Interaction of Proteins with Ultrafiltration Membranes: Development of a Nonfouling Index Test

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ABSTRACT: Ultrafiltration membranes were prepared from homopolymer [polyacrylonitrile (PAN), polyethersulfone (PES), and polyvivylidenefluoride (PVDF)] and acrylonitrile copolymers with increasing acrylamide content. The membranes containing acrylamide were more hydrophilic and had a smaller dispersive surface energy than those prepared from the acrylonitrile homopolymer. A new nonfouling index (NFI) test was devised and appears to distinguish well between ultrafiltration membranes of different hydrophilicity–hydrophobicity balance. The NFI indices of acrylamide containing copolymer membranes were much higher than those of membranes cast with commercial membrane materials such as PAN, PES, and PVDF. The NFI of ultrafiltration membranes increased as acrylamide substitution in the copolymer increased. The use of acrylamide containing copolymers substantially eliminated intrinsic fouling. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1600–1606, 2000

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INTRODUCTION

Synthetic ultrafiltration (UF) membranes based on cellulose acetate and other derivatives were well developed by the mid-1930s. Today, the synthetic membrane range includes polyvinylidine fluoride (PVDF), polyacrylonitrile (PAN), polyethersulfone (PES), and the nylons. In spite of the many kinds of UF materials available today, the large scale commercial utilization of UF has been hampered by the costs involved, largely because of the occurrence of membrane fouling, namely the adhesion of dissolved and suspended materials onto the hydrophobic polymer surfaces and the resulting flux decline. This is difficult to reverse except by extensive and often severe cleansing methods that add substantial costs to the process.[1]

Fouling by native proteins is important of itself and also demonstrates many of the phenomena operative. Globular proteins consist of coiled, long-chain molecules, with a hydrophilic exterior and a hydrophobic interior. The hydrophilic exterior contains the predominantly ionic portions of the protein, namely its amino and carboxylic moieties. The hydrophobic regions are in the interior of the protein, and the coiled structure is held together largely by hydrophobic and hydrogen bonds, so that in its native state the protein can be highly soluble in water and stable in it. However, when a protein is exposed to a hydrophobic surface, it literally is "turned inside out," with the hydrophilic outside exposed to the aqueous medium and the hydrophobic part adhering to the

membrane. The bonds that are operative are largely of hydrophobic-bonding character. Most proteins become irreversibly denatured and permanently deformed and being insoluble adhere strongly to the hydrophobic interface. A thin film of denatured protein is formed, usually much less than 1 μm in thickness and rather impermeable to both solvent and solute transfer. Such films can be removed only by degrading the protein with acid, base, or enzymes.

There are several routes that can be used to reduce or control fouling. One is to make and use hydrophilic polymers so as to alter the surface characteristics of the membrane. One can improve feed pretreatment, modify the crossflow rate and turbulence, or improve membrane-cleaning procedures. We selected the first route, which involved altering the nature of the monomers and polymers so that adhesive or adsorption forces would be minimized.[2,3]

EXPERIMENTAL

Materials

Polyacrylonitrile (MW 730,000) was obtained from Monsanto Co. (Dayton, OH). PVDF and PES with the commercial name of Radel A-100 were obtained from Amoco Chemicals. Three copolymers based on acrylonitrile and acrylamide in the ratios of 90 : 10 (A-1), 80 : 20 (A-2), and 70 : 30 (A-3) were prepared in our laboratory by free radical polymerization of these two monomers using potassium persulfate and sodium hydrogensulfite as initiators.[4] All above polymers were used as membrane materials.

PES membranes HZ-15 were obtained from Osmonics, Inc. (Minnetonka, MN). Nonwoven, porous poly(ethylene terephthalate) cloth (Hollytex 3396) was obtained from Eaton-Dikeman Co. *N, N*-dimethylformamide (DMF), sodium azide, potassium hydrogen phosphate, and sodium dihydrogen phosphate were obtained from Aldrich Chemicals (Milwaukee, WI). Bovine serum albumin (BSA) was obtained from Sigma Chemical Co. (St. Louis, MO).

