molecular weight cutoff ratings of 10,000 and 20,000, respectively, although the permeate flux of the latter sample was almost twice that of the former sample. It was found that glucose molecules were not rejected by the membrane.

INTRODUCTION

Charged ultrafiltration (UF) membranes are unique and more versatile from the industrial applications point of view in comparison to conventional neutral UF membranes. Charged UF membranes having a fixed

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charge on the polymeric matrix have three variables: ion-exchange capacity (IEC), charge sign, and pore size as compared to only pore size in conventional UF membranes. Since conventional UF membranes separate solutes solely on the basis of the difference in their molecular sizes, they are incapable of separating a mixture of solutes having more or less similar molecular sizes. However, a charged UF membrane can be used as a conventional UF membrane besides being capable of rejecting macromolecules bearing charges of the same sign as that of the membrane. Thus it may be possible to separate charged solutes from neutral solutes even though both types of solutes are of similar molecular size. This characteristic of charged UF membranes may be exploited in the practical application of the separation of various solutes having different isoelectric points. Based on this nature of charged UF membranes, a protein mixture of myoglobin and cytochrome has been separated by charged UF membranes made of sulfonated polysulfone at the isoelectric point of one of the proteins (1).

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Charged UF membranes made of sulfonated polysulfone have been used to reject various inorganic salts even though the average pore size of the membrane was much larger than that of the salts (2). A commercially available (Millipore PSAL) noncellulosic charged UF membrane (fixed negatively charged groups) has been employed in an experimental investigation of the rejection of several ionic inorganic solutes (3, 4). The sulfonated polysulfone membrane has also been used to separate amino acids having molecular weights ranging from 75 to 200 (5).

Amino acids in aqueous solutions exist as amphoteric dipolar ions (zwitterions) to different extents. The net charge on the molecule of an amino acid is dependent on the solution pH. At the isoelectric point the net charge on the molecule in solution is zero. As solution pH increases beyond the isoelectric point, the net charge on the molecule starts changing to negative values; at a sufficiently high pH value, the amino acid molecule acquires a total negative charge. At pH values below the isoelectric point the net charge gradually changes to positive values, and at a certain value it changes completely to a positive charge.

$$\mathrm{HAH^+} \leftarrow \mathrm{HA} \rightarrow \mathrm{A^-} + \mathrm{H^+}$$

Isoelectric Point

← Decreasing pH Increasing →

During the past few years the amino acid L-phenylalanine has enjoyed great commercial success as one of the raw materials of the nonnutritive sweetener aspartame (brand name Nutrasweet). Presently it is being produced by the microbial fermentation process. It is separated from the fermentation broth by complicated and costly ion-exchange schemes due to low fermentation titer and very low solubility in organic media. Separation and purification costs are 80–90% of the total production costs (6). A schematic flow diagram of the recovery process of L-phenylalanine on the basis of the patent literature is given in Fig. 1 (7, 8).

The main purpose of this investigation is to determine the feasibility of separating L-phenylalanine by a novel approach from a fermentation broth containing various inorganic and organic solutes. This approach consists of using our newly developed thin-film composite (TFC) charged UF membranes made of sulfonated poly(phenylene oxide) (SPPO) in a membrane separation process as an alternative to the various unit operations involved in the downstream processing after removing microbial cells, $CaCO_3$, and any other suspended materials from the fermentation broth by centrifuge.

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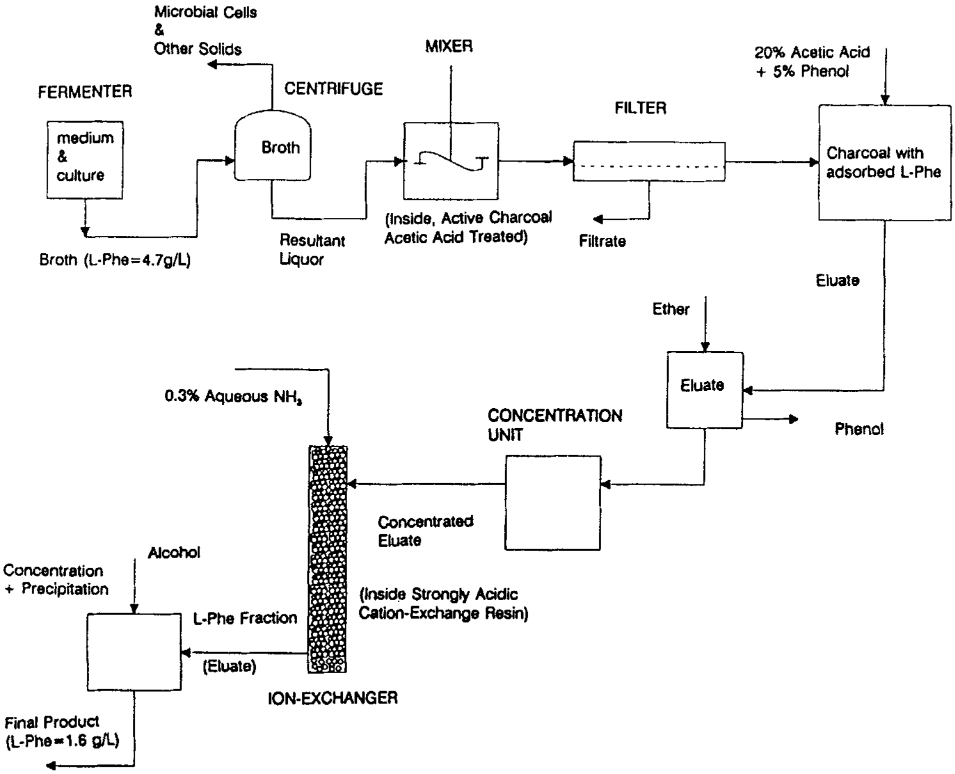

FIG. 1 Schematic flow diagram for the recovery process of L-phenylalanine from fermentation broth.

TABLE 1
Composition of Fermentation Medium (7, 8)

Solute	Concentration (wt%)
Glucose	10.00
Potassium phosphate (monobasic)	0.05
Potassium phosphate (dibasic)	0.05
Magnesium sulfate (hydrated)	0.025
Ammonium sulfate	2.0

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This process scheme, which is now being used, is shown in Fig. 1. The composition of the fermentation medium is given in Table 1 according to the literature (7, 8). Because the composition of the broth is not mentioned in this literature, for the purpose of this investigation it is assumed to be that of the fermentation medium.

