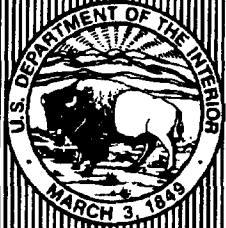# ENHANCEMENT OF MEMBRANE FOULING RESISTANCE THROUGH SURFACE MODIFICATION

Water Treatment Technology Program Report No. 22

March 1997

U.S. DEPARTMENT OF THE INTERIOR
Bureau of Reclamation
Technical Service Center
Environmental Resources Team
Water Treatment Engineering and Research Group

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ENHANCEMENT OF MEMBRANE FOULING RESISTANCE THROUGH SURFACE MODIFICATION

A study using the principles of membrane fouling and cleaning to develop ways to enhance membrane fouling resistance.

Water Treatment Technology Program Report No. 22

by

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UNITED STATES DEPARTMENT OF THE INTERIOR ★ BUREAU OF RECLAMATION

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U.S. Department of the Interior
Mission Statement

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy.and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

ABSTRACT

Commercial samples of cellulose acetate and polyamide reverse osmosis (RO) and nanofiltration (NF) membranes were treated with an homologous series of polyethylene-oxide based surfactants to improve fouling resistance. Various characterization methods were used to quantify membrane surface changes with treatment and fouling with a vegetable broth solution. Streaming potential was used to characterize changes in zeta potential. Atomic force microscopy was used to evaluate changes in surface topography. Water flux and salt rejection were evaluated using a bench scale "swatch-testing" apparatus. Fouling layer thickness was evaluated using acoustic time domain reflectometry. Results from these methods were compared with performance changes.

The fouling solution degraded the untreated cellulose acetate (CA) blend membrane. Therefore any surface protection provided by the surfactant was dramatically illustrated. Triton Xl00 and Pluronic P84 provided significant protection. Polyamide (PA) membranes treated with surfactant experienced a severe flux decline. A similar decline was caused by fouling of the untreated PA membrane. The treated PA membrane did not have further flux decline with fouling. These results suggest a need for further studies on whether or not a surfactant pretreatment will result in improved membrane flux and rejection over many operating and cleaning cycles when exposed to fouling waters.

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ACRONYMS

AFM	atomic force microscopy
ATDR	acoustic time-domain reflectometry
CA	cellulose acetate
CMC	critical micelle concentration
CP	concentration polarization
DI	deionize
EKA	electrokinetic analysis
EPS	extra-cellular polymeric substance
HLB	hydrophilic-lipophilic balance
IP	isoelectric point
LB	Langmuir-Blodgett
LDPE	low density polyethylene
MGD	million gallons per day
MHz	megahertz
NF	nanofiltration
NIST	National Institute of Standards and Technology
NPF	normalized permeate flow
PA	polyamide
PA/TFC	polyamide/thin film composite
PEG	polyethylene glycol
PEO	polyethylene oxide
PEU	polyetherurea
RMS	root mean square
RO	reverse osmosis
ROWPU	Reverse Osmosis Water Purification Unit
SDS	sodium dodecylsulfate
SEM	scanning electron microscopy
TACOM	Tank Automotive Command (U.S. Army)
TDS	total dissolved solids
TSC	Technical Service Center
UF	ultrafiltration
YDP	Yuma Desalting Plant

1. INTRODUCTION

The Water Treatment Membrane Cleaning Project has been a cooperative project between the Bureau of Reclamation Technology Service Center (TSC), Bureau of Reclamation Yuma Desalting Plant (YDP), and the U.S. Army Tank Automotive Command (TACOM), Mobility Technology Center. Until 1994, the two types of membranes used in TACOM's Reverse Osmosis Water Purification Units (ROWPU) were incompatible with each other. One was an aromatic polyamide (PA) membrane from FilmTec with a negative surface charge, and the other was a polyetherurea (PEU) membrane from Fluid Systems with a positive surface charge. Since the membranes were oppositely charged, they could not be cleaned with the same surfactants. The PA membrane cannot be exposed to cationic cleaning agents, and the PEU membrane cannot be exposed to anionic or nonionic cleaning agents. TACOM had funded Separation Systems to find a cleaning solution that would work on both membranes (Separation Systems, 1993), but they were unable to identify such a solution though over a hundred formulations were tested. As a result of their work, they did make the following observations:

- The PEU membrane is not durable enough for use in ROWPU elements. Newly developed PA seawater membranes would be more viable.

. The construction of membrane elements is inadequate for use in ROWPUs. Feed channel spacers need to be redesigned to improve turbulence, minimize fouling, provide a minimum pressure drop, and increase the ability to clean elements without damaging the membrane.

- Pretreatment to the ROWPUs is inadequate. Without improvement, element operation will be limited to a few hundred hours.

To address these observations, TACOM initiated four separate projects. One was to use the Separation Systems study results to support their argument to their procurement officers that new membranes needed to be qualified for use in the ROWPUs. This was accomplished finally in 1994. TACOM now has a wider variety of membranes to choose from for the ROWPUs. The second was to fund development of a new membrane spacer design. The third was to develop a new ROWPU design to improve pretreatment without increasing the size or weight of the unit. The forth was to fund this project to identify cleaning, operating, or other methods to extend membrane life expectancy in the field.

As owner of the world's largest spiral wound membrane water treatment facility, the Bureau of Reclamation is interested in identifying the causes of membrane fouling and in developing methods to extend membrane life through fouling prevention and proper cleaning techniques.

1.1 Objectives

There were three objectives for this study. The first was to find out how membranes were being maintained in water treatment plants. The second was to review literature on membrane fouling and cleaning to identify technological changes that could improve membrane life. Then, to find

ways to implement the changes once the improvements were identified. The focus for the third objective for this study was to identify ways to enhance the fouling resistance of membrane materials.

1.2   Assessing the Problem-Membrane Plant Cleaning Survey

As part of the preliminary investigations, operators of membrane water treatment plants were surveyed to find out what the current practices in membrane maintenance were. The survey was designed to be simple and quick to fill out. The questions were all short answer or multiple choice. Participants were asked for the following plant data:

- Type of membrane process
- Membrane manufacturer
- Year of startup
- Capacity
- Water composition
- Source of water
- Pretreatment used
- Quality of product water
- Percent recovery
- Shutdown frequency
- Fouling or scaling problems and symptoms
- Cleaning procedure
- Cleaning effectiveness
- Whether mechanical cleaning had been used

Out of 77 surveys mailed out, there were 20 responses and 4 that were returned by the post office.   Figure 1.1 is a graphical representation of the responses summarized in table 1.1.

Table 1 **.1** .-Tally of membrane fouling problems and cleaning practices

Fouling problem	Number of problems	Have cleaned	Have not cleaned
Silica scaling	5	3	2
Metal scaling	1 0	7	2
Biofouling	6	6	0
No problem	5	3	3
Totals	26	1 9	7

Appendix A contains a copy of the survey. Respondents that were having problems with their systems also expressed frustration with their lack of success in cleaning.   All responding plants,
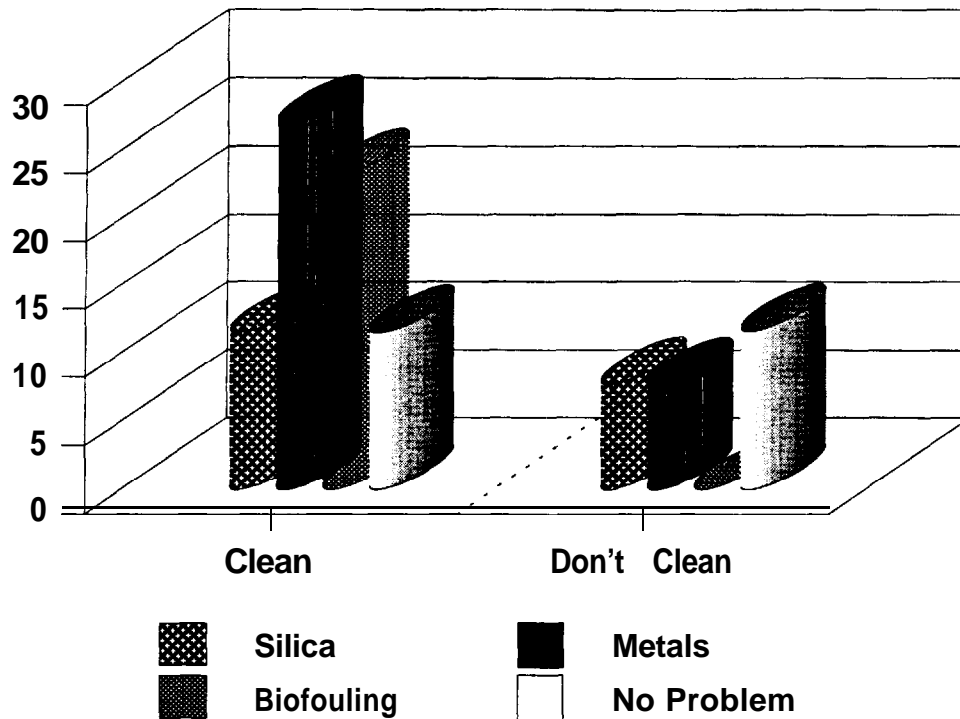
Figure 1.1 .-Cleaning practices and fouling problems as a percentage of problems reported.

except the Yuma facility, were treating well water with total dissolved solids (TDS) ranging from 260-36,000. All but one had at least cartridge filtration for pretreatment. All but four' had problems with biofouling and/or scaling. Three of these four had been on line for 2 years and had not cleaned their membranes. The fourth plant was established in 1978. There, a weekly pH 4.5 rinse was used to keep the system in good condition. One seawater emergency plant that had been on line for 1 year had 100 percent flux and salt rejection return after cleaning with Floclean (PA41 1), citric acid, and $NaHSO_4$. Four plants were able to achieve 93-99 percent flux and salt rejection return. Of these, three used only high and low pH rinses for cleaning. The other one sent theirs out for reconditioning every 2 years. The rest of the respondents had less than satisfactory results (<83 percent flux and salt rejection return).

1.3   Plan of Attack-How to Prevent or Minimize Fouling and Scaling?

Three types of solutions to the problem of keeping membrane systems in operation were developed from information gathered in the literature search reviewed in chapter 2:

1. *Modification of the membrane* surface: The membrane material can be modified using surfactants or a more permanent method, to produce an entropic barrier at the surface to protect it from poisons in the feed stream. After review of the literature on fouling mechanisms, it was hypothesized that a low energy surface with near neutral charge would be fouling resistant.

2. *Improved performance monitoring:* Another solution is to track real time normalized performance data. This would require monitoring each stage for conductivity and

flow rate of feed, concentrate and permeate streams, pressure of feed and concentrate streams, and temperature of the feed stream. Data acquisition software could be used to calculate real time normalized performance data. Two levels of action thresholds would be set at 5 and 15 percent change in any of the normalized parameters (or thereabouts). The lower-level threshold would signal the need for passive cleaning techniques described in chapter 2. When the upper-level threshold is reached, chemical cleaning procedures would be initiated.

3. *Clarify cleaning procedures:* Procedures and monitoring requirements for membrane cleaning must be established. Cleaning is often unsuccessful because it is carried out for too short or too long a time with the wrong cleaning solution. Recommended cleaning solutions are specific for a particular type of fouling, but it is not always clear which solution is needed in a specific situation. Manufacturers describe indicating symptoms with vague, subjective terms, such as "marked," "significant," and "rapid." A method should be developed to tie real-time normalized performance changes to a fouling problem and hence a cleaning solution.

At the start of this project, the problem of membrane cleaning was believed to have a chemical solution so chemical manufacturers were contacted to find out what products were available for membrane cleaning. After the literature review, however, chemicals ceased to be the focus of study, but the fruits of the effort are presented in appendix B. The list of chemicals is modest in comparison to the number available for the job, and surely, many more are available today.

1.4 How to Increase a Membrane's Natural Fouling Resistance?

After reviewing the literature on the mechanisms of membrane fouling, it appeared that work in the medical field on prevention of protein adsorption might be applicable to membrane fouling as well. Lee et al. (1989, 1990) had success using a variety of surfactants to create an entropic barrier on the surface of medical instruments. Membranes could easily be treated with surfactants and tested to see if fouling could be reduced in the same manner. Tests were performed on small sheets, or swatches, of membrane with five different surfactants and tested for changes in performance and fouling resistance. The results of this study are presented in chapter 3.