Membrane Casting

The membranes described below were prepared using standard casting techniques. Ultrafiltration membranes were prepared from 3 wt % polymer solutions in DMF by casting the solution onto

Table I Properties of the Liquids at 20°C (ergs/cm^2)

Liquid	γ_l^d	γ_l^p	γ_{lv}
Water	21.8	51.0	72.8
Formamide	39.5	18.7	58.2

Hollytex, with a 5-mil (127 μm) gate opening on a casting knife, followed by immediate coagulation in 2–5°C water to minimize skin formation. The membranes were rinsed several times in deionized water and kept at 5°C until used.

Membrane Characterization

Surface Characterization

The surface characterization of each polymer could be done using dried clean membrane. The intrinsic hydrophilicity of the membrane materials was determined from the advancing contact angles measured by a goniometer (model 100-00; Rame-Hart, Mountain Lakes, NJ).[5]

Prior to the contact angle measurement, the membrane sample was rinsed three times for 10 min in double-distilled water, and the sample was then cleaned with double-distilled water in an ultrasound bath for two 15-min periods. The angles were evaluated from photographs using video-enhanced image processing. The values of the contact angles are the average of the 10 air bubbles (two angles per bubble), giving a total of 20 angles for each membrane sample.[6]

The polar and dispersion force components of the surface energy were determined from the following equation[7] using the reported parameters in Table I and measured contact angles for water and formamide:

$$1 + \cos \theta = 2(\gamma_s^d)^{0.5} \lfloor (\gamma_l^d)^{0.5}/\gamma_{lv} \rfloor$$
$$+ 2(\gamma_s^p)^{0.5} \lfloor (\gamma_l^p)^{0.5}/\gamma_{lv} \rfloor \quad (1)$$

where γ is the contact angle, γ_{lv} is the surface free energy of the liquid in equilibrium with the vapor of the liquid, γ_s^d and γ_s^p are the dispersion force component and the polar component of the surface free energies of the solid, respectively, and γ_l^d and γ_l^p are the dispersion force component and the polar component of the surface free energies of the liquid, respectively.

Determination of Membrane Flux

The flux of membranes was usually determined in the Amicon (Beverly, MA) stirred cell 8050.[8] An
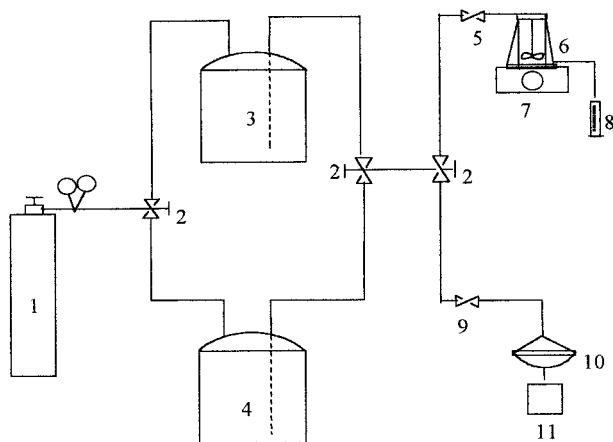
Figure 1 Experimental set-up of NFI measurement. 1, nitrogen tank; 2, three-way valve; 3, pure water; 4, pure water; 5 and 9, two-way valve; 6, Amicon cell; 7, magnetic stirrer; 8, 50-mL graduate; 10, Millipore cell; 11, 5-mL collection cup.

applied pressure (30 psig) of nitrogen in the pure water feed tank enabled us to measure the flux of water. The flux of water through the membrane was calculated according to the following equation:

$$J \ (\mu \text{sa}) = \frac{V \times 10^4}{t \times A \times P} \tag{2}$$

where V (cm^3) is the volume of the permeate water received during the time t (s), the area A (cm^2) is the effective filtration area , and P (atm) is the pressure applied. Here flux is given as μsa, which is the abbreviation of micrometers/s-atm.

Nonfouling Index Test

The lack of a test that can be used by all laboratories and that makes use of a standard fouling feed has hindered progress in the UF field. In spite of the importance of fouling in a membrane process, no standard test for fouling has as yet been devised.[9–13] Those in industry are forced to carry out empirical laboratory or bench scale studies on virtually all feed streams before estimating equipment requirements. Fouling industrial feeds are subject to almost limitless variations. Repetitive runs of several hours are needed to show significant differences.