In this work, poly(phenylene oxide) (PPO) was first sulfonated to give a negatively charged polymer according to a method reported earlier (9, 10). Sulfonated poly(phenylene oxide) (SPPO) polymer was then used to prepare the charged UF membranes. These newly developed charged UF membranes are of the thin-film composite type, consisting of a top thin layer of SPPO polymer coated onto a porous polysulfone substrate. Then the effect of the feed concentration of various solutes (inorganic and organic) in a single component system on the rejection of various solutes was studied. The effect of pH on the feed solution over a wide range of pH values on the rejection of L-phenylalanine was also investigated in order to study the changes in its rejection behavior with solution pH.

EXPERIMENTAL

Polymer Synthesis

The sulfonation of poly(2,6-dimethyl-1,4 phenylene oxide) (PPO, electrical grade, supplied by General Electric Co.) was carried out in a chloroform solvent system at ambient conditions to the desired ion-exchange capacity by using chlorosulfonic acid as the sulfonating agent. The SPPO thus obtained was neutralized with sodium hydroxide to convert the hydrogen form of SPPO polymer into a thermally stable sodium form. The synthesis scheme has been discussed in detail in the literature (10), and the chemical reaction is shown in Fig. 2. The SPPO polymer (sodium salt form) thus prepared was exhaustively dried at 70°C in a vacuum oven.

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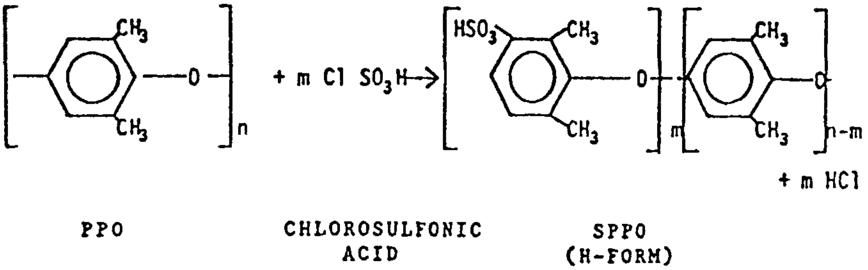

FIG. 2 The chemical reaction for the synthesis of sulfonated poly(phenylene oxide) (SPPO) polymer.

TFC-SPPO Charged Ultrafiltration Membrane Preparation Method

The polysulfone (PS) substrate was first prepared. For this a casting solution containing 12.5 wt% PS (Udel grade, P-3500, supplied by Amoco Performance Products) and 12.5 wt% methyl cellosolve in dimethylformamide was prepared. This solution was cast onto a nonwoven polyester cloth (Hollytex 3329) held on a glass plate with the help of a newly designed "adjustable casting knife" having the capability of adjustment to variable widths and thicknesses. The thickness of the wet film was 250–275 μm. The ambient conditions were: temperature, 22°C; relative humidity, 40–50%. After casting, the glass plate was immediately immersed into a gelling bath containing a 50% by weight solution of dimethylformamide in deionized water. The film gelled quickly. This PS substrate was washed several times with deionized water and then put in deionized water for 4–5 hours. Then the PS substrate was air-dried for at least 12 hours and examined for any defects by using a light box.

A coating solution of SPPO polymer having IEC = 2.38 meq/g dry polymer was prepared in anhydrous methanol. The composition of the coating solution was: SPPO = 0.5 g, methanol (anhydrous) = 20 mL, isobutyl alcohol = 2 mL, glycerin = 0.2 mL.

This coating solution of SPPO was then applied to the top layer of the dried PS substrate with the help of the adjustable casting knife to give a composite membrane having a dried film thickness of about 2–3 μm. This composite membrane was then allowed to dry for 4–5 hours in air. Samples of the membrane having the exact size necessary to fit properly in the UF test cells were then cut out at random with the help of a die cutter in a hand-operated hydraulic press. These membrane samples can be stored either in a dry condition or in a wet condition in water for an extended time period.

Apparatus and Materials

The UF experiments were conducted in an apparatus consisting of six identical UF cells as shown in Fig. 3 and described elsewhere (11). The effective membrane area was 14.43×10^{-4} m^2 (diameter = 4.286×10^{-2} m).

The molecular weight cut-off (MWCO) of the various membrane samples was measured by studying the rejection of polyethylene glycol molecules having molecular weights ranging from 600 to 10,000. In particular, PEG-600, PEG-1000, PEG-1540, PEG-6000, and PEG-10,000 (J. T. Baker, New Jersey, USA) were used. L-Phenylalanine was obtained from Sigma, and its physical properties are given in Table 2. Various other inorganic salts, such as NaCl, KH_2PO_4, $(NH_4)_2SO_4$, $MgSO_4 \cdot 7H_2O$, and glucose, were also used.

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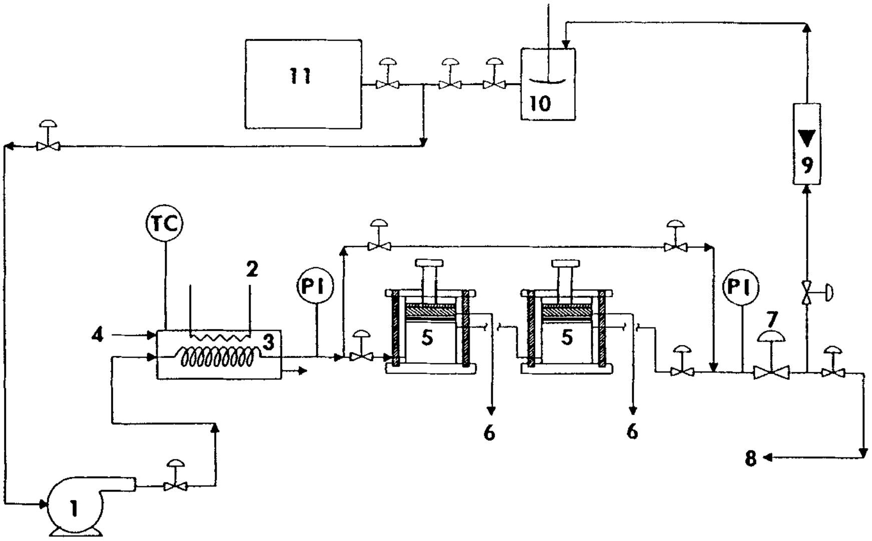

FIG. 3 Schematic diagram of the ultrafiltration experimental unit. 1: "BIF Prosuperb" metering pump; 2: heating element; 3: thermostated water bath; 4: cooling water; 5: ultrafiltration cells (in actual six cells used); 6: permeate; 7: backpressure regulator; 8: sink; 9: flowmeter; 10: feed solution tank; 11: deionized water tank. TC: temperature controller; PI: pressure gauge.