1.5 Membrane Characterization

Three novel characterization techniques were used to help quantify and qualify the surface changes caused by surfactant adsorption. They were zeta potential analysis, atomic force microscopy, and acoustic time-domain reflectometry. The first two were available at the National Institute of Standards and Technology, the last was under development at the University of Colorado, Boulder. As an application is always of great assistance in development of novel methods, the membrane surface modification study was used to try these techniques with membrane materials. The procedures and results of these analyses are presented in chapters 4, 5, and 6.

2. CLASSIFICATION AND MECHANISMS OF MEMBRANE FOULING AND CLEANING

Sources of information for this review have been published studies on protein and bacterial fouling, models of scale formation, and membrane cleaning studies geared toward a variety of applications ranging from medical implants to cooling tower maintenance.

2.1 Categorization of Membrane Obstructions

The typical categories of membrane obstructions are fouling and scaling. Fouling refers to material that accumulates without a precipitation reaction. Examples are particulate and organic matter that adheres to the surface through hydraulic or other physical or electrical forces. Scaling, on the other hand, is the result of a chemical change in state which prevents the material from leaving the module. For instance, when carbonates crystallize in bulk solution, they tend to settle out in low flow areas within the module. Scaling can occur at the same time and in the same system as fouling. Without chemical analysis of the membrane deposit, one must rely on changes in performance and operating parameters to deduce which has occurred to the greatest extent. Even with an analysis, one could find carbonate scale in intimate contact with biological fouling. Particulate matter can form the nucleus of scale formation; likewise, scale formation can provide back-water areas where fouling can occur. Therefore, in this study, when referring to the joint processes of fouling and scaling, the term membrane obstruction will be used.

A.A. Baran (1990) published a study on obstructions of reverse osmosis (RO) and ultrafiltration (UF) membranes that based categorization on the chemical composition of the constituents. Table 2.1 summarizes some aspects of each group. For cleaning purposes, two major categories are sufficient: one for each of the two basic cleaning strategies. However, to best understand the nature of the foulant, how it is attached, and why it should be expected to be removed with a particular cleaning strategy, it is necessary to include Baran's groups as subcategories. The two-tiered classification system in table 2.2 is proposed.

It is a simple thing to devise a system of categories and procedures for dealing with each. The difficulties arise in the application of the system. One problem is that the obstruction layer changes both spatially and temporally. As the character of the feed water and/or operating conditions change, the obstruction layer will form strata reflecting the changes, just like geological strata. A layer that may be rather permeable at first will in time be compressed as the organic matter within it is broken down. These condition changes are difficult to duplicate in a laboratory setting. Destructive methods of determining the nature of the obstructing layer are helpful, but the next module may be completely different.

Further difficulties stem from the fact that adsorption to the membrane surface and cleaning procedures are dependent on the membrane's surface characteristics of hydrophobicity, surface charge, surface energy and roughness. The first time a membrane comes in contact with natural water, however, there is a spontaneous adsorption of colloidal and/or biological materials onto the surface (Baier, 1980). The original surface chemistry is manifested above the "conditioning

Table 2.1 .—Foulant characterization based on chemical composition (adapted from Baran, A.A. 1990)

	Soluble inorganic substances	Soluble organic substances	Colloid materials (water insoluble inorganic compounds: silica, iron hydroxides, etc.)	Biological materials (bacteria, algae, fungi, etc.)
Causes	Over saturation Presence of crystallization centers	Humic and fulvlc acids natural to surface waters Lack of adequate pretreatment Over utflization	Over utilization Inadequate sedimentation period	Inadequate pretreatment Inadequate flow through module . dead spaces Hydrophobic attraction between cell and membrane surfaces Production of extracellular polymeric substances Cell fimbriae may help attach bacteria to molecular matrix of the membrane
Effects	Decrease in salt rejection in end stages Increase in pressure drop in end stages Decrease normalized permeate flow (NPF) Scale formation on membrane surface or In bulk w/ subsequent deposition Formation of "salt bridge" facilitating protein adsorption High concentration at membrane surface can cause denaturatton of protelns which then are more of a fouling problem	Formation of H bonds on contact w/membrane Partial diffusion through membrane - dependent on degree of branching	Gel formation on membrane surface Decrease in NPF Decrease In salt rejection Symptoms most likely to appear in last stage	Decrease in NPF Initial increase in salt rejection Increase in pressure drop Symptoms most likely to appear in first stage (DHP') Accumulation of byproducts of *metabolism* Eventual deterioration of the membrane resulting in a decrease in rejection Decrease in flow at membrane surface can exacerbate concentration polarization phenomena
Prevention	Softening Acidification Use of chelating agents	Ultrafiltration Coagulation/sedimentation	Softening	Prefiltration Use of surfactants during normal operation has been shown to prevent bacterial attachment Reduce recovery rate
Remediation	Low pH w/chelate Normal operating temperature Soak cycle (DHP) Physical methods: ultrasound, magnetic, hydrodynamlc	Same as colloids (DHP)	High pH High temperature High flow rate Detergent (DHP)	Same as colloids (DHP) Use of enzymes has been shown to help loosen biofilm

' DHP: Paul, 1993

2.2

Table 2.2.—Two tiered classification for membrane obstructions

	Low temperature, low pH	High temperature, high pH
W/chelate	Soluble inorganic substances (carbonates, sulfates)	
W/detergent		Inorganic colloidal materials (e.g., silica, metallic hydroxides)
		Soluble organic substances (precursors of trihalomethanes)
W/chelate and/or enzymes		Microorganisms (bacteria, protozoa, fungi, algae)

layer," but some aspects are lost as the layer becomes thicker. This phenomena could produce benefits in surface treatment applications. But it may also interfere with cleaning products that are chosen according to the surface chemistry of clean membranes.

2.2 Soluble Inorganic Material

Soluble inorganic materials are the most predictable of all the constituents present in an RO module. Solubilities for all inorganic salts are well known within a restricted range of conditions. Antiscalants and/or pH adjustment are used to extend recovery levels above the point of saturation in the concentrate stream. Even without these additives, salts can be concentrated above the solubility level due to the time lag between over saturation and precipitation. Problems do arise, however, due to several factors. Some causes for scale formation are:

- Failure of the antiscalant or acid feed systems
- Foulant build-up resulting in channelized flow patterns
- Change in the composition of the feed water
- Increase in recovery rate due to increase in applied pressure

There may be other causes that are not so obvious. Assumptions may be made during the design process that are not appropriate in RO. For instance, solubility constants are normally listed for 25 "C, 1 atmosphere (atm), and zero ionic strength, but conditions in an RO system are substantially different. There are corrections to allow for ionic strength, but these are limited to ionic strengths below 0.5 M.

Another potential problem can arise from operating at inappropriate recovery rates. Product recovery rates are determined during the design phase based on the solubility of the limiting constituent. Then the recovery rate is calculated in the following manner:

$$recovery = 1 - \frac{C_f}{C_c}$$

Where C_f is the feed water concentration of the limiting species and C_c is the maximum concentration of that species to avoid exceeding its solubility limit. To manage a higher recovery rate, the concentration of the limiting constituent must be lowered through pretreatment or complexing with antiscalants. The design recovery rate determines the number of stages in the RO system. Once the system is installed, and the operation parameters set, the recovery rate is supposed to follow.

One would hope that RO systems are not designed to operate at their maximum limit. However, if there are changes in the feed water, if there is fouling at the membrane surface, or if the normal solubility limits are not appropriate in some cases, the safety margin may not be wide enough. Under these circumstances, an exploration of the effects of ionic strength, pressure and temperature is in order.

2.2.1 Effect of Temperature. The relationship between solubility constant and temperature is as follows:

$$\ln\left[\frac{K_T}{K_o}\right] = -\frac{\Delta H^o}{R}\left[\frac{1}{T} - \frac{1}{T_o}\right]$$

Where: K_T = Solubility constant at T
K_o = Solubility constant at 25 °C
ΔH = Change in enthalpy with solution (cal/mole)
R = Universal gas constant. (cal/mole-K)
T = Temperature ('Kelvin)
T_o = Temperature for known solubility (298.15 ° K)

Whether the solubility constant is increased (increasing solubility) or decreased with temperature depends on the sign of the **enthalpy** change. For some, such as calcium carbonate, solubility decreases with temperature. In most RO systems, temperature rises in the afternoon and falls at night. There are seasonal changes as well. Even in the range of 20" to **30°C,** the adjusted solubility of calcium carbonate varies from 1.12 to 0.89 times its normal solubility. The average daily temperature used in determining solubility is not sufficient. It would be more accurate to use the maximum and minimum annual temperatures to calculate the limiting solubility when determining maximum recovery rate.

2.2.2   Effect of Pressure. The effect of pressure on solubility is dependent on the change in volume of the reactants. At low pressures, the effect is very small. Deep in the ocean, however, at pressures approaching 1,000 atm, solubility can be increased by a few percent. The relationship is as follows:

$$\ln\left[\frac{K_P}{K_o}\right] = -\frac{\Delta V^o}{RT}[P - P_o]$$

W h e r e : K_P = Solubility constant at pressure P
         K_o = Solubility constant at 1 atm
         A V   = Change in volume with solubilization
         R   = Universal gas constant (Cal/mole-K)
         T   = Temperature in °K

Volume normally decreases by a small amount with dissolution; therefore, K_P is greater than K_o with higher pressures. The increase in the solubility of calcium carbonate is approximately 0.2 **percent/atm** near 1 atm. Brackish water RO systems operate at about 27 atm, resulting in a 7.4 percent increase in calcium carbonate solubility.

2.2.3   Effect of ionic strength. Ionic strength (I) is a property of an electrolyte solution that measures the effect of the total concentration of ions and their charge on the behavior of any one species of ion in the solution (**G.M.Barrow,** 1988, p. 328).

$$I = 0.5 * \sum c_i * Z_i^2$$

W h e r e : c_i = Concentration of the ith ionic species
         Z_i = Charge of the ith ionic species

Activity coefficients are calculated for each charge species from some form of the **Debye-Hückel** equation. The following is an approximation for solutions with I < 0.5 M:

$$\log y, = A*Z_+Z_-\left[\frac{\sqrt{I}}{1 + \sqrt{I}} - B*I\right]$$

Where: y   = Activity coefficient
         A   = 0.509 1 for water at 25 °C
         B   = 0.2 for monovalent species
         Z_+ = Charge of cation
         Z_- = Charge of anion

Coefficients A and B depend on temperature and the dielectric constant. B is also related to the radius of the ion. Activity coefficients are used to modify ionic concentrations in determining saturation concentrations. For instance, if $C^+ + D^- \rightleftharpoons CD,,,,$ then:

$$K_{sp} = \gamma^+[C^+]^* \ y\text{-}p^{-}]$$

Figure 2.1 shows the variation of activity coefficient with ionic strength for different electrolyte charge ratios. Activity coefficients less than one increase solubility by decreasing the effective concentration of the ion species. When I > 0.01, however, the activity of different ionic solutions begins to deviate from the predicted values. Above I=0.5, ionic strength and charge no longer describe the observed activity.
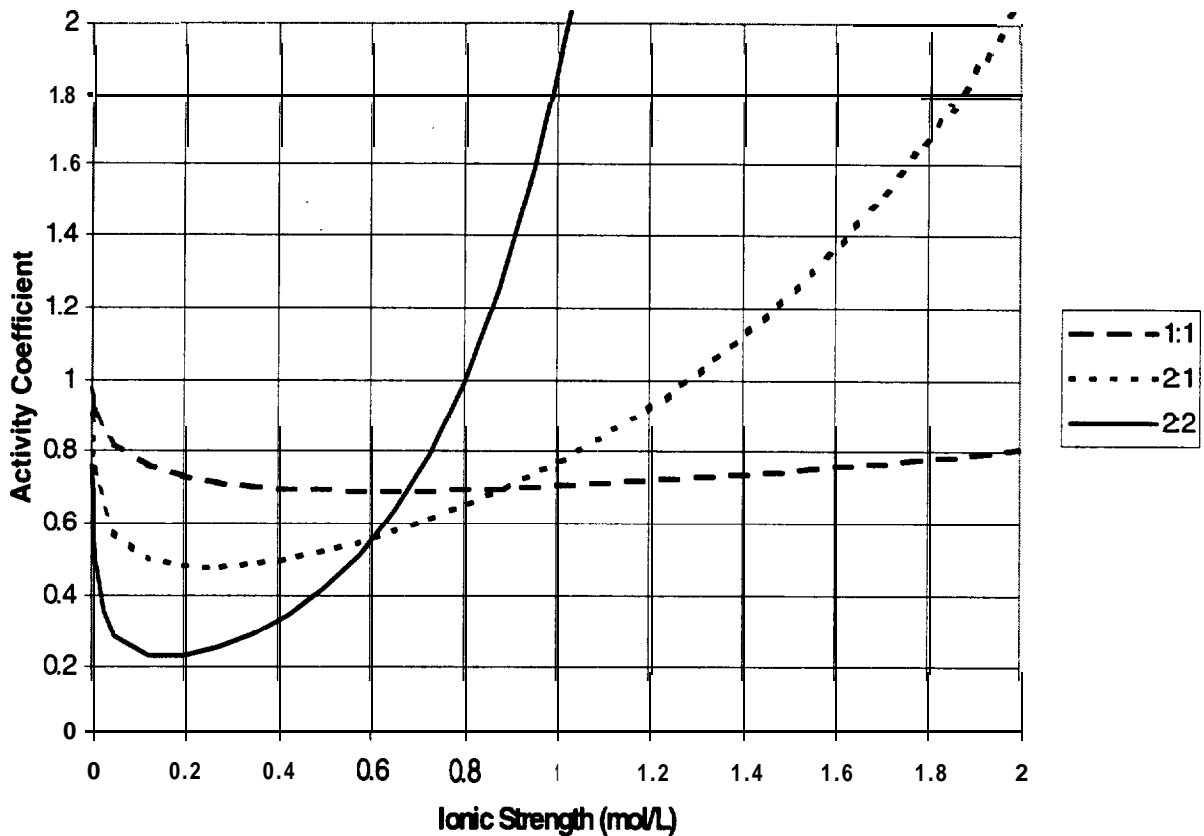
Figure 2.1 .-Comparison of mean activity coefficients of one to one, two to one, and two to two electrolytes using the Debye-Hückel limiting law.