We have already shown that an NFI can be measured by (1) challenging a given membrane by pure water, measuring its steady-state flux J_1; (2) substituting a dilute solution of BSA at 1 mg/mL in pH 7 buffer, observing the sharp drop in flux which follows and measuring the lowered protein flux J_p; (3) washing the protein out of the system with pure water and observing the steady-state water flux J_2. The NFI has been defined as

$$NFI = \frac{J_2 - J_p}{J_1 - J_p} \tag{3}$$

where J is the steady-state flux at constant pressure (usually 30 psig), with J_1 the initial steady-state pure water flux, J_2 that after the protein-challenged membrane has been rinsed thoroughly with buffer, and J_p is its protein solution steady-state flux.

This NFI test can be performed in almost any laboratory UF cell, preferably one with some form of stirring (Fig. 1). The same sample of membrane must be used because 1- to 2-inch samples cut from most commercial rolls differ by as much as a factor of two in flux from one another. Steady-state fluxes take about 4–6 h to be reached, depending on the method of membrane preparation and conditioning. The choice of protein and the buffer pH are important factors in the test. Dilute solutions of BSA at 1 mg/mL in pH 7 buffer appear to be the most useful.

Membrane Backwash

Membrane backwash experiments were conducted using a bench scale UF device. It is shown diagrammatically in Figure 2. The cell design has been used for several years in carrying out bench scale tests.[15] The cell, while small and simple in design, allows one to test a relatively small UF membrane under conditions under which the results translate directly into the performance of full sale, spiral-wound equipment. Entrance ef-
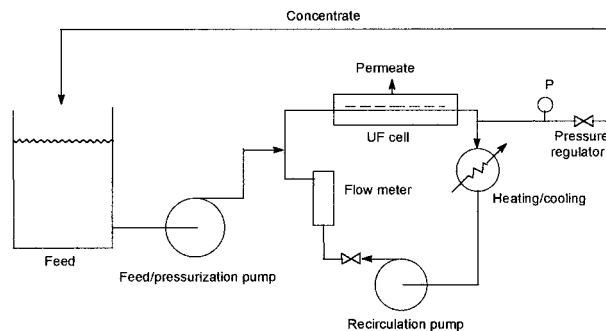

Figure 2 Schematic of ultrafiltration bench scale device.

Table II   Surface Characterization

Membrane	AM in Feed (mol %)	Contact Angle (°)		Surface Free Energy (erg/cm^2)		
		Water	Formamide	γ_s^p	γ_s^d	γ_s
PAN	0	72	47	8	34	42
A-1	10	68	44	11	33	44
A-2	20	61	37	15	32	47
A-3	30	54	35	22	27	49

fects are eliminated by the wide entrance and exit ports.

The system design is of the "feed and bleed" configuration. A limited volume (2–4 L) of feed is placed in the tank. The feed pressurization pump supplies a pressure adequate for the UF process. The flow rate is determined primarily by the pump characteristics and to a smaller extent by the hydraulic resistance of the circuit. The pump is selected to deliver enough flow to have only a small concentration gradient across the face of the membrane and much more than enough to replenish the feed to the cell.

RESULTS AND DISCUSSION

Surface Characterization of Membranes

As would be expected from the chemical modification, Table II shows that the polymer/water contact angles decrease with an increasing acrylamide content. The polar component of the surface energy increases with increasing acrylamide content; whereas the dispersion force component of all acrylamide-containing membranes is less than that of the PAN membrane.
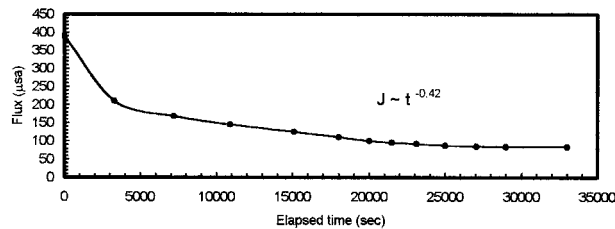
Fouling Evaluation

Effect of Time on Water Flux

Figure 3 shows a declined flux with a pure water feed of a typical PAN membrane, freshly prepared and soaked in water for a few days. The behavior is typical of many membranes. The curve drawn through points results in a good fit to the equation shown in Figure 3, obtained by a mathematically linear regression. This curve is similar in shape to many different kinds of membranes produced by the phase inversion or coagulation technique.