TABLE 2
Physical Properties of L-Phenylalanine Amino Acid

Zwitterion between pHs 3.5 and 9.0
Molecular weight = 165
Isoelectric point = 5.48
Water solubility = 2.97 g per 100 g (25°C)

Conditions and Procedure

The experimental conditions were as follows: feed recirculation rate, 3 L/min; feed temperature, 25°C; pressure, 0.345 MPa (50 psi).

The following experimental procedure was used:

1. The pure water flux of the membrane was determined by collecting permeated water over 1000 seconds.
2. The rejections of various inorganic salts, glucose, polyethylene glycol, and L-phenylalanine were determined by recirculating the feed solution for about 1.0 hour and then connecting the permeated product sample for 1000 seconds. This feed recirculating time of 1.0 hour has been found sufficient to give a steady-state condition.
3. The feed and product solutions were analyzed for their inorganic salt concentrations by using a Water Associates Differential refractometer model R403. The same refractometer was used to determine the concentration of polyethylene glycol and glucose solutions.
4. After each run, before starting the next run, the whole system was flushed with deionized water for about 2000 seconds.
5. The pH of L-phenylalanine feed solution was adjusted by using a NaOH or HCl solution.
6. The concentrations of L-phenylalanine in the feed and permeated solutions were determined by using an UV-VIS spectrophotometer (Perkin-Elmer) model Lambda 3 at a wavelength of λ = 257.5 nm.

The solution rejection was calculated by using

$$R\ (\%) = [(C_{\text{feed}} - C_{\text{permeate}})/C_{\text{feed}}] \times 100$$

RESULTS AND DISCUSSION

Membrane Characteristics

The IEC of the SPPO polymer was determined by using the acid-base titration method. It was found to be equal to 2.38 meq/g of dry polymer.

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FIG. 4 Scanning electron microscope (SEM) photomicrograph of the cross section of a thin-film composite (TFC) charged SPPO ultrafiltration membrane.

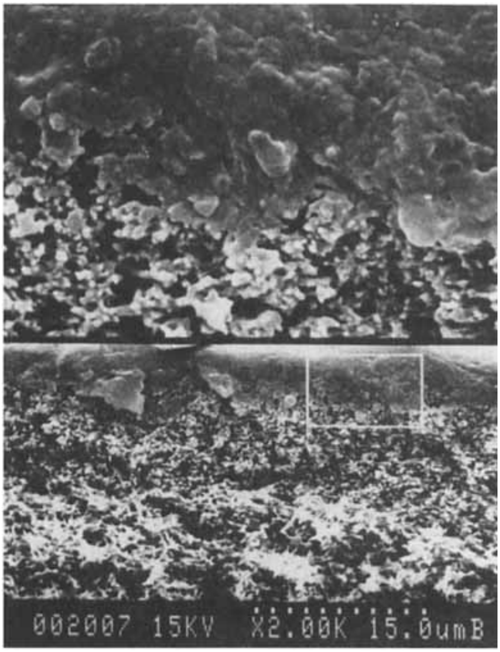

FIG. 5 SEM photomicrograph of the cross section of a TFC-SPPO charged ultrafiltration membrane at two magnifications (lower one at 2000× and upper one at 10,000×).

The morphology of the thin-film composite ultrafiltration membrane of SPPO polymer coated onto a microsporous substructure of polysulfone was examined by using a scanning electron microscope (SEM) (Hitachi model S-570). These photomicrographs are shown in Figs. 4, 5, 6, 7, and 8. Figure 4 shows the cross section of a TFC-SPPO charged UF membrane. It is obvious from Fig. 4 that the PS substrate has a highly spongy structure. The coated layer of SPPO polymer has a uniform thickness of about 3.0 μm and does not penetrate deeply into the porous substructure. Figure 5 shows the cross section of the same membrane sample at two magnifications in order to give better insight into the structure of the membrane. Figure 5 indicates an unconventional dense structure of the top coated layer of the SPPO polymer as compared to the asymmetric fingerlike structure usually found in conventional UF membranes. Figure 6 shows a further close examination of the cross section of the same TFC-SPPO charged membrane sample at a higher magnification. This SEM photomicrograph reveals a very thin and highly tortuous path through an otherwise top coated dense layer of SPPO polymer for liquid permeation

FIG. 6 SEM photomicrograph of the cross section of the top coated layer of SPPO polymer of the same TFC-SPPO membrane sample as shown in Figs. 4 and 5 at a higher magnification of 25,000×.

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through the TFC-SPPO charged UF membrane. This tortuous path is indicated by the arrows in Fig. 6 and has a width of about 0.12 μm. Figure 7 shows an SEM photomicrograph of the top surface of the membrane sample; it indicates the presence of a dense skin layer whose integrity has been breached at numerous places (visible as circular spots). Figure 8 is an SEM photomicrograph at a higher magnification of the same top surface of the membrane sample taken to indicate the structure of the breached spots on the surface. The cross-sectional views of this sublayer are shown in Figs. 4, 5, and 6. Most of the permeation of the liquid through the membrane occurs via these breached spots. In order to better understand the mechanism of the formation of the structure of this novel TFC-SPPO ultrafiltration membrane and its effect on the transport properties of the membrane, a more detailed investigation is currently underway.