Despite the model's limitations, RO solubility graphs (Dupont's for calcium, barium, and strontium sulfate, Bulletin 502, 12/1/82) show adjusted K_{sp} increasing over the whole range of ionic strengths up to 2 M. In figure 2.1, it is apparent that solubility of divalent electrolytes decreases after 0.8 M. The values calculated for these figures are only valid under 0.5 M. Beyond that point, the activity coefficient should be adjusted with factors that account for specific interactions between ion pairs and triplets (Morel and Hering, 1993 p.78).

2.2.4 Effect of surface microenvironment development. Crucial changes in condition develop across the flow channel within the membrane element. At a point very close to the surface, flow changes from moving parallel to the membrane to moving perpendicular to the membrane. In this region, dissolved and suspended matter are concentrated as solvent permeates through the membrane. There is a lag time between arrival at the surface and diffusion back into the bulk stream. This phenomena is called concentration polarization (CP). The extent of CP depends on the concentration of the bulk stream, presence of surfactants or polymers, the diffusivity of the solution, and the operating conditions (Baran, 1990). At some point along the RO system, CP can cause concentration at the membrane surface to exceed the solubility limit of scaling salts under prevalent conditions.

The microenvironment at the membrane surface is further altered by the presence of scale build-up. When precipitates of slightly soluble salts are present in solution with their ions, the solid serves as a nucleus to facilitate further precipitation. The chemistry in this microenvironment becomes very complex. There are several things going on: uncharged species may be permeating through the membrane, the pH may be elevated by the presence of the solid, flow is obstructed, etc. The net effect of all these interactions is not well understood. Even if conditions at the membrane surface were known, it is not clear that we would be able to predict what would occur.

2.2.5 Strategy for scale removal. There are three approaches to preventing scale in RO membranes. The best solution is to operate the system with a lower recovery rate. If this is not an attractive alternative, the metal cations can be removed from solution by softening, or they can be complexed with chelating agents or antiscalants. Complexing is not the best solution since the cations are still in the system. The scaling problem may be averted, but the additives may cause other types of fouling. One other form of prevention is to add acid to shift the equilibrium balance toward dissolution. With cellulose acetate (CA) membranes, the pH must be in the range of about 3 to 8 to avoid membrane hydrolysis. This range may be low enough to prevent scaling under most conditions, but whether scaling occurs depends on the water chemistry.

Cleaning strategies for scale removal are similar to those for prevention:

- Use a corrosive rinse, permeate water if possible

- Add acid to drive the solubility equilibrium toward dissolution

- Use high flow rate and low pressure to maximize flow across the membrane and minimize flow through the membrane

- Use normal operation temperature as some slightly soluble salts are less soluble at high temperatures

- Tie up metal ions with chelate to prevent reprecipitation

2.3 Biological Fouling

Biological fouling is defined by Characklis (1991) as the accumulation and metabolism of macroorganisms and/or microorganisms. Included in this definition are algae, fungi, protozoa, and bacteria. Table 2.3 outlines some basic differences between these major groups. One must keep in mind the diversity of organisms being discussed here. Within each of these subdivisions, there are thousands of species that are found in water. The groups are as different from each other as thistles are from people. The problem of finding an effective biocide or cleaning agent to simultaneously remove any combination of organisms is similar to the problem of finding a way to prevent both thistles and people from living on a plot of fertile land.

Larger microorganisms, e.g. protozoa, larger algae, and fungus cells, can be removed easily from feed water with prefilters. Bacteria are another matter though. Argo and Ridgway (1982) monitored numbers of bacteria throughout the pretreatment system of Water Factory 2 1 with interesting results. Various media incubation techniques were used to determine viable cell numbers, and scanning electron microscopy (SEM) was used to determine total cell numbers. The only processes that removed any significant number of bacteria were lime softening and RO. The other processes in the system were recarbonation, mixed media filtration, granular activated carbon filtration, and chlorination. To be sure, chlorination does kill most of the bacteria, but the dead cells are not removed, and the live ones rebound quickly. The interesting part is the comparison of what went into the RO with what came out. The feedwater had a total bacteria count of 7.5 x 10^6 cells/mL and a viable cell count of 1 x 10^5 cells/mL, while the permeate had a total cell count of 1x10" cells/mL, all viable (99.9 percent rejection!).

Unfortunately, Argo and Ridgway did not monitor the concentrate stream (85 percent recovery). It would be interesting to know what the cell count there would be. At the cell counts reported in Ridgway's study, if all of the cells were retained in the system, it would take only 7.6 minutes to completely cover the membrane surface of a 4-inch element. In 2.6 days the module would be completely filled. This does not happen though, because while there are forces acting to retain cells on the membrane, there are other forces removing them. In this section the processes of transport, attachment, and detachment will be examined.

2.3.1 Transport to the membrane surface. Marshall and Blainey (199 1) describe the forces which transport bacteria to a surface. Fluid dynamic forces are the major transport mechanism in RO systems. The vexar spacer between membrane envelopes is designed to create turbulence to aid in transport back to the bulk stream. However, in creating turbulence, areas with low flow develop just downstream from each crossmember in the spacer. Several studies include images of membrane material with fouling build-up in these areas (Ridgway and Argo, 198 1; Milstead and Riley, 1993). Matter that is caught in the spacer is trapped until the flow pattern changes. During this time other forces are in operation. **Brownian** motion, random movement caused by

Table 2.3.—Physiological differences between microorganisms

	Microalgae	Fungi	Protozoa	Bacteria	virus
Size	Unicellular or multicellular	2-5 pm dia cells forming mycelium	5 µm to 1 mm	0.5-3 pm 0.2-0.5 pm starved	1 O-300 nm
Life cycle	Free living, or plant-like	Spore/mycelium or motile cells/ mycelium	Free living or parasitic, w/encystment	Sporulation after active reproductive cycle	Reproduction phase w/in host cells, dispersed phages
Metabolism	Photosynthetic	Simple carbohydrates, some can produce enzymes that enable them to utilize complex carbos	Omnivorous	Photosynthesis, oxidation of inorganics, or carbon w/wo 0,	None
Reproductive rate	Asexual fission, or thru spores, dependent on conditions	Vegetative from hyphal fragments, sexual or asexual spores	Dependent on nutrient level	0.3-l 5 hour mean generation time dependent on nutrient level	100 new phages w/in 30 min of infection
Attachment	W/acidic polysaccharide mucilaginous materials'	Rhizoid holdfasts	W/adhesive holdfast appendages, suction mechanism'	Hydrophobic interactions, surfaceappendages	No
Motility	W/flagella or free drifting	Reproductive cells	Flagella, pseudopodia, cilia, or nonmotile w/spores	Some do	No
EPS[2]	No	Yes	No	Some do	No
Cell Composition	Cellulase, diatoms w/silica	Chitin-cellulose	Some have calcareous or silica shells	Phospholipids, protein, peptidoglycan	Protein, may have lipoprotein capsid

[1] Corpe, 1980
[2] Extra-cellular polymeric substance

the movement of the water molecules, aids in transporting nonmotile cells to the vicinity of the membrane surface. Cells that are motile exhibit chemotaxis, movement toward beneficial chemical stimulus. As nutrients are concentrated at the surface of the membrane, especially in the back water areas, chemotaxis will proceed in the direction of the membrane surface.

2.3.2 Adsorption processes. Once the cell is in the vicinity of the membrane surface, it is held by a combination of forces. Hydraulic forces, electrostatic forces, mechanical attachment with polymeric surface structures, or hydrophobic attractive forces between the bacterial cell wall and the surface, have been indicated. At this point the cell is said to be reversibly attached. It can be dislodged by a moderate change in the shear force (Marshall and Blainey, 1991). After a certain amount of time, the bonds between cell and surface, whatever their nature, become more permanent. The pili, or fimbriae, protrude from the cell wall, piercing the membrane structure like tent stakes These structures are thought to grow faster when in the vicinity of an acceptable adsorption surface. The extra-cellular polymeric substance (EPS) surrounding the cell helps form a polymer bridge between the cell and the surface which becomes more secure with time. The extent of adsorption depends on three aspects of the system: the microorganism; surface characteristics; and liquid characteristics. There are several variables for each. Table 2.4 lists some of these factors (Flemming and Schaule, 1988b).

Ridgway et al. (1984) found that species of *Mycobacterium* seemed to be the colonizing bacteria at Water Factory 2 1. *Mycobucterium* were the sole species in colonies isolated from RO membranes for up to 57 days of operation. By the time 215 days had passed, the *Mycobacterium* had been superseded by species of *Acinetobacter, Shigella, Alcaligenes, Pseudomonas, Klebsiella,* and *Flavobacterium/Moraxella*. There are a couple possible reasons for this change in population. It could be that the flora and fauna of the feed water had changed over time. Or, as a filamentous, branching type of bacteria, *Mycobacterium* may be better adapted than the others to adsorption onto membrane surfaces. Once the surface has been modified by the presence of the *Mycobacterium* layer, other bacteria are able to attach.

In a study of how bacterial health and membrane material affect adhesion, Flemming and Schaule (1988b) found polyethersulfone to be resistant to *Pseudomonas vesicularis* and *Acinetobacter calcoaceticus,* but only slightly resistant to *Staphylococcus wameri* regardless of health.

How membrane surface characteristics affect cell adhesion is important. It has been shown that many types of biological fouling are minimized on surfaces with critical surface tension in the range of 20 to 30 dynes/cm (Baier, 1980). Membrane surface charge can also affect adhesion. Though net cell surface charge is negative, it is not evenly distributed over the cell surface. Complimentary charge arrangements between cell and membrane form electrostatic bonds (Daniels, 1980). The charge arrangements vary among bacteria types, which may explain Flemming and Schaule's results discussed above.

Another complicating factor is the phenomena of conditioning films. When a surface is exposed to natural water, organic molecules are spontaneously adsorbed onto the surface. As the accumulation increases, the surface characteristics of charge and surface tension are masked by the characteristics of the film itself. There is a measurable effect on cell adhesion when conditioning films are present, but it is not clear how or why. Fletcher and Marshall (1982)

Table **2.4.—Factors** affecting adsorption to membrane surfaces

Microorganism	Surface	Liquid
Species	Chemical composition	Temperature
Composition of mixed population	Surface charge	**pH**
Population density	Surface tension	Dissolved organic substances
Growth phase	Hydrophobicity	Dissolved **inorganic** substances
Nutrient status	Conditioning film	Suspended matter
Hydrophobicity	Roughness	Viscosity
Surface charge	Porosity	Shear forces
Physiological responses		Boundary layer
		Flux

found that adsorption of proteins to petri dish and tissue culture dish surfaces inhibited bacterial attachment when protein adsorption occurred prior to bacteria exposure. When exposure to bacteria and protein was concurrent, however, the inhibitory effect was much less. Characklis (1990) reviewed unpublished results showing that microbial adsorption is inversely proportional to the concentration of adsorbed organics, indicating that cells may be interacting with surface areas that have no adsorbed film as yet. In natural systems, the processes of organic or protein absorption and cell adsorption, are going on simultaneously. Characklis refers to the development of a "fuzzy" conditioning film in natural systems that may enhance cell adsorption by creating hooks, handles, and protected spaces that interact with pili, and/or EPS coatings.