A number of membranes were cast from a variety of polymers at different concentrations in DMF or NMP and at different percent of solids and gate openings onto nonwoven polyester fabrics. The fabric used is known as Hollytex. A number of polymers were used, including PAN, PVDF, PES, and several hydrophilic polymers. Similar curves were obtained but with different periods of time to achieve the steady-state flux.[15]

NFI Comparison among Different Types of Membranes

A few results are now given of flux/time curves and NFI values. For the highly hydrophobic PAN membrane in Figure 4, NFI is 28%; similar behavior is observed for the extremely hydrophobic
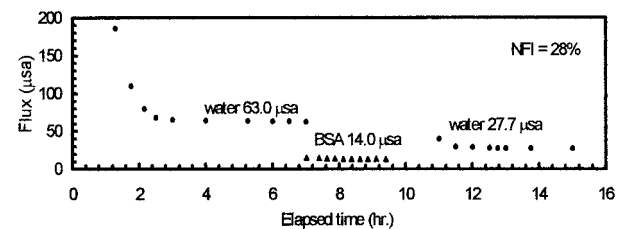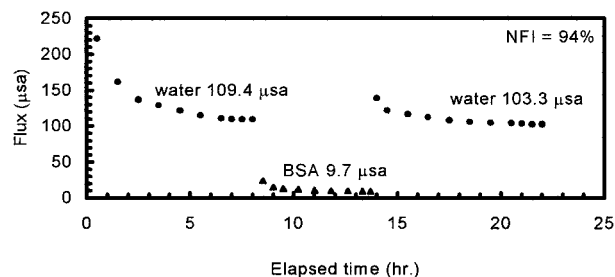

Figure 3   Typical flux behavior for PAN membrane with pure water feed.

Figure 4   Fouling test of PAN membrane.

Figure 5 Fouling test of A-2 membrane.

Figure 6 Ultrafiltration of tap water (Brooklyn) at flat-sheet bench scale. A-2 membrane. Solid line, ultrafiltration at 14.5 psig; dashed line, back-wash at 14.5 psig.

membrane made from PES (Radel A), with an NFI of 11%. The fluxes and calculated pore diameters of these differ widely, but the sharp drop in flux with BSA is quite similar. PVDF membranes also show a sharp drop of flux with BSA, but with a greater flux recovery with NFI 37%.

In sharp contrast, a membrane made from 80-20 AM showed a sharp drop in flux with BSA but recovered it almost completely in pure water for an NFI of 94% (Fig. 5). Increasing the AM content of the polymer to 70-30 AM led to a NFI of 100%. Lowering the AM content of the polymer to 90-10 AM also led to a NFI of 79%.

Thus, the new NFI test appears to distinguish well between UF membranes of different hydrophilic–hydrophobic balance.

Effect of Washing Time on NFI of Commercial Polysulfone Membrane

Many commercial polysulfone membranes are either made from a casting solution to which polyvinylpyrrolidone (PVP) was added or coagulated in an aqueous solution of the latter to render
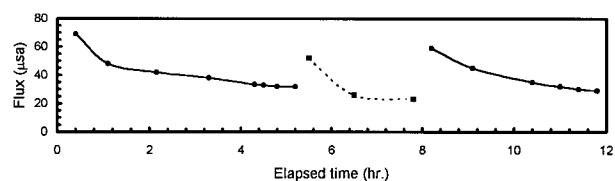
them hydrophilic for initial use. But it is known that this effect is temporary, because the water soluble polymer is slowly leached from the membrane. As shown in Table III, a number of similar samples of the PES Osmonics HZ-15 series membranes having fluxes of 12–19 μsa initially show an NFI of 73%, which fell to 38% after 1 week of soaking in water at room temperature, to 19% after 2 weeks, and to 10% after 4 weeks. Treatment with warm water at 60°C for 1 day lowered the NFI to 21%.

Membrane Backwash on Bench Scale

The backwash with the hydrophilic membrane A-2 is shown in Figure 6. This was performed in the flat-sheet bench scale cell shown earlier, with a feed of Brooklyn tap water. This is typical city water and contains both dissolved and suspending fouling agents.