The MWCO curves for two membrane samples (A and B) as determined by using a series of polyethylene glycol (PEG) molecules having different molecular weights are shown in Fig. 9. According to this figure, the MWCO rating of membrane sample A is 10,000 while that of sample B is about 20,000.

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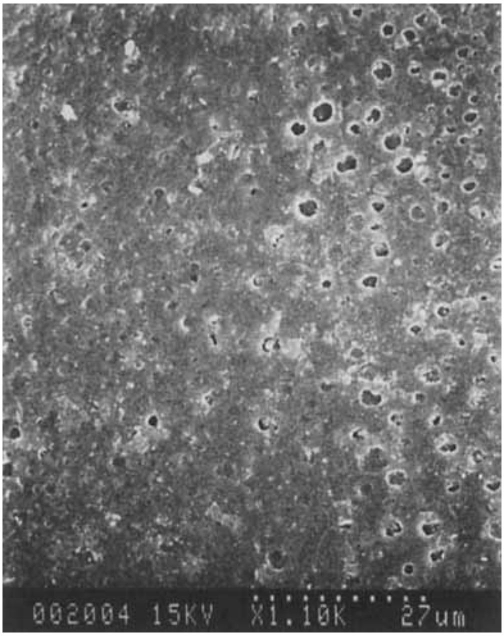

FIG. 7 SEM photomicrograph of the top surface of a TFC-SPPO charged ultrafiltration membrane sample.

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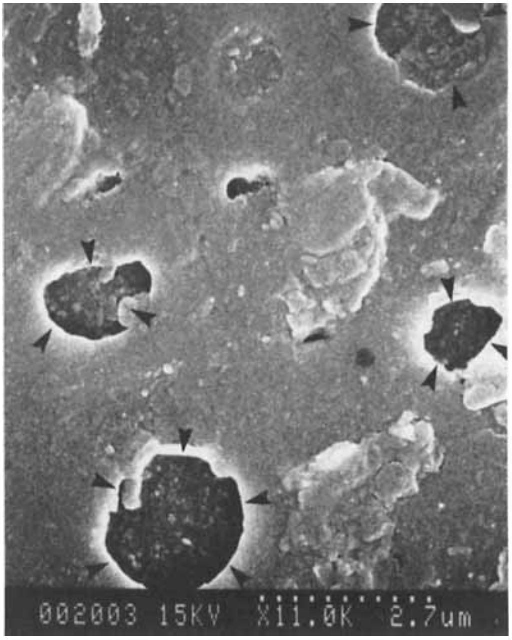

FIG. 8 SEM photomicrograph of the top surface of the same TFC-SPPO ultrafiltration membrane sample as shown in Fig. 7 at a higher magnification (11,000×) to indicate the structure of the surface of breached spots.

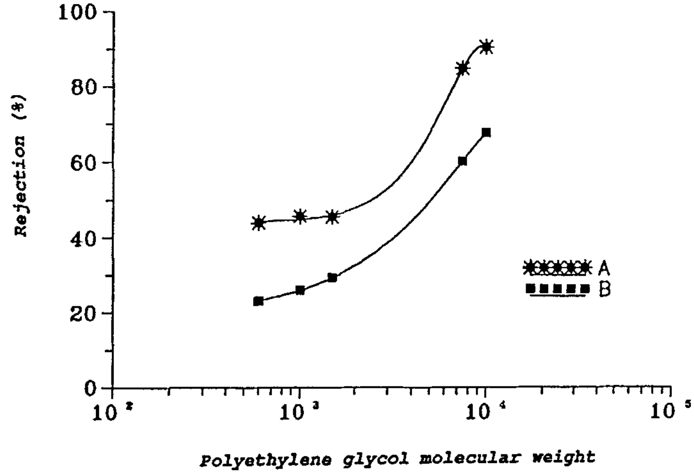

FIG. 9 TFC-SPPO charged ultrafiltration (UF) membranes characterization in terms of molecular weight cut-off (MWCO).

Effect of Inorganic Solutes Feed Concentration on Rejection Characteristics of Membranes

The effects of the concentration of the feed solution of various inorganic solutes, which are present in fermentation broth, on the rejection characteristics of membrane samples A and B were studied in a single component system of inorganic solute. Membrane samples A and B, which have different MWCO ratings, were chosen to see the effect of pore size on the rejection characteristics of these solutes. Figure 10 shows the effect of the NaCl feed concentration on the rejection characteristics of the membrane samples. Although NaCl is not present in the fermentation medium, its effect was studied because it is usually considered as a reference solute. From Fig. 10 it is obvious that the rejection of NaCl for both membrane samples decreases as its concentration in the feed solution increases. However, the permeate flux for both samples remains quite steady as the feed concentration increases. From the same figure it can also be seen that although the permeate flux of membrane B is almost twice that of

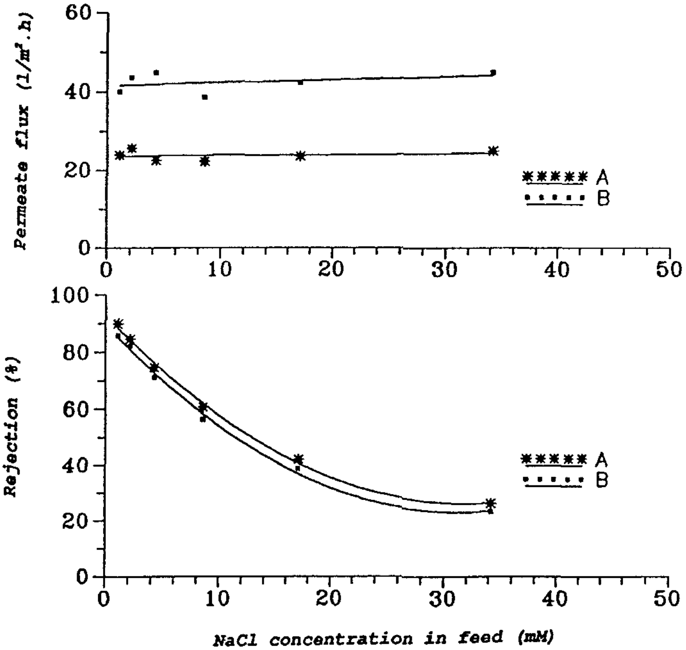

FIG. 10 Effect of NaCl feed concentration on rejection characteristics of the TFC-SPPO charged UF membranes.