2.3.3 Detachment of biofilms. It should be emphasized that the objective in alleviating biofilm obstructions is the removal of the biofilm, which is not the same as killing the bacteria. Flemming and Schaule (1988a) found that dead cells adhered just as securely as live cells. There are uncertainties about this, though. Whittaker et al. (1984) found that biofilms that had developed under high chlorine conditions were more effectively cleaned with a number of different formulations than biofilms developed under low chlorine conditions. However dead cells may have more of an obstructing effect on RO performance than live cells.

In the same study, Whittaker et al. found that the high chlorine system experienced a steady decline in productivity over time, while the low chlorine system maintained productivity over the period of the study (Ridgway et al., 1984). On SEM inspection, both membranes had developed a biofilm. The high chlorine system membrane was covered with lysed cells, while those on the low chlorine membrane were intact. There are two possible reasons for these results. It may be that the dead biofilm by itself was simply more obstructive to water flux. Or, the high chlorine concentration could have altered the chemical structure of the membrane, allowing the biofilm to penetrate further into the membrane structure.

One approach to finding ways to induce detachment of microorganisms, or to prevent their attachment, is to examine ways in which they are observed to detached. Perhaps one or more of these natural processes can be enhanced in an RO system without damaging the membrane. There are at least six causes of bacterial detachment from surfaces (Marshall and Blainey, 1991):

- Sloughing, detachment by shear forces when film exceeds critical thickness
- Changes in bacterial surface properties
- Changes in substratum surface properties
- Polymer cleavage, chemical, or enzymatic disruption of attachment polymers
- Change in metabolic state of bacteria, sporulation
- Release of daughter cells

2.3.3.1 *Mechanical removal.* The critical thickness of a fouling layer depends on the flow conditions and the roughness of the surface. Sloughing could be encouraged to occur sooner by periodically increasing the flow velocity. This is precisely what Kuepper (1982) did in studying the effectiveness of ultrasonic activation in improving RO productivity under fouling conditions. It was found that flow pulsing, increasing the flow rate while decreasing pressure, had more effect on productivity than the ultrasonic activation. Adding pulsed flow to the cleaning cycle has been shown to aid in lifting fouling films from the membrane surface (Milstead & Riley, 1993). Applying permeate back pressure also had a cleaning effect. Even shutting down the system periodically and restarting improved water flux. At the Yuma Desalting Plant, it has been found that permeate water left in the system on shutdown undergoes osmosis back to the feed side of the membrane. This gentle reverse flow seems to have a cleansing effect (E. Lohman, personal communication, 1993). These techniques cause changes in the flow pattern and, thus, enable matter caught in low flow areas to be carried away.

2.3.3.2 *Bacterial surface alteration.* Bacterial cell surface properties can be changed by reaction with constituents of the water. Due to the spatial variation in surface charge, bacteria are adsorbed onto a variety of charged particles. They have even been likened to biological ion exchange resins (Daniels, 1980). Unfortunately, they are so small that they are carried off by the particle. Consequently, bacteria are not so good for removing particles, but particles can be used to remove cells. There have been a couple studies using this phenomena to identify substances that prevent adhesion (Ridgway, Roger, and Argo, 1986; Flemming and Schaule, 1988b).

Ridgway tested several compounds for effect on adhesion of gram-positive, acid-fast, filamentous Mycobacterium species, strain **BT2-4,** on cellulose diacetate membrane material. The objective was to react attachment sites with the compound before exposing the cell to the membrane. They had fairly good results for octylphenoxy-polyethoxy-ethanol (Triton X 100, 63 percent inhibition), dodecyl sodium sulfate (40.9 percent), and hexadecyl-trimethylammonium bromide (49 percent). However, dodecylbenzyl-dimethylammonium chloride, and dodecyl-trimethylammonium bromide both enhanced adhesion (196.3 percent and 448.3 percent of control adhesion, respectively).

Flemming tried dodecylguanidine acetate (Dodigen), Triton X-100, and sodium bisulfite. Sodium bisulfite had the least effect. Dodigen had a better inhibiting effect than Triton X-100. There were significant differences between effects on the different membrane materials and bacteria species (2 gram-negative rod type species, *Pseudomonas vesicularis* and *Acinetobacter calcoaceticus*; a gram-positive *coccus* type, *Staphylococcus warneri*; and a mixed culture). Both Triton X 100 and Dodigen inhibited attachment to polyethersulfone, but were not effective against adhesion of the same strains to polyamide. They even enhanced adhesion in some cases. $NaHSO_3$ was best with *Staphylococcus wameri* on polysulfone. The other two worked against

Staphylococcus warneri on polyethersulfone. Polyetherurea showed mixed results. All worked well against gram-negative species; dodigen was good at 0.05 percent, and Triton X 100 and NaHSO₃ at 1 .O percent.

In both of these studies, the compound was dissolved in the water with the bacteria before exposure to the membrane surface. The compounds seem to be reacting with bacterial attachment sites. These studies do not reveal whether the results were due to reaction with attachment sites on the bacteria or competition for reaction sites on the membrane. Was sufficient compound concentration used to completely react with the bacteria or the membrane? Most likely there are different types of reaction sites on both surfaces. Are the different compounds reacting with different sites? Could a combination of surfactants be more effective?

2.3.3.3 *Changes in substratum surface properties.* An alternative to changing the bacterial surface properties is to change the membrane surface properties via protein-resistant surface coatings. The compounds most studied in this capacity are copolymers with polyethylene oxide (PEO) side chains, such as Triton X 100. The idea behind this approach is to use a hydrophobic backbone polymer that will adsorb onto the membrane surface, and to add coiled hydrophilic side chains that will be repelled from the membrane surface and wave about in the solution. There are three forces at work between the surface coating and approaching cells. First, there is stearic repulsion. The PEO chains are like springs; they can be compressed to only a certain point before they release forcefully, thereby preventing cells from getting close enough to the surface to form irreversible bonds. Secondly, van der Waals forces attract cells to the surface, but they are much weaker than the stearic repulsion forces. The third force is hydrophobic attraction. Hydrophobic attraction of a particle to the membrane surface can overcome the stearic repulsion forces in some cases; it is mostly dependent on the density of the PEO side chains on the copolymer (Jeon et al., 1991). While bacterial cell walls do have hydrophobic patches, the EPS surrounding the cell is hydrophilic (Marshall and Blainey, 1991). So, there should not be strong hydrophobic interactions between cell and membrane surface.

Before surface coatings can do any good in preventing cell adhesion, they must be securely adsorbed onto the membrane surface. Lee et al. (1990) studied the degree of adsorption of copolymers of alkyl methacrylates with methoxy (polyethylene oxide) methacrylates on low density polyethylene (LDPE) surfaces. Surfaces were exposed to the copolymers for 30 minutes, then rinsed for 30 minutes before protein resistance testing. They found that the extent of adsorption was dependent on the hydrophobicity of the copolymer. The ones that were least soluble in water were more extensively adsorbed onto the surface. LDPE surfaces coated with these copolymers also exhibited the lowest degree of protein adsorption. Evidently, protein resistance was limited to areas coated with copolymer. When the amount of adsorbed polymer left after protein resistance testing was compared to pretest levels, it was found that the highest performer lost over 25 percent coverage. The strong hydrophobicity of the copolymer allowed it to be de-adsorbed by interaction with the hydrophobic protein molecules.

In previous studies, commercial PEO containing block copolymer surfactants with different structures were tested in the same manner (Lee et al., 1989). Synperonic PE-L64C proved to be best at both adsorbing to the surface and inhibiting protein adsorption. Synperonic has an alternating structure of hydrophilic and hydrophobic blocks, such that short hydrophobic

sections are connected with hydrophilic loops. The other products tested where Pluronic L64, Butronic 184, and Tetronic 1504. Pluronic and Butonic have a hydrophobic center block with hydrophilic sections on each end. Tetronic is a hydrophobic four pointed star-shaped block with hydrophilic sections on each arm. Surface concentration of Pluronic and Butronic were too low after rinsing to affect protein adsorption. Tetronic had a good adsorption rate at high concentrations and remained adsorbed after rinsing. Low concentrations of Synperonic formed just as good a coating, though, and performed better in the protein resistance test.

Adsorbance of these copolymers resulted in a **decrease** in surface energy from near 70 dynes/cm, to between 30 to 40 dynes/cm, close to the optimum for biofouling resistance. The degree of hydrophobicity was also changed, one way or the other, by the attachment of the copolymer. The net result was a resistance to protein adsorption. Fletcher and Marshall (1982) tested the effect of protein adsorption on surface energy and bacterial adhesion. They found that protein adsorption **also** decreased the surface energy and increased the hydrophilicity of petri dish and tissue culture dish surfaces. As with copolymer coatings, the result of these changes was a drastic drop in subsequent bacterial adhesion. From these two studies, it appears that, generally, a decrease in hydrophobicity and surface charge promotes resistance to adsorption. It is strange that in one case the hydrophilic and structural nature of a polymeric coating aids in resisting protein adsorption, and in the other, a hydrophilic protein coating resists bacterial adhesion. It could be that the attachment mechanisms, and therefore the resistance mechanisms, are the same. Bacterial EPS is hydrophilic, while the cell is hydrophobic. Cells with an EPS envelope would not be attracted to a hydrophilic surface because it would "look" the same as the surrounding liquid media, and also like the EPS itself. If it is not coated with EPS, the hydrophilic appearance of the surface should prevent hydrophobic attraction between the membrane and the cell.

In a study on the role of cell-surface carbohydrates in adhesion processes, mammalian cells adhered to surfaces with adsorbed galactose, yet did not adhere to surfaces with glucose or N-acteylglucosamine coatings (Chipowsky et al.,1973). It is interesting that bacterial cell walls contain N-acteylglucosamine (Carpenter, 1977), and glucose makes up a portion of the EPS in coagulase-negative *Staphylococci* species (Hussain et al., 1991) and most likely other slime producing bacteria. Could the lack of adhesion of mammalian cells to bacterial EPS components be a defensive mechanism, or would bacterial cells behave similarly? Are these two components in mammalian cell membranes as well? Could a coating similar to mammalian cell membranes help in RO membrane treatment?

Whether any of these results can be applied to water treatment membranes is unknown. Membrane surfaces are hydrophobic, but not as hydrophobic as tissue culture dishes. Also, adsorbed proteins, sugars, or polymers may not remain on the surface when exposed to the flow rate used in RO. Owens, Gingel, and Rutter (1987) measured shear stress needed to remove red blood cells and *Escherichia coli* cells from glass slides treated with Pluronic (a copolymer that did not adsorb strongly to LDPE) and found that 0.03 N/m^2 was sufficient to remove 97-99.5 percent of the cells. In comparison, the wall shear stress in a 10 cm diameter RO module with a AP of 70 kPa (max $\Delta P=138$ kPa, specified by Fluid Systems) would be roughly 130 N/m*. What shear stress can the adsorbed coating withstand?

There is some indication that surfactants do bind irreversibly to membrane surfaces. Milstead and Riley (1993), in a study performed for Fort Belvoir RD&E Center, found that all the nonionic surfactants that they tested caused a marked decrease in productivity in FilmTec membranes (polyamide, negative surface charge). To find out if the fouling was reversible, they induced osmotic flow backwards through the membrane by exposing the feed side to urea and the permeate side to distilled water. After 30 minutes of this treatment, the membrane was tested under seawater feed conditions. Productivity was improved from 48 percent of control to 60 percent. Only 23 percent of the obstruction was removed with the other 77 percent irreversibly bound to the membrane surface. The trouble is that surfactants used in the studies mentioned above did not prevent adhesion very well on polyamide membranes. It would be interesting to find out if the surfactants irreversibly bind to the other membrane types and if so, do they maintain productivity while preventing biological adhesion.

2.3.3.4 Disruption of attachmentpolymers. The goal of the disruption strategy is to break as many bonds as possible in hopes that many attachment bonds will be among them. Whittacker et al. (1984) tested several different types of compounds and combinations in this capacity. Table 2.5 lists the types, their mode of action, and some popular examples of each.