The typical loss in flux reflecting partial compression of membrane and partial accumulation of fouling agents followed the usual curves and leveled off at about 30–35 μsa. The membrane

Table III   Effect of Pretreatment on NFI of Commercial PES Membranes

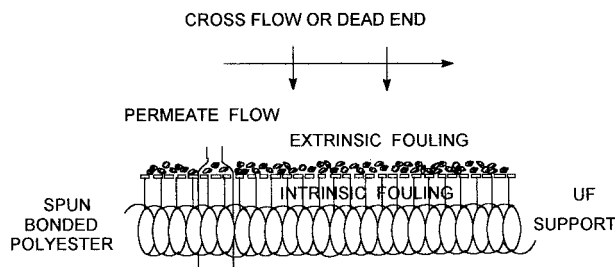| No.	Water J_1 (μsa)	BSA* J_p (μsa)	Water J_2 (μsa)	NFI (%)	Comment
Radel A-100[a]	8.0	3.5	4.0	11.1	No additives
HZ-15-0	11.6	5.4	9.9	72.6	1 day in H_2O at RT
HZ-15-1	14.1	6.8	9.6	38.4	1 week in H_2O at RT
HZ-15-2	19.2	7.8	10.0	19.3	2 weeks in H_2O at RT
HZ-15-5	15.0	6.7	7.5	9.6	4 weeks in H_2O at RT
HZ-15-10	14.3	6.5	8.1	20.5	1 day in H_2O at 60°C

[a] Radel A-100: laboratory-made.

Figure 7 Ultrafiltration membrane fouling.

was left in water, and next day it was reversed with membrane side down and the nonwoven polyester face up. Here is seen a drop in flux probably due to membrane compression. Then, the membrane was reversed in the cell with flow in the usual direction and the flux decline also was observed.

This behavior is typical of many membranes, but this case shows a leveling off of the flux characteristics of hydrophilic membranes. Compression of the membrane is seen for a long period of time.

When the polymer of the UF membrane is hydrophobic and causes fouling, this is termed intrinsic and can be removed only by chemical treatment. The use of back-washing is most important because it eliminates extrinsic fouling, whereas the use of our polymers substantially eliminates intrinsic fouling. These phenomena are illustrated in Figure 7. When a feed contains soluble and particulate fouling agents, as is invariably the case with waste waters, the particulates cause a decrease in flux by being concentrated at the surface of the membrane and held there by permeate flow. Even a very high rate of cross flow does not prevent this, at high energy consumption. Only a frequent and periodic backwash to the concentrate can substantially eliminate this kind of flux reduction. To achieve anything like the capability of UF membrane systems, the use of both nonfouling polymers and backwashing is essential.

In Figure 7 the cast and coagulated polymers are easily locked into the surface of the support, be it spun-bonded polyester cloth or microporous plastic. Because back-washing tends to force the support upward, the bond between the membrane and support and between support and pipe tube, if any, must have adequate strength.

Given the above conditions, UF systems could fulfill their promise to provide inexpensive (in terms of equipment and power) devices for both the Navy and manifold civilian applications.

CONCLUSIONS

In comparison with PAN, the AM-containing copolymers yield membranes with higher polarity and hydrophilicity and smaller dispersive surface energy. A new NFI test was devised and appears to distinguish well between UF membranes of different hydrophilicity–hydrophobicity balance. The NFI indices of AM-containing copolymer membranes were much higher than those of membranes cast with commercial membrane materials such as PAN, PES, and PVDF. The NFI of UF membranes increased as AM substitution in the copolymer increased. The use of AM-containing copolymers substantially eliminated intrinsic fouling.

NOMENCLATURE

A effective filtration area (cm^2)
J flux of feed through membrane (μsa)
J_1 water steady-state flux at first measurement (μsa)
J_2 water steady-state flux at second measurement (μsa)
J_p protein steady-state flux (μsa)
P operation pressure (atm)
t collection time (second)
V collected volume (ml)
θ contact angle (°)
γ_s^p polar (H-bonded) component of surface free energy of solid (erg cm^{-2})
γ_s^d dispersion force component of surface free energy of solid (erg cm^{-2})
γ_l^p polar (H-bonded) component of surface free energy of liquid (erg cm^{-2})
γ_l^d dispersion force component of surface free energy of liquid (erg cm^{-2})
γ_s surface free energy of solid (erg cm^{-2})
γ_{lv} interfacial tension (liquid/vapor) (dynes cm^{-1})
γ_{sv} interfacial tension (solid/vapor) (dynes cm^{-1})
γ_{sl} interfacial tension (solid/liquid) (dynes cm^{-1})

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