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membrane A, their salt rejection behaviors are almost identical quantitatively as well as qualitatively. On the basis of this observation it can be inferred that the pore size of the charged membrane does not have any appreciable effect on salt rejection, at least within the limits of the pore sizes of these two membrane samples, and that rejection is governed by the electrostatic forces due to the fixed charged groups on the membrane.

The decrease in salt rejection with an increase in the concentration in the feed solution may be explained in light of the fact that due to electrostatic forces between the fixed membrane negative charges (sulfonic groups) and the ions present in the aqueous solution (Na^+ and Cl^-), the coions (Cl^-) are repelled (excluded) from the membrane phase, while the counterions (Na^+) are attracted toward the membrane phase. Thus, the number of coions which invade the membrane's high-pressure face is low compared to counterions. But due to the Donnan potential, the number of counterions reaching the membrane's high-pressure face is reduced compared to that of coions at steady state (equilibrium). Thus, in the steady state the counterion and coion fluxes through the membrane are in a stoichiometric ratio and together are equivalent to a salt flow due to the electroneutrality requirement. This salt flow and, hence, its rejection or exclusion from the membrane phase are limited by the coion flow. The coion flow is influenced by several factors such as the ion-exchange capacity of dry polymer, the degree of swelling, the crosslinking density, and solute concentration in the solution. Coion flow usually increases with an increase in salt concentration and, therefore, its permeability through the membrane also increases. This increase in solute (salt) permeability results in a decrease in salt rejection or exclusion. Therefore, a decrease in salt rejection with a corresponding increase in feed concentration is observed.

Permeate flux usually depends on the porosity of the membrane in the absence of any concentration polarization and fouling of the membrane surface. In this experiment there is no fouling, and concentration polarization is minimal due to crossflow conditions and a high feed recirculation rate. Therefore, permeate flux remains almost constant and only increases with membrane porosity.

Figures 11 and 12 show the effect of the feed concentrations of monobasic and dibasic potassium phosphate, respectively, on the rejection of solute. Again, it can be observed that as the solute concentration in the feed increases, the rejection decreases accordingly for both solutes. However, at a particular level of the feed concentration, the rejection of dibasic potassium phosphate is higher than that of monobasic potassium phosphate. These results are to be expected considering the fact that an ion-exchange membrane excludes the coion of an electrolyte due to electro-

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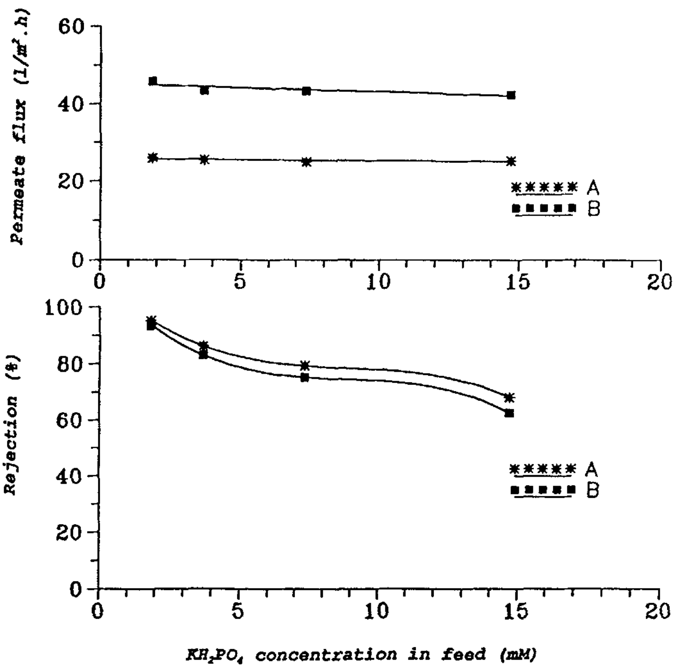

FIG. 11 Effect of KH_2PO_4 feed concentration on rejection characteristics of the TFC-SPPO charged UF membranes.

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static forces. The magnitude of coion exclusion depends upon the charge density of the coions and generally increases with an increase in the charge density. Therefore, dibasic ($HPO_4^=$) coions are rejected more than $H_2PO_4^-$ coions, and consequently their salts containing the common counterion (K^+) are rejected correspondingly.

Figures 13 and 14 illustrate the effect of the feed concentration of magnesium sulfate (hydrated) and ammonium sulfate, respectively, on the solute rejection characteristics of the membrane samples. In general, a trend similar to the rejection behavior of other inorganic solutes, as discussed earlier, was also observed in the case of these solutes. The rejection of ammonium sulfate at any particular value of the feed solution concentration was found to be much higher than the corresponding value of the rejection of magnesium sulfate (hydrated). This phenomenon may be explained by the fact that in the case of electrolytes having a common anion (in this case the counterion $SO_4^=$), rejection by an ion-exchange membrane will be higher in the case of an electrolyte having a lower cation charge

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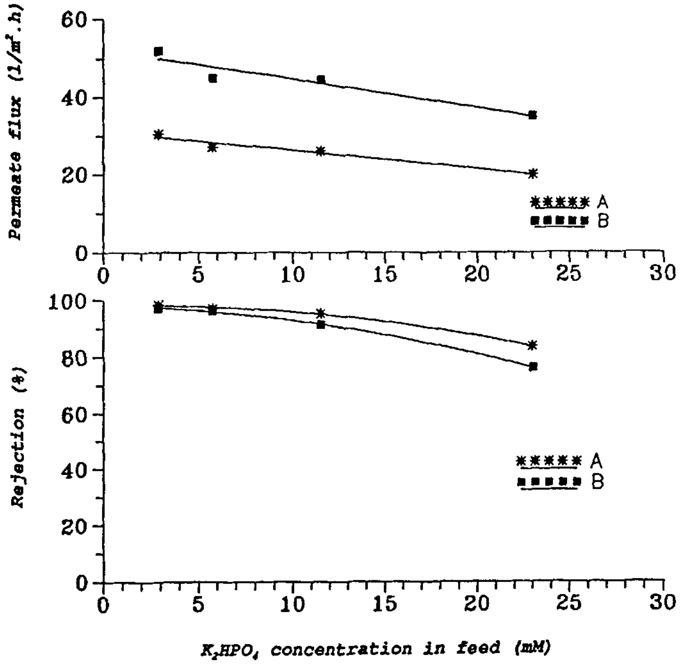

FIG. 12 Effect of K_2HPO_4 feed concentration on rejection characteristics of the TFC-SPPO charged UF membranes.

density in comparison to an electrolyte having a higher cation charge density. In the electrolyte $MgSO_4{\cdot}7H_2O$ the cation Mg^{2+} has a higher charge density than the NH_4^+ cation present in the electrolyte $(NH_4)_2SO_4$. Therefore, the rejection of $(NH_4)_2SO_4$ solute is much higher than that of $MgSO_4{\cdot}7H_2O$.