Of all the examples listed, none would work well as a cleaning agent by itself. This is because there are three different tasks to be performed in the disruption strategy. First, complex usubstances, such as EPS, must be broken down. Metallic ions, especially calcium, are integral components of extracellular structures. Once released, metallic ions must be complexed with a sequesterant or surfactant to prevent redeposition. Finally, the whole mess must be transported out of the module. In Whittaker's study, the top five performers for biofouling removal were combinations of two or more of the classes listed above. Urea and sodium dodecylsulfate (SDS) worked the best; Biz, which is a combination itself, was next; then there were a few enzyme-sequesterant combinations that did well. In another cleaning study, mild abrasives were also added (Milstead and Riley, 1993)

2.3.3.5 Change in metabolic state. After an active reproductive phase, many species of bacteria go into a sporulation stage. It is believed to be initiated by deteriorating nutrient supplies. Half of the DNA of the cell is partitioned off into one end of the cell. Through a series of stages, a membrane forms around the DNA, thickens, and becomes highly thermoresistant. The whole process can take from 6 to 7 hours (Carpenter, 1977). After the cell spore is complete, it detaches, and is carried away by the current to better grazing grounds (Marshall and Blainey, 199 1). It may be possible to induce sporulation in a monoculture, but with the mixed population likely to be found in an RO module, it would be difficult. There would be a different chemical trigger for each trophic type.

2.3.3.6 Release of daughter cells. This last detachment scenario may not seem to be too helpful at first glance. However, if daughter cells are released into the bulk stream, it would be advantageous to prevent them from reattaching within the RO system. The "schange cell surface" strategy could be useful. If a low dose of surfactant is used during normal operation, daughter cells may be prevented from reattaching.

Table **2.5.—Biological** agents of disruption

Class	Mode of Action	Examples
Bactericides	Kills microorganisms through cell lysis or dissolution	CTAB', GuHCl*, MBTC', Urea, ZDDC"
Chaotropic-denaturing agents	Denatures proteins rendering their organic constituents readily soluble	Urea, GuHCl, SDS'
Enzymes	Hydrolysis of the proteinaceous and glycoprotein exopolymers surrounding the microorganisms	Trypsin, Protease, Thermolysin, Papain, Esterase, Pancreatin, Biz'
Surfactants-detergents	Neutralizes charged colloidal particles and resolublizes or resuspends them	Triton X-100, Biz, CTAP TSP*, STP', SDS
Sequesterants	Forms complexes with metal ions	EDTA, Citric Acid

. CTAB. cetyltrimethylammonium bromide; GuHCl, guanidine hydochloride; MBTC, methylene bisthiocyanate; SDS, sodium dodecylsulfate; STP, sodium triphosphate; TSP, trisodium phosphate; ZDDC, zinc dimethyldiihiocarbamate. Biz is a laundry presoaking detergent containing broad spectrum enzymes and bleaching compounds. Adapted from Whittaker, Ridgway, and Olson, 1984.

2.4 Interactions Between Obstruction Components

There are dismally few studies on the interactive effects between components in natural water undergoing RO compression. There is acknowledgment that scale and particulate build up do provide attachment sites for biological fouling. Biological fouling is acknowledged to change pH, dissolved gas, and ion concentrations at the membrane surface (Paul, 1993; Ramakrishna and Desai, 1991). However, studies are usually conducted during normal operating mode (Ridgway's work), with pure bacterial cultures (Ridgway and Flemming's work), or with limited mixed cultures (Flemming). Ridgway does report complete water analyses for each step of their water reclamation process, but there is no speculation about the contribution of components other than the bacteria. Part of the problem is the inability to measure parameters at the membrane surface during operation.

To study obstruction development using complex feed water under real operating conditions, one would need real time information to establish the interaction pathway. A pathway is the series of events that led to the development of the final result. Alternatively, one could look at the final result, and compare it to the results of the many possible pathways that could occur. All the possible pathways would need to be defined, though. Even then, many pathways may appear to lead to the same result. If the object is to find a way to stop the reaction, or divert it, one needs to know the actual pathway. The task grows geometrically.

As yet, investigations have no model for the behavior of multiple component inorganic solutions. For instance, if there is an inorganic salt solution with species that have multiple pH

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dependent dissociation states, what happens? Uncharged species are only rejected through size exclusion. For many important compounds, uncharged intermediates may form and pass through the membrane. Does this drive the balance toward formation of more uncharged species, or does the water leave the system before any change can take place? How does this affect the pH? This problem is even more puzzling in nanofiltration (NF) systems where multivalent species are being separated from monovalent species. Interactions of this sort can be calculated from the concentrations of the ions involved and their interaction coefficients. It is a very tedious calculation, but could be automated. A method for including pressure and temperature effects would have to be devised.

What happens to large organic molecules in an RO system? Are they embedded in the membrane? Do they provide nutrients for biogrowth, or are they too large for bacteria to metabolize? It is likely that these huge molecules are involved in film conditioning. If so, they would definitely have an impact on the RO system. Is it good, or bad? The most aggressive response to fouling prevention may not be the best solution. Perhaps a certain amount of "conditioning" is beneficial, as long as a lower productivity is acceptable. It may be that membrane producers are quoting an unrealistic expectation for productivity.

2.5 Recommendations

Based on the literature search, the following recommendations are offered for alleviating membrane fouling and/or improving the effectiveness of cleaning procedures.

- Look for ways to modify the membrane surface to make it less prone to fouling.

  It is beyond the resources of the project and the lab to study the efficacy of using natural cell components to inhibit membrane fouling. With the joint sponsorship of TACOM it was possible to contract with Professor A. Zydney to identify surfactants that can be used to modify the membrane surface to hinder adsorption of foulants on the membrane. This study will be discussed in chapter 4.

- Devise a method for monitoring operating parameters at the membrane surface during operation or in simulation of operating conditions. Parameters of interest are pH, temperature, pressure, flow rate, and conductivity.

  Optical fiber sensors are available that could be used to monitor these parameters. Testing these sensors has been an objective of TSC's "New Investigative Techniques" research project.

- Determine how solubility of major water constituents is affected by pressure up to 8,000 kPa and ionic strength expected at membrane surface under sea water conditions.

The solubility of many solutes increases with moderately high pressure and ionic strength. Whether this trend continues under conditions found in a seawater RO systems is unknown. But the complexity of the problems is beyond the scope of this project.

- Measure microbial cell concentration in the effluent of each pretreatment process and in concentrate and permeate streams of an RO system to determine points where microbes are being introduced or removed from the system. Such a study could help refine water treatment process sequencing to minimize biological fouling. Another benefit would be to prove or disprove the idea that membrane processes form a microbial barrier.

  Heterotrophic plate counts were taken for samples drawn from the source, detention tank, after cartridge filtration, interstage NF, permeate and reject streams during NF testing at Lake Havasu City, Arizona, and in RO testing at Avondale. Results have been published in R-95-09 (Boegli et al., 1995). The only significant loss of microbial population occurred in the cartridge filter. The NF provided only a 30 percent rejection of live bacteria.

- Perform experiments to complete a three dimensional graph relating bacterial cell type, membrane polymer, and surface active coatings. A chart of this information would be valuable in choosing a membrane to match fauna or feed water and in developing surface coatings and new membranes.

  This task is part of a current research project being performed at Water Factory 2 1.

- Explore the possibilities for an oscillating pressure pump for use with membrane applications. Automatic flow changes during operation may reduce fouling and may not be detrimental to the system.

  The idea of using an oscillating pump in microfiltration is being pursued by a group at University of Colorado, Boulder under the Water Treatment Technology Program.

Since the literature search was completed, further developments have been made in some of these areas.

3. Membrane Treatment and Performance Testing

3.1 Introduction

This portion of the project focuses on modifying existing membrane surfaces so as to reduce the extent of fouling from organic, biological, and colloidal sources during membrane filtration. Fouling materials are transported to the membrane surface during RO and NF and accumulate in the boundary layer. Material that comes in close contact with the surface, while in the boundary layer, can become adsorbed. The control of biofouling during membrane filtration is an extraordinarily complex problem due to the enormous range (and properties) of the biofoulants which may be present in any given aqueous system. Biofoulants include both macromolecular species like humic acids, polysaccharides, lipids, and glycoproteins, as well as a variety of microorganisms, particularly bacteria. The macromolecular components tend to have a broad range of chemical groups on their surfaces. The chemical groups can interact with the membrane through van der Waals, electrostatic, hydrophobic, and/or hydrogen bonding. Bacterial cells can be an even greater problem.

A variety of surface modification strategies have been reported which can be roughly grouped into four distinct "strategies," based on the underlying philosophy of the approaches used to improve the fouling resistance:

- Increased hydrophilicity
- Introduction of negatively charged surface groups
- Steric repulsion
- Biomimetic (biological) modifications

Increased hydrophilicity: A large number of attempts have been made to improve the fouling behavior of available membranes by increasing the hydrophilic character of the membrane surface. The logic behind this approach is clear: for any protein or cell to adsorb (or adhere) to the membrane, it must first displace the water molecules that are chemically associated with the surface groups on the membrane. Several studies have specifically demonstrated that increased hydrophilicity can result in a significant reduction in both protein adsorption and cell adhesion (e.g., Baier, 1980; Fletcher and Loeb, 1979) and in turn biofouling.

Introduction of negative charges: Most proteins and cells are negatively charged in aqueous solution, thus the introduction of negative charges on the membrane surface should (at least in principle) increase the electrostatic repulsion between the membrane and the cells/proteins. Most studies of surfactant-modified membranes provide very clear evidence for this general phenomena, with negatively charged surfactants being much more effective at reducing fouling than the corresponding cationic surfactants (Chen et al., 1992.)

Biological modifications (biomimetic surfaces): Many biological surfaces (e.g., the surface of endothelial cells) are naturally nonadhesive to most proteins and bacteria. It should, at least in principle, be possible to modify existing membrane surfaces to "mimic" the chemistry of these natural biological surfaces, thereby reducing the extent of biofouling. The attachment of heparin

or heparin analogs to polyurethanes has been shown to reduce the extent of protein adsorption and in turn blood clotting (Casu, 1994). In addition, Chapman (1993) has demonstrated the attractiveness of this technique for the preparation of nonfouling membranes using phosphorylcholine (one of the primary phospholipids in the outer surface of the mammalian cell membrane.) Note that most of these biological modifications are hydrophilic in nature, and they may also introduce negatively charged side groups onto the membrane surface.

Steric hindrance: Protein and cell attachment to the membrane can also be reduced by grafting large polymer chains to the membrane surface so as to sterically exclude the cells/proteins from the immediate vicinity of the membrane. This type of approach has been used extensively in the stabilization of colloidal particles, and it has also been shown to be effective at reducing protein adsorption (Amiji and Park, 1994.) Stearic hindrance is the primary mechanism involved with the surfactant-treated membrane tested here.

There have been several studies of membrane modification with surface active molecules to minimize the effects of "foulants." Speaker (1993) summarized the use of Langmuir-Blodgett (LB) or self-assembled monolayers on RO and UF membranes with a variety of hydrocarbon and fluorocarbon surfactants to counter fouling from humic substances. Less flux decline was observed in many cases. Kim et al. (1989) have also examined the effects of LB layers on the fouling characteristics of several UF membranes using a variety of nonionic surfactants (Polyether oxide (PEO) -based with nonyl phenol hydrocarbon chain). They observed significant reduction in fouling during protein ultrafiltration. The best results were obtained for a PEO chain length of 13 and hydrophilic-lipophilic balance (HLB) of 14.4. The flux decline was somewhat greater for membranes modified with surfactants having both higher and lower HLB numbers (12.3 and 16.0), although all modified membranes exhibited improved performance relative to the untreated ones.

Brink and Romjin (1990) coated a large number of different surfactants onto UF membranes from bulk solution. They then analyzed the effects on membrane fouling from protein solutions. They found a significant reduction in protein adsorption on the surfactant-modified membranes, but only a very slight improvement in fouling resistance during actual protein ultrafiltration. Chen et al. (1992) also used coating from bulk solution to adsorb small anionic surfactants, both alone and in combination with nonionic ones, as pretreatments of UF membranes. They reasoned that synergistic mixtures of surfactants could provide combinations of electrostatic, steric, and hydration interactions that could be optimized for the particular solutes and membranes. Their results with protein ultrafiltration did indicate substantial improvements in fouling resistance from combinations of surfactants. The improvements were pH dependent, thereby confirming the role of the electrostatic interactions.

Flemming and Schaule (1988b) examined the effects of a specific octyl phenol-PEG surfactant (Triton X-100) on bacterial adhesion to polysulfone, polyethersulfone, polyamide, and polyetherurea reverse osmosis membranes. Studies were performed using both 0.1 percent and 1 .O percent Triton X- 100, with better results found for the higher concentration solution.   It should be noted, however, that these experiments were done by adding the surfactant to the process water, thus it is impossible to determine if the reduction in bacterial adhesion seen in

these experiments was due to the actual modification of the membrane or to an alteration in the surface properties of the bacteria themselves (e.g., a reduction in bacterial hydrophobicity due to the adsorption of the Triton X-100 onto the bacterial surface).