Effect of Glucose Feed Concentration on Rejection Characteristics of Membrane

Figure 15 depicts the effect of glucose feed solution concentration on the rejection characteristics of membrane samples A and B. As expected, the effect of feed concentration is negligible. This can be attributed to the fact that glucose is a neutral organic molecule and, therefore, the electrostatic forces due to the charged membrane do not have any effect on the rejection of the glucose neutral molecules. The MWCO ratings of membrane samples A and B are 10,000 and 20,000, respectively, which are much higher than the molecular weight of the permeating glucose

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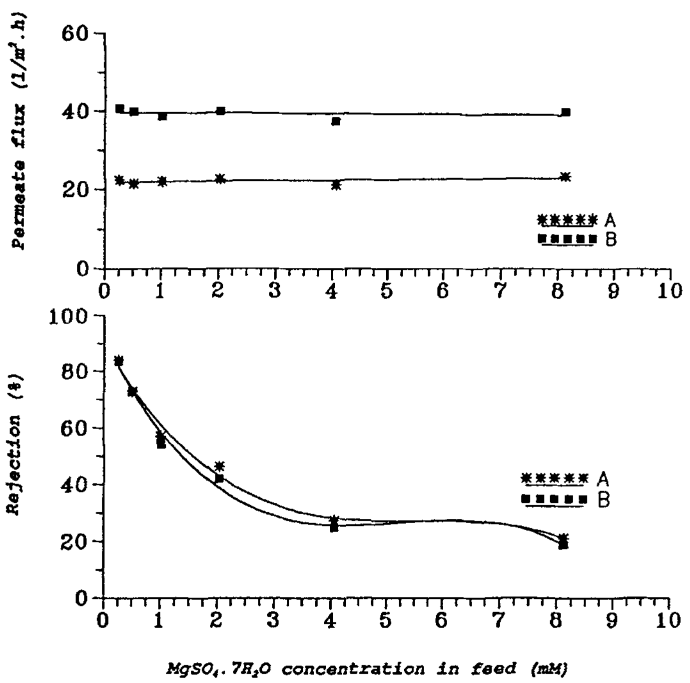

FIG. 13 Effect of $MgSO_4{\cdot}7H_2O$ feed concentration on rejection characteristics of the TFC-SPPO charged UF membranes.

molecules (MW = 180.2). Therefore, there is no resistance to permeation and, hence, no glucose molecule rejection occurs due to the sieving effect. The small amount of rejection observed can be attributed to the pore size distribution of the membrane samples.

Effect of L-Phenylalanine Feed Concentration on Rejection Characteristics of Membrane

Figure 16 shows the effect of L-phenylalanine feed solution concentration on the rejection characteristics of the membrane. It is evident from this figure that the rejection and permeation rates are unaffected by the change in concentration, and rejection is virtually negligible by membrane samples A and B. These results are in accordance with expectation because the pH of the feed solution was near its isoelectric point (5.48) and, therefore, the L-phenylalanine molecules were neutral (nonionic). Due to the nonionic nature of L-phenylalanine molecules, they are not subjected

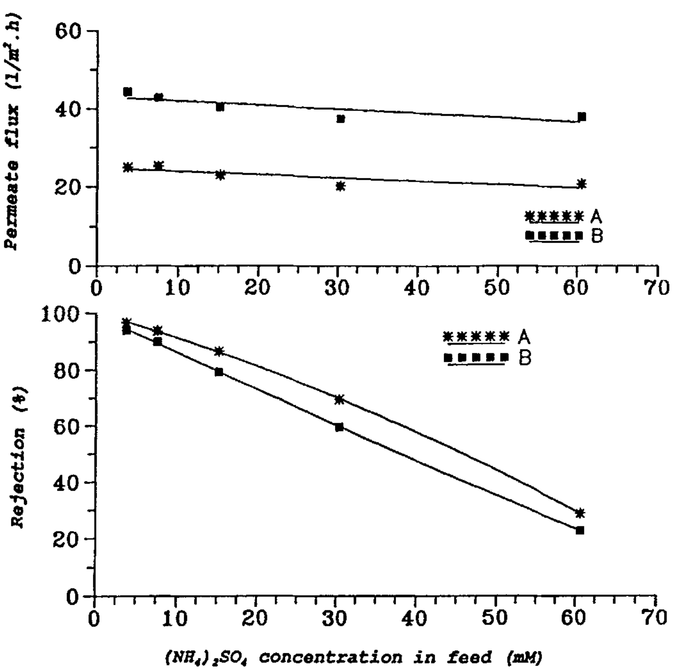

FIG. 14 Effect of $(NH_4)_2SO_4$ feed concentration on rejection characteristics of the TFC-SPPO charged UF membranes.

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to electrostatic forces by the charged membrane and, therefore, are not rejected. The molecular weight of L-phenylalanine is 165, which is very small in comparison to the MWCO of membrane samples A and B. Therefore, these molecules are also not rejected due to the sieving effect of the charged ultrafiltration membrane samples.

Effect of pH of L-Phenylalanine Feed Solution on Rejection Characteristics

Figures 17 and 18 show the effect of the pH of the L-phenylalanine feed solution on the rejection characteristics at feed concentration levels of 0.605 and 6.05 mM, respectively. It is evident from both figures that pH has a strong effect on the rejection behavior of L-phenylalanine while the permeate flux is independent of it. The rejection varies from − 10 to 90%, depending on the pH level. It can also be noted from these figures that the difference in the pore size of membrane samples A and B does not cause any appreciable change in the rejection behavior of L-phenylalanine,

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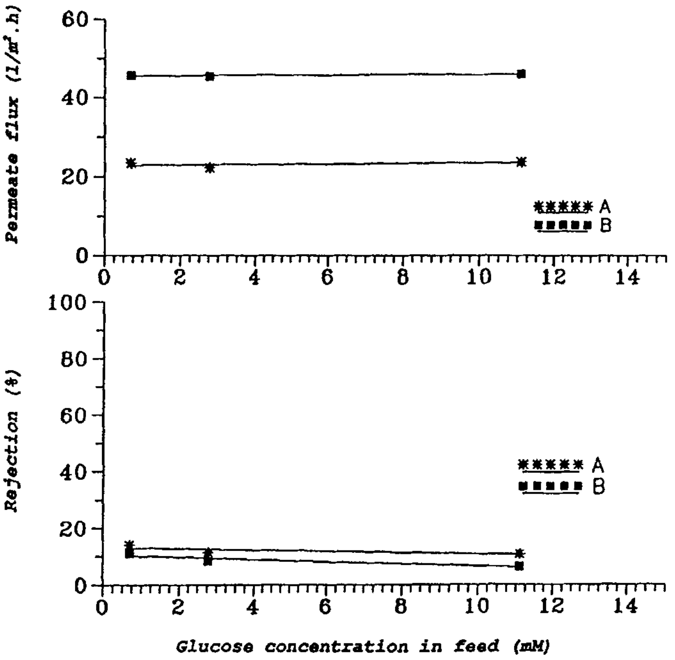

FIG. 15 Effect of glucose feed concentration on rejection characteristics of the TFC-SPPO charged UF membranes.

at least within the limits of the pore sizes of the two membrane samples tested. Further, it can also be seen from these two figures that changes in the rejection behavior of L-phenylalanine with the pH of the feed solution at the two concentration levels are almost identical qualitatively and do not differ by much quantitatively.

The above results may be explained in light of the fact that the ionic nature of the L-phenylalanine molecules changes profoundly with the change in pH of the feed solution. At the isoelectric point of L-phenylalanine, i.e., at pH 5.48, the molecules are neutral and have a net zero charge, and thus are unaffected by electrostatic forces due to the charged membrane. Therefore, their rejection at pH values in the neighborhood of the isoelectric point is negligible. However, L-phenylalanine molecules in aqueous solution behave as zwitterions between pH values of 3.5 and 9.0. Therefore, as the pH of the aqueous solution increases beyond its isoelectric point, the net charge on the molecules starts changing gradually to negative values, and at pH values 9.0 and higher the molecules acquire a total negative charge. Therefore, these negatively charged molecules

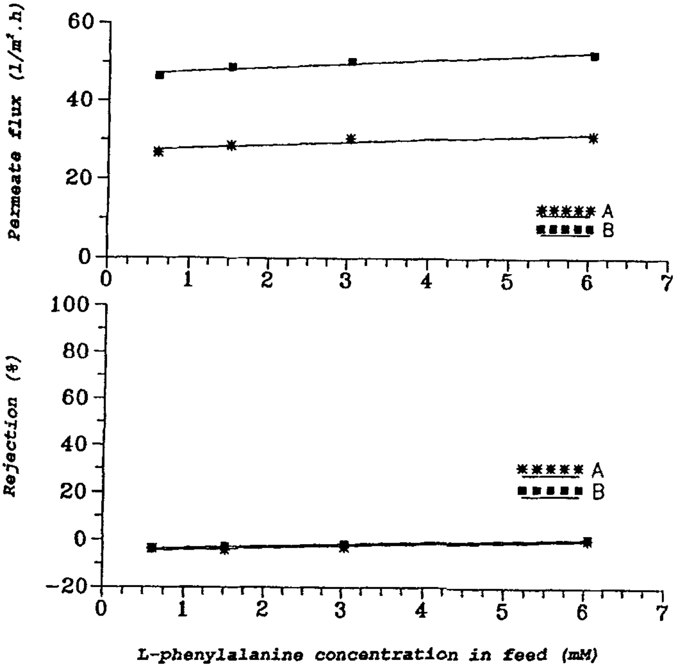

FIG. 16 Effect of L-phenylalanine feed concentration on rejection characteristics of the TFC-SPPO charged UF membranes.

are rejected by the negatively charged membrane. At pH values below the isoelectric point the net charge gradually changes to positive values, and at pH 3.5 and below it changes completely to positive charge. The positively charged L-phenylalanine molecules are attracted toward the negatively charged membrane surface. In this process the permeability of L-phenylalanine molecules through the membrane is increased to such an extent that enrichment of L-phenylalanine molecules in the permeate stream occurs, which gives negative rejection values. Identical rejection behaviors by membrane samples A and B, which have different MWCO values, show that the rejection is controlled more by the ionic nature of the membrane samples than by the sieving effect.

CONCLUSIONS

Two membrane samples of a newly developed charged (fixed negatively charged sulfonic groups) TFC ultrafiltration membrane made of SPPO and

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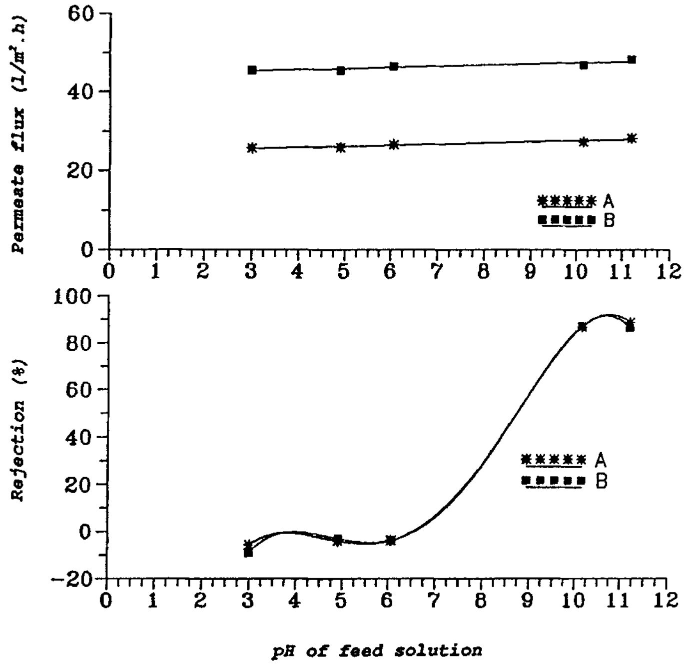