There is currently no widespread agreement with regards to the relative advantages of these different surface modification strategies, nor is there any agreement as to the specific chemical group(s) or additive(s) that would be best at satisfying the different objectives of each of these approaches. But an extensive amount of prior work on increasing the biocompatibility of materials has shown that polyethylene oxides are able to reduce protein adsorption and cell adhesion. PEO can both increase the surface hydrophilicity and sterically exclude the proteins/cells from the immediate vicinity of the membrane (Lee et al., 1989 and 1990; Jeon et al., 1991).

PEO groups have been both surface adsorbed and covalently bonded. The latter attachment strategy certainly minimizes the uncertainties with regards to the integrity and extent of surface coverage, but can be difficult to accomplish. Surface adsorption using block copolymer surfactants, where the more hydrophobic portion of the surfactant has favorable free energy of attraction for the polymeric surface, can be accomplished with **simple** coating approaches. By taking this approach, one can make systematic chemical changes in a relatively straightforward fashion, **perform** transport evaluations and some material characterizations on the laboratory bench scale, and then continue on to larger scale pilot evaluations with relatively modest resources.

Surface-adsorbed polyethylene oxides with differing PEO chain lengths and **hydrophilic-**lipophilic balance (HLB) were chosen for this study. Current efforts included surface-adsorbing, from bulk solution, five PEO-based surfactants onto commercial flat sheet membranes of CA and **PA/TFC**. These membranes were then evaluated in salt water permeation measurements, with and without preadsorption of complex foulants.

3.1.1 Methods for Evaluating Success. To determine whether a surface treatment was successful, several questions have to be answered.

- Will the surfactant adsorb to the membrane surface evenly and remain adsorbed?
- Will it decrease the water permeation rate?
- Will it decrease the rejection rate?
- Will it prevent fouling or other forms of membrane performance degradation?

Swatch testing can provide information to answer all these questions, but there have been reproducibility problems with swatch testing in the past. The membrane has to be placed in exactly the same position each time. The permeate carrier has to be cut precisely or fibers will cut into the active surface area. The spacer material, or turbulence promoter, is left out for the same reason. With these changes, the hydraulic conditions in the swatch test system are not analogous to conditions in a spiral wound element. For these reasons, other methods of evaluation were sought to back up the swatch testing results. Zeta potential was chosen as a qualitative measure of the extent of change in surface energy of the treated membrane. An ultrasonic measurement technique was chosen as a qualitative measure of differences in fouling

layer thickness. Atomic force microscopy (AFM) was chosen to provide information about changes in surface roughness and the uniformity of the surface treatments. Finally, scanning electron microscopy was used as a visual aid in verifying information from the other methods.

3.2 Experimental Methods

3.2.1   Surfactant selection and application. Factors influencing the effect of a surfactant on membrane surface properties are the hydrophilic-lipophilic balance (HLB), charge, size of the molecule, and length of hydrophilic branches. Two types of surfactants were selected, the Triton-X and Pluronics varieties.   Surfactants of each type with a range of HLB values were selected to determine the effect of HLB value. Table 3.1 lists the surfactants tested and their characteristics. Their molecular structures are shown in figures 3.1 and 3.2.

Table   3.1   .-Surfactants   and   their   characteristics

Surfactant	m	n	% PEO	HLB	Total MW
Triton-X 35	N/A	3	39	7.8	340
Triton-X 100	N/A	9	66	13.5	604
Triton-X 705	N/A	70	94	---	3288
Pluronics P84	30	34	40	12-18	3750
Pluronics F87	-30	119	70	24	7500

The lipophilic (hydrophobic) portion of the surfactant, polypropylene oxide, for the Pluronics and the octylphenol group for the Triton-X series, adsorbs strongly to the hydrophobic membrane surface. Polyethylene oxide (PEO) is the hydrophilic group on both of these surfactants. It extends away from the membrane surface into the boundary layer. The PEO side chains are not rigid, nor are they entirely free to move. Ideally, intermolecular forces between groups would cause them to repel each other so that they stand up from the surface, rather than tangling together. When compressed, the side chains would give to a certain extent, but then spring back forcefully, repelling particles back into the bulk stream.

Surfactants were mixed with deionized (DI) water and buffered to pH 6 in a water bath held at 298°K. A concentration of 0.1 weight percent was used initially for swatch testing. Later, the polyamide membranes were tested at a concentration of 0.001 weight percent. Membrane elements were also treated with the lower concentration. Swatch test samples were attached to a Plexiglas plate so that only the active surface would be in contact with the surfactant solution. Plates were suspended in the water bath for 24 hours. The solution was gently agitated to maintain circulation past the membranes.
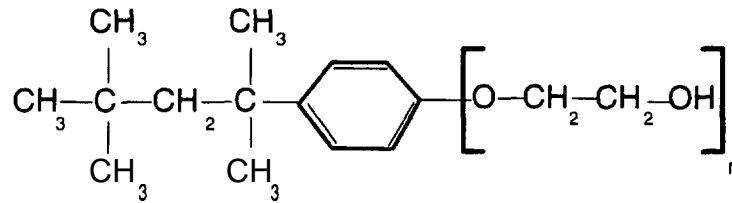
Figure 3.1 .-Triton-X series surfactants.

$$(C_3H_6O)_m(C_2H_4O)_nH$$

Figure 3.2 .-Pluronics series sutfactants.

3.2.2   Standard fouling solution. The standard foulant mixture was a commercial vegetable protein mixture. The choice of this mixture was based on the following criteria:

- A complex and reproducible mixture containing biological compounds (cells, proteins, and small and large organic molecules)

. Water soluble

- Inexpensive and available in large enough quantities so as to be viable for scaling up to larger water volume transport tests

Reproducibility was not considered a problem with this fouling solution for two reasons: first, it was inexpensive enough that several pounds were purchased immediately; and second, the manufacturer's product quality control (being based on taste) would help insure that future batches would likely be very similar.

The fouling solution was prepared by mixing the-powder with boiling water and letting it steep until cool enough to handle. The solution was then filtered through cheese cloth to remove particulates. The solution pH was raised from <3 to 6 with sodium bicarbonate before use.

To evaluate the "fouled" condition transport properties for swatch testing, membranes were returned to the water bath, as for surfactant treatment, with a 0.1 percent weight fouling solution. This method was chosen for two reasons:

- Every membrane would be exposed to the same "fouling conditions." Fouling the membranes under filtration conditions allows differences in hydrodynamic conditions and membrane permeability from cell to cell to contribute more uncertainty to the data interpretation.

3.5

- Also, once the foulant mixture has been recirculated in the swatch testing apparatus, it requires a very lengthy cleaning period before it is completely removed. This situation diminishes the amount of data that can be collected in a reasonable time period.

3.2.3 Swatch testing. Flat sheet cellulose acetate blend RO (CD series) and NF (CG series) membranes were purchased from Desalination Systems, Inc. Polyamide thin film composite RO (BW-30 series) and NF (NF40 series) membranes were purchased from Dow Chemical.

Six sets of three rectangular "swatches" (mass transfer area of 189 cm^2) of each type of RO membrane were cut and treated as described above with one of the five surfactant solutions. The control set, without surfactant, was placed in a DI water bath in the same manner and at the same pH and temperature as the treated sets, After surfactant treatment, a set of membrane swatches was tested in an Osmonics test cell system (see figure 3.3) at the appropriate pressure and flow rate (see table 3.2). The test solution contained 2,200 mg/L NaCl in RO permeate. The pH was kept within the range of 5.5-6.4 with HCl. Swatches were labeled with a test cell number and code for surfactant treatment.

Table 3.2.—Operating conditions for swatch testing

Membrane	Operating pressure (kPa)	Reject flow rate (L/min)	pH
CA RO	2757	5.3	6
CA NF	950	5.3	6
PA RO	1750	5.3	6
PA NF	950	5.3	6

Measurements were made every hour over 3 to 5 hours. Retentate flow rate, feed pH and temperature, and pressure before and after each test cell were recorded. Samples were taken of the retentate, feed, and each product stream. Flow rates were determined by weighing samples that had been collected in a container for 30 seconds to 10 minutes, depending on the amount of flow. A sample size of at least 50 mL is needed for accurate conductivity and temperature measurements. Conductivity was measured with a Beckman model RC-18 conductivity bridge. Temperature was measured to within a tenth of a degree centigrade. Testing was continued until product flow had leveled off for at least three sample periods.

After testing clean membrane performance, the swatches were returned to the water bath, in the same manner as for surfactant treatment, with a 0.1 weight percent fouling solution prepared as described above. The swatches were left in the fouling bath for 24 hours, after which they were returned to the test cell system for performance re-evaluation. Swatches were placed in the same cells as they had been in during initial testing. While awaiting their turn, swatches were refrigerated in DI water.
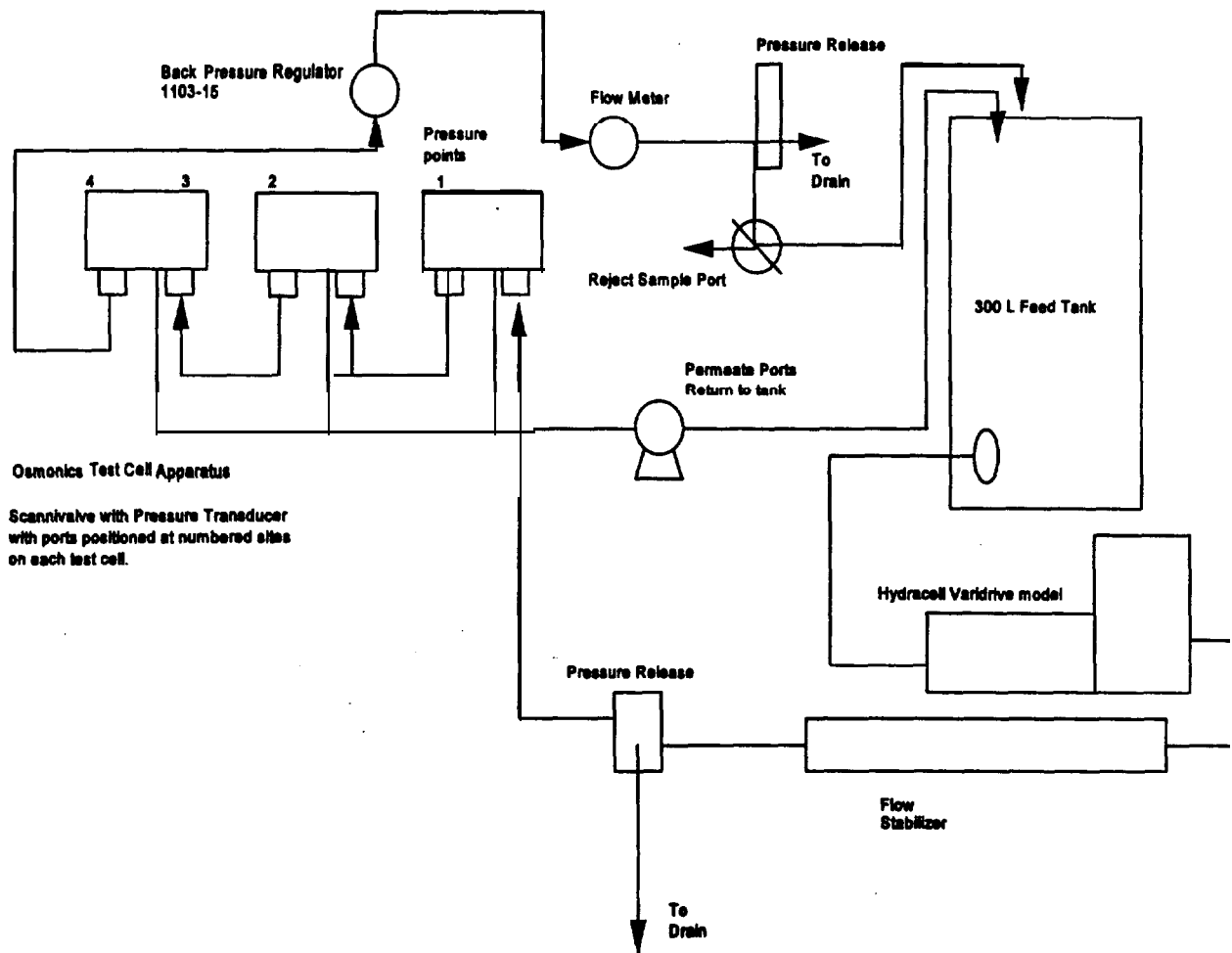
Figure 3.3.—Swatch test system with three Osmonics test cells in series.

3.2.4 Transport evaluation. Feed flow rate is calculated as the sum of the product flow from each test cell plus the concentrate flow:

$$Q_{F_1} = Q_r + \sum Q_i$$

1)

Conductivity is normalized to 25 °C with the following relationship for NaCl solutions:

$$X_{25} = X_T \cdot 1.0213^{(25-T)}$$

2)

Where T is the temperature in °C, and X_T is the conductivity at temperature "T."

X_{25} is converted to mmoles/L:

$$C_{F|} = \frac{0.4682 *X_{25_{F_1}} *(1+1.964e-3*\sqrt{X_{25_{F1}}})}{58.44} \qquad 3)$$

Feed concentration to the second and third cells is estimated as follows:

$$C_{F_i} = \frac{Q_{F_{(i-1)}} C_{F_{(i-1)}} - Q_{P_{(i-1)}} C_{P_{(i-1)}}}{Q_{F_{(i-1)}} - Q_{P_{(i-1)}}} \qquad 4)$$

Where Q is the flow rate and C is the concentration of the feed stream (subscript "F") and product stream (subscript "P"). The denominator, $Q_{F(I-1)}-Q_{P(I-1)}$, is the feed flow rate for the ith test cell.

A mass balance is calculated as follows for use in monitoring observation accuracy:

$$1 \approx \frac{Q_{F_1} C_{F_1}}{Q_{P_1} C_{P_1} + Q_{P_2} C_{P_2} + Q_{P_3} C_{P_3} + Q_R C_R} \qquad 5)$$

Normalized water flux and rejection were used as the evaluation variables. Rejection is calculated for each cell as follows:

$$R_i = 1 - \frac{C_{pi}}{C_{f_i}} \qquad 6)$$

and for the system overall:

$$R_{overall} = 1 - \frac{(Q_{P_1} C_{P_1} + Q_{P_2} C_{P_2} + Q_{P_3} C_{P_3})}{Q_{P_{total}} * C_{F_1}} \qquad 7)$$

The water flux (NPF_i) is the permeate flow normalized for net driving pressure (NDP) and temperature:

$$NPF_i = \frac{NDP_i}{NDP_{i_o}} * \frac{TCF*Q_i}{A*P_{Fi}} \qquad 8)$$

$$\qquad 9)$$

$$NDP_i = P_{F_i} - \left[\frac{C_{F_i}+C_{F_{(i+1)}}}{2} - C_{P_i}\right]*8.314e^{-3}T$$

Where: NDP_i is the NDP for cell I at sample time
               NDP_{oi} is the initial NDP for cell I
               TCF is the temperature correction factor
               Q_i is the volume per second of the ith product sample
               A is the active membrane area in cm^2
               P_{Fi} is the pressure to test cell "I" in kPa
               T is temperature in degrees Kelvin
               $8.314e^{-3}$ $kPa{\cdot}dm^3{\cdot}mmole^{-1}{\cdot}K^{-1}$ is the universal gas constant

For cellulose acetate NF and RO membrane with T in $°K$:

$$TCF_{CA} = e^{[2333.17*(1/298.15 \quad 1/T)]} \qquad 10)$$

For polyamide thin film composite NF and RO membrane when $T< 25$ "C:

$$TCF_{PA} = \frac{1}{0.35 + 0.026*T} \qquad 11)$$

When $T> 25°C$ (T in $°K$):

$$TCF_{PA} = e^{-[2640*(1/298.15 - 1/T)]} \qquad 12)$$

3.2.5 Element testing. Having acknowledged the "perils" of adding the foulant mixture to the swatch testing apparatus, element testing was done at the last stages of the current studies to verify the effects of the best performing surfactant treatment. Two sets of four · 6.35mm (2.5 inches) CA RO elements were tested in the RO Test System of Reclamation's Water Treatment Engineering and Research Group (see figure 3.4). DI water was circulated through the

control set for 24 hours. A 0.001 weight percent Triton X-100 solution buffered to pH 6 was circulated through the other set for the same period of time. Both sets were evaluated with a 0.04M NaCl solution for 24 hours at 2,757 kPa feed pressure, then with the same salt solution - to which a 0.001 weight percent foulant mixture was added - for another 24 hours. The elements were then rinsed with RO permeate for 3 hours and retested with the 0.04 M NaCl solution for another 24 hours. Feed conductivity and temperature, reject flow and conductivity, and permeate flow and conduc-tivity data from each element were collected automatically at 20 minute intervals throughout the test period.
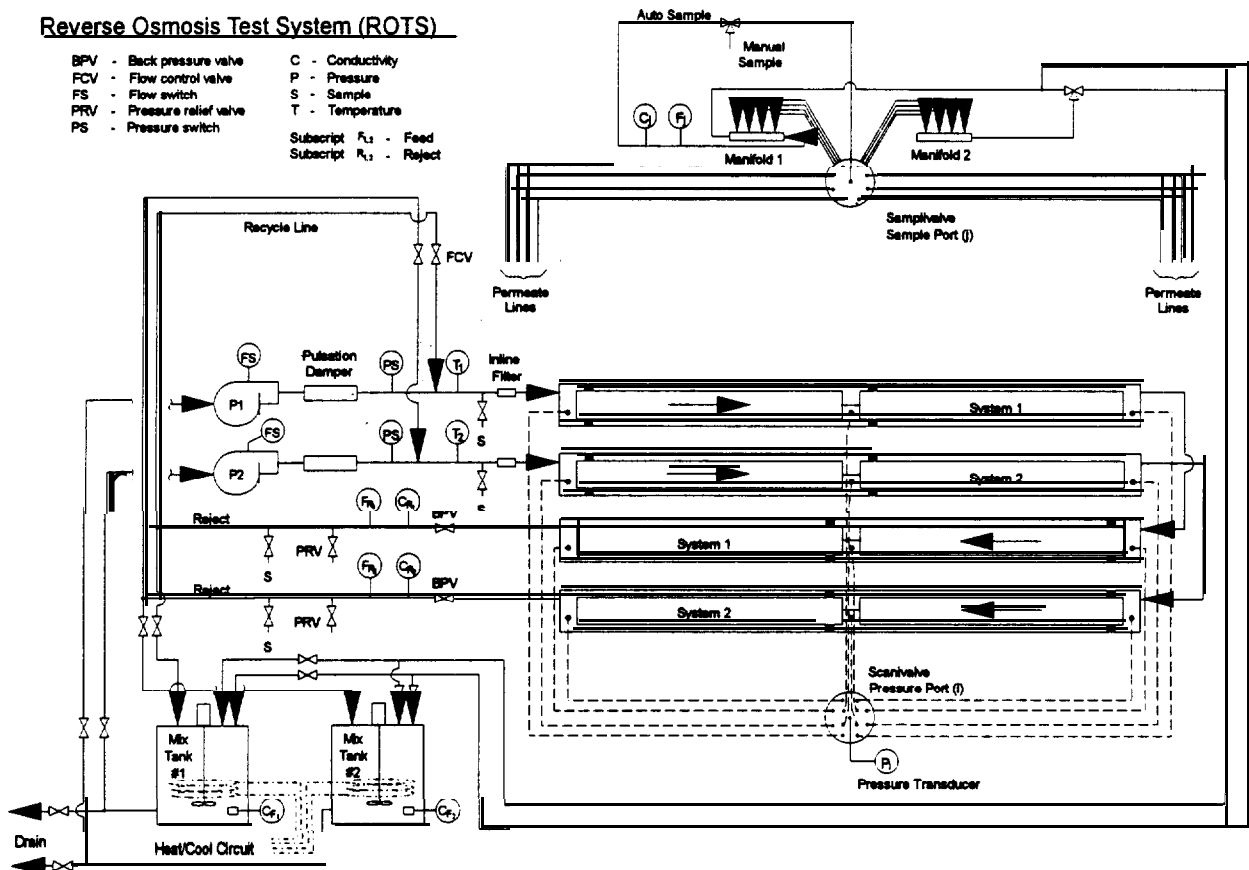

Figure 3.4.—Water Treatment Engineering and Research RO Test System used for element performance testing.

3.3 Results

3.3.1 Swatch Testing. Figures C. 1-C.5, in appendix C, show the change in normalized permeate flow (NPF) and rejection for cellulose acetate RO membrane untreated and treated with each surfactant before and after fouling. Figures C.6-C. 10 show the same for polyamide RO membrane. The results for CA and PA nanofiltration membrane untreated and treated with

Triton-X 100 are presented in figures C. 11-C. 12. Each point represents one swatch of a set of three tested in series. The open symbols, denoted with an "(F)" in the legends, represent data collected after fouling. The time between removal from the fouling bath and retesting ranged from one-half hour up to 1 week. If the swatches were not going to be tested right away, they were stored in distilled water in the refrigerator.

In some cases, there was a great deal of variation between the performance of swatches within a set. The worst case was the baseline CA RO membrane. If the three observations are averaged, any of the treatments would be an improvement. If the failed membrane is thrown out, then, to be fair, the other poor performers would have to be thrown out too. The result of that exercise would be no difference between tests! To avoid that trouble, all the data for the three swatches in each test were averaged together. The results are given in table 3.3 and depicted in figures 3.5 and 3.6, (figures 3.5 through 3.12 are at the end of this chapter) with the maximum and minimum values indicated by the error bars. This method of analysis lumps effects from 'compaction in with changes in the equilibrium performance due to treatment and/or fouling. To minimize the compaction time differences, the average of the three swatch's performance at the last sample time is listed in table 3.3 as well. In many cases, as seen in the appendix C figures, the rejection and flux data do not indicate that equilibrium had been reached by the end of the test. It would have been best if the tests could have been continued for a full 24 hours or more, but equipment limitations prevented overnight testing.

3.3.1.1 *Cellulose acetate blend.* The overall average flux and rejection for CA RO membrane swatches are plotted in figure 3.7. None of the surfactant treatments had a significant effect on permeation rate. Triton X-35, Triton X-100, and Pluronic F87 improved rejection over the control membrane. The fouling solution degraded the control membrane to the extent that one of the fouled membranes completely failed. Compared to the control, all treatments provided some improvement.

3.3.1.2 *Polyamide thin film composite.* The overall average flux and rejection for PA RO membrane swatches are plotted in figure 3.8. With the exception of one sample treated with Pluronic F87, all the PA RO membranes maintained an excellent rejection throughout the clean testing and after fouling. Flux declined miserably, though, with treatment and with fouling of the control membrane. The treated membranes did not experience significant further flux decline after fouling. To test whether a thinner layer of surfactant would allow a higher permeation rate while still protecting membrane integrity, Pluronic P84 was adsorbed onto PA RO membrane from a 0.001 percent weight solution. This set of membranes did have a 70 percent increase in flux accompanied by a slight increase in rejection over the higher concentration treatment. The flux was still 60 percent lower than the clean control set, but only 34 percent lower after fouling. It may be that PA membrane treated with an even lower concentration of surfactant would perform acceptably.

3.3.1.3 *Nanofiltration CA and PA membrane.* The overall average flux and rejection for CA and PA-NF membrane swatches are plotted with their respective RO counterparts in figures 3.5 and 3.6. The CA NF membrane was not improved by treatment with Triton X-100. The flux increased and the rejection dropped with treatment. After fouling, the treated and untreated sets had the same average flux and rejection.

Table 3.3.—Performance parameters for swatch test data before and after fouling

| Membrane | Test | Clean | | | | Fouled | | | |
| | | Rejection | | Flux' | | Rejection | | Flux | |
		Ave	Last	Ave	Last	Ave	Last	Ave	Last
CA RO	Control	66.0	95.2	2.24	1.91	56.6	61.1	46.6	53.7
	Triton X 35	95.6	96.3	1.79	1.76	53.6	60.4	3.44	2.61
	Triton X 100	92.7	95.2	2.03	1.95	66.6	95.4	2.16	3.25
	Triton X 705	62.7	69.0	2.10	1.92	64.0	76.7	2.01	2.16
	Pluronic P84	62.1	66.0	2.36	2.06	75.6	79.2	2.66	2.36
	Pluronic F67	97.2	97.1	1.60	1.57	79.6	67.6	2.01	1.75
PA RO	Control	96.0	96.6	6.06	5.50	96.2	96.4	3.24	3.29
	Triton X 35	96.7	96.3	1.07	1.46	96.1	97.5	0.61	0.52
	Triton X 100	96.1	96.3	2.79	3.21	96.0	97.5	2.01	2.26
	Triton X 705	96.7	97.2	1.44	1.52	97.5	97.6	1.26	1.30
	Pluronic P64	97.0	97.3	1.44	1.60	96.9	97.1	1.36	1.40
	Pluronic F67	97.9	96.1	1.14	1.16	67.1	67.5	4.34	3.64
	Pluronic P84.001%	97.6	97.6	2.45	2.50	96.1	96.2	2.14	2.17
CANF	Control	62.1	69.4	6.41	5.76	56.5	61.4	6.69	6.30
	Triton X 100	52.6	54.7	6.11	7.36	56.7	62.2	6.60	6.56
PANF	Control	34.1	35.1	9.66	9.92	24.7	24.7	10.4	10.4
	Triton X 100	46.5	46.6	11.6	11.6	27.9	29.3	11.3	11.4

^{1} $m^3 m^{-2} sec^{-1} Pa^{-1}$ x 10^{12}

The PA NF membrane results are much different, though. The set treated with Triton X- 100 had a higher rejection rate and higher flux rate than the untreated set. Flux was not changed significantly with fouling, but rejection was reduced from 48.6 to 29.3 percent, still higher than the untreated set. This is contrary to expected behavior. Normally, one expects an increase in rejection to be accompanied by a decrease in flux. The surfactant may be able to penetrate the NF membrane pore structure, enhancing water transport and salt rejection mechanisms. Of course, another explanation is that the NF40 membrane is spotty, with some areas having higher flux characteristics than others.

3.3.2   Element Testing. There were some technical difficulties during the element testing, but with automatic data acquisition, they are all documented. Considering that a full scale system might suffer the same problems, the test still provided a good comparison of the treated and untreated membranes. In fact, if operations had been smoother, the treated membrane would most likely have performed even better than it did. Figures 3.9 and 3.10 show normalized water permeation rate and salt rejection for the control and treated sets of CA RO elements over the duration of testing. Results are summarized in table 3.4.

During the first 48 hours of testing, one set of elements was tested at a time. The untreated set was tested first; then the next day, testing of the treated set was begun. Apparently, the untreated set had radically different compaction characteristics, because the pressure did not stabilize until the fouling solution was added after 28 hours of testing. The glitch in the system occurred during the retest of rinsed elements after the fouling period. The valve that shunts product water from

the two systems to separate tanks failed, allowing the product water from the treated set in system 2 to be diverted to the feed tank for the untreated set in system 1. Consequently, the treated elements were dealing with increasingly concentrated feed solution until the tank was finally emptied at the 70-hour mark. The flow switch shut the system down, and the elements sat for the rest of the night in greater than 10,000 μS/cm salt solution. Meanwhile, the control membranes were receiving a purer feed solution as time went on. The next day, more salt was added to the system 1 feed tank and both systems were operated off the same feed source.

Table 3.4.—Performance of the treated and untreated sets of CA RO elements before, during, and after fouling and rinsing with RO permeate

Sample	Untreated			Treated		
	Initial	Fouled	Cleaned	Initial	Fouled	Cleaned
Rejection (%)	95.54	96.13	94.71	95.13	95.65	93.21
Flux $(10^{12} m^3 m^{-2} sec^{-1} Pa^{-1})$	2.37	2.53	2.77	3.17	2.91	3.5

The treated membrane maintain a 15 to 30 percent higher flux rate throughout testing. Rejection stayed very close to the untreated membrane until after the cleaning cycle, when it lost 1.5 percentage points. This change could be the result of having been operated under such high salinity and then being shut off for a number of hours. High salinity may enhance desorption of the surfactant from the membrane surface.

3.3.3 Effect of performance changes on operating costs. It is difficult to access the importance of changes in rejection and permeation rates without a clear connection to cost. To bring some meaning to the data, the USBR-NIST Water Treatment Cost Estimation Program model for membrane costs was used to estimate operating and maintenance costs for a system experiencing the changes in rejection and permeation rates found in the swatch and element tests (Chapman Wilbert and Pellegrino, 1995). A hypothetical situation where a plant must produce a certain quantity of acceptable water was used as a basis for defining the assumptions needed for the model. If the rejection falls such that the membranes cannot produce 500 mg/L product, then make-up water of 80 mg/L must be purchased at \$0.50/m^3. If the membrane productivity falls below acceptable levels, then the model calculates operating costs for a larger sized plant. Table 3.5 lists the assumptions used in the model.

The blend ratio is calculated as follows:

$$Q_b = Q_t * (C_t - C_f(1-R))/(C_b - C_f(1-R))$$

Where: Q_b = Volume of blend per sec
$\quad\quad\quad Q_t$ = Target volume produced
$\quad\quad\quad C_t$ = Target concentration
$\quad\quad\quad C_f$ = Feed concentration
$\quad\quad\quad C_b$ = Blend concentration = C_f if RO product <500 mg/L, otherwise 80 mg/L
$\quad\quad\quad R$ = Rejection

This model represents a best case scenario. If longer term data were available, the cost of decreased membrane life and increased cleaning costs could be included. From the results of this rather harsh test of membrane durability, the life of untreated membrane would be much shorter than the treated membrane. Thus, the operating costs would be higher for the control membrane.

Table 3.5.—Assumptions used assessing operating cost
of changes in membrane performance

Parameter	Assumed Value
Feed TDS	2000 mg/L
Target TDS	500 mg/L
Target volume	2 MGD
Make-up TDS	80 mg/L
Make-up water cost	$0.50/m³
Recovery	75%
Operation pressure	2757 kPa
Energy cost	$0.1 0/kWhr
Interest	8%
Loan lifetime	20 years
Downtime	15%
Membrane life	3 years
Membrane productivity and rejection	Variable

3.3.3.1 *Operating cost based on swatch test performance.* Figure 3.11 shows the change in operating costs based on CA blend, PA thin film composite, and NF membrane swatch test performance. The operating costs for the CA RO membrane double when fouled, due to the loss in rejection. In this model, loss of rejection is much more costly than a loss in productivity, since the amortized cost of a larger plant is not as great as the annual cost of purchasing good quality make-up water. Since the treated membranes did not suffer large losses in rejection, their costs remain stable even though there is a small loss in productivity.

The polyamide thin film composite membrane lost much of its productivity, with surfactant treatment causing costs to increase relative to the untreated membrane. The untreated PA membrane had an increase in productivity with a small decrease in rejection, and so its operating costs did not change much with fouling.

Treatment improved costs for both types of nanofiltration membrane. Costs improved due to an increase in rejection with treatment in the case of the PA membrane and an increase in flux with

a small decrease in rejection for the CA membrane. The treated CA NF membrane performance matched the untreated membrane performance after fouling, so costs with treated and untreated membrane are identical. The treated PA NF membrane experienced a large decrease in rejection after fouling, but not as much as the untreated membrane. As a result, operating costs for treated PA NF membrane are favorable.

3.3.3.2 Operating cost based on element testperformance. In all conditions, the CA RO membrane elements treated with Triton X- 100 have lower costs than the untreated membrane due to the improvement in productivity without loss in rejection. Figure 3.12 shows the operating cost model results based on element data performance in a clean condition, fouled condition, and after cleaning with RO permeate.

3.4 Conclusions

Cellulose acetate RO membranes with adsorbed PEO surfactant do show increased resistance to deterioration and fouling. The data suggest an optimum PEO chain length in the midrange of those tested. Triton X-100, Pluronics P84, and Pluronics F87 were the top three performers, with the Triton X- 100 being best even with one failed sample averaged in. From the element data, treatment results in a more consistent product. This could be due to the creation of a more uniform active surface and the filling in of larger voids in the membrane. Untreated membrane adsorbs matter from the feed stream and eventually the benefit of a more uniform surface is realized. With treatment, this process is controlled. Excess surface energy is taken up with adsorption of the entropic barrier formed by the PEO side chains rather than detrimental colloids or biological material that may encourage further fouling.

Polyamide RO membrane, on the other hand, is not improved by adsorption of PEO surfactants. Fouling resistance may be improved, but it is difficult to tell when the flux has already been decreased by 1/2 to 5/6 the untreated flux rate. Organic colloidal fouling has the same affect on performance as adsorption of the surfactants. This suggests that permeation is being blocked physically by either type of molecule.

Surfactant adsorption has marginal benefit for CA NF membrane. There was an improvement in the flux of the treated membrane, but it was accompanied by a decrease in rejection. This indicates that the surfactant has increased the wetability of the pore structure and thereby decreased resistance to mass flow through the pores.

The performance of the PA NF membrane is the most surprising result of this part of the study. Anything that increases flux and rejection is worth further examination. Compared to past experience with the NF70 and NF90 membranes, of the same series as the NF40 tested in this study, the flux of this membrane is low. The NF70 and NF90 membrane element tests had flux rates twice as high as the NF40 swatch test data. There are a few possible explanations for the results with surfactant tests:

- Either the swatch test membrane was an inferior batch and the treated membrane happened to be slightly better than the untreated section, or

3.15

- Dow Chemical normally treats their membrane with something similar to the Triton X-100 surfactant which improves flux and rejection, or

- Dow Chemical relies on natural components of the feed source to improve flux and rejection characteristics of their membrane and treatment with Triton X- 100 would be an improvement.
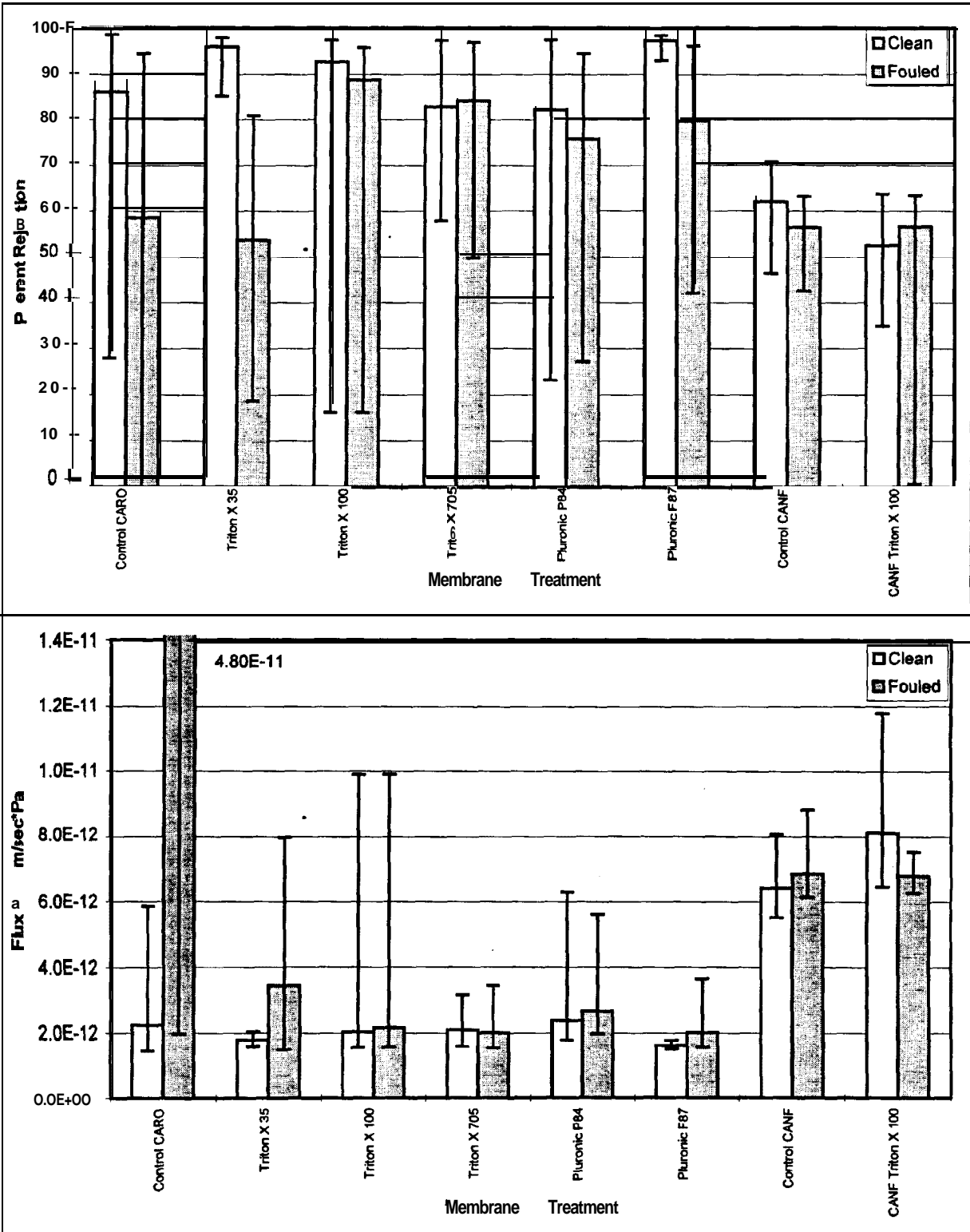