FIG. 17 Effect of pH of feed solution of L-phenylalanine on rejection characteristics of the TFC-SPPO charged UF membranes (feed concentration = 0.605 mM).

having MWCO ratings of 10,000 and 20,000 were used to study the rejection of various components which are usually present in fermentation broth by using a single solute system. The rejection of various salts was found to be strongly dependent on the concentration of the salts in the feed solution. This is a typical characteristic of charged ultrafiltration membranes. The rejection was observed to decrease with an increase in the salt concentration, while the permeate flux remained virtually constant. The rejection behaviors of two membrane samples with different MWCO ratings were almost identical, both qualitatively and quantitatively, while the permeate flux of one sample was almost twice that of the other. These results indicate that the pore size of the membrane does not have any significant influence on the rejection of salts for the two different samples tested. Therefore, the ionic nature of the charged membrane may be a strong controlling factor in the rejection of salts.

Glucose and L-phenylalanine (at or near its isoelectric point), which are neutral molecules, were not rejected by the charged membrane, and their rejection behaviors were found to be independent of the solute feed solu-

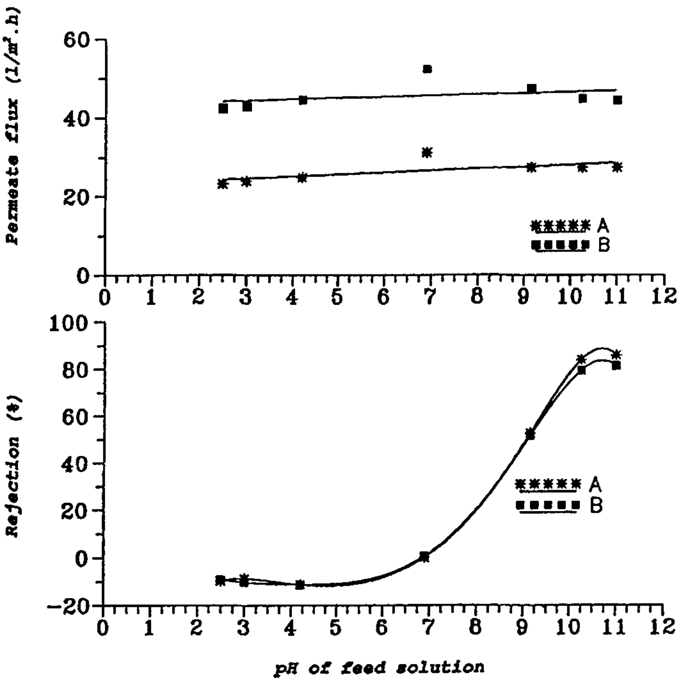

FIG. 18 Effect of pH of feed solution of L-phenylalanine on rejection characteristics of the TFC-SPPO charged UF membranes (feed concentration = 6.05 mM).

tion concentration. The pH of the feed solution containing L-phenylalanine changed from − 10 to 90%, depending on the pH. Rejections of two membrane samples having MWCOs of 10,000 and 20,000, respectively, were found to be exactly the same although the permeate flux of one sample was almost twice that of the other sample. This result indicates that rejection is very strongly governed by the electrostatic forces caused by the fixed negative charges due to sulfonic groups on the membrane for the two membrane samples tested.

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REFERENCES

1. S. Nakao, H. Osada, H. Kurta, T. Tsuru, and S. Kimura, "Separation of Proteins by Charged Ultrafiltration Membranes," *Desalination*, *70*, 191–205 (1988).

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2. I. Jitsuhara and S. Kimura, "Rejection of Inorganic Salts by Charged Ultrafiltration Membranes Made of Sulfonated Polysulfone," *J. Chem. Eng. Jpn.*, *16*(5), 394–399 (1983).
3. D. Bhattacharyya, J. M. McCarthy, and R. B. Grieves, "Charged Membrane Ultrafiltration of Inorganic Ions in Single and Multi-Salt Systems," *AIChE J.*, *20*(6), 1206–1212 (1974).
4. D. Bhattacharyya and R. B. Grieves, "Charged Membrane Ultrafiltration," in *Recent Dev. Sep. Sci.*, *3*, 261–283 (1977).
5. S. Kimura and A. Tamano, "Separation of Amino Acids by Charged Ultrafiltration Membranes," *Membranes and Membrane Processes* (E. Drioli and M. Nakagaki, Eds.), Plenum Press, New York, 1986, pp. 191–197.
6. M. P. Thien, T. A. Hatton, and D. I. C. Wang, "Liquid Emulsion Membranes and Their Applications in Biochemical Separations," in *Separation, Recovery, and Purification in Biotechnology* (ACS Symposium Series 314), (J. A. Asenjo and J. Hong, Eds.), American Chemical Society, 1986, pp. 67–77.
7. N. Kiyoshi and H. Hiroshi, U.S. Patent 3,917,511 (1975).
8. N. Kiyoshi and H. Hiroshi, U.S. Patent 3,759,790 (1973).
9. C. W. Plummer, G. Kimura, and A. B. Laconti, *Development of Sulfonated Poly(Phenylene Oxide) Membranes for Reverse Osmosis*, Office of Saline Water Research and Development, Progress Report 551, General Electric Co., Lynn, Massachusetts, 1970.
10. P. J. Chludzinski, J. F. Austin, and J. F. Enos, *Development of Poly(Phenylene Oxide) Membranes*, Office of Saline Water Research and Development, Progress Report 697, General Electric Co., Lynn, Massachusetts, 1971.
11. S. Sourirajan and T. Matsuura, *Reverse Osmosis/Ultrafiltration Process Principles*, National Research Council of Canada Publications, Ottawa, 1985, pp. 680–682.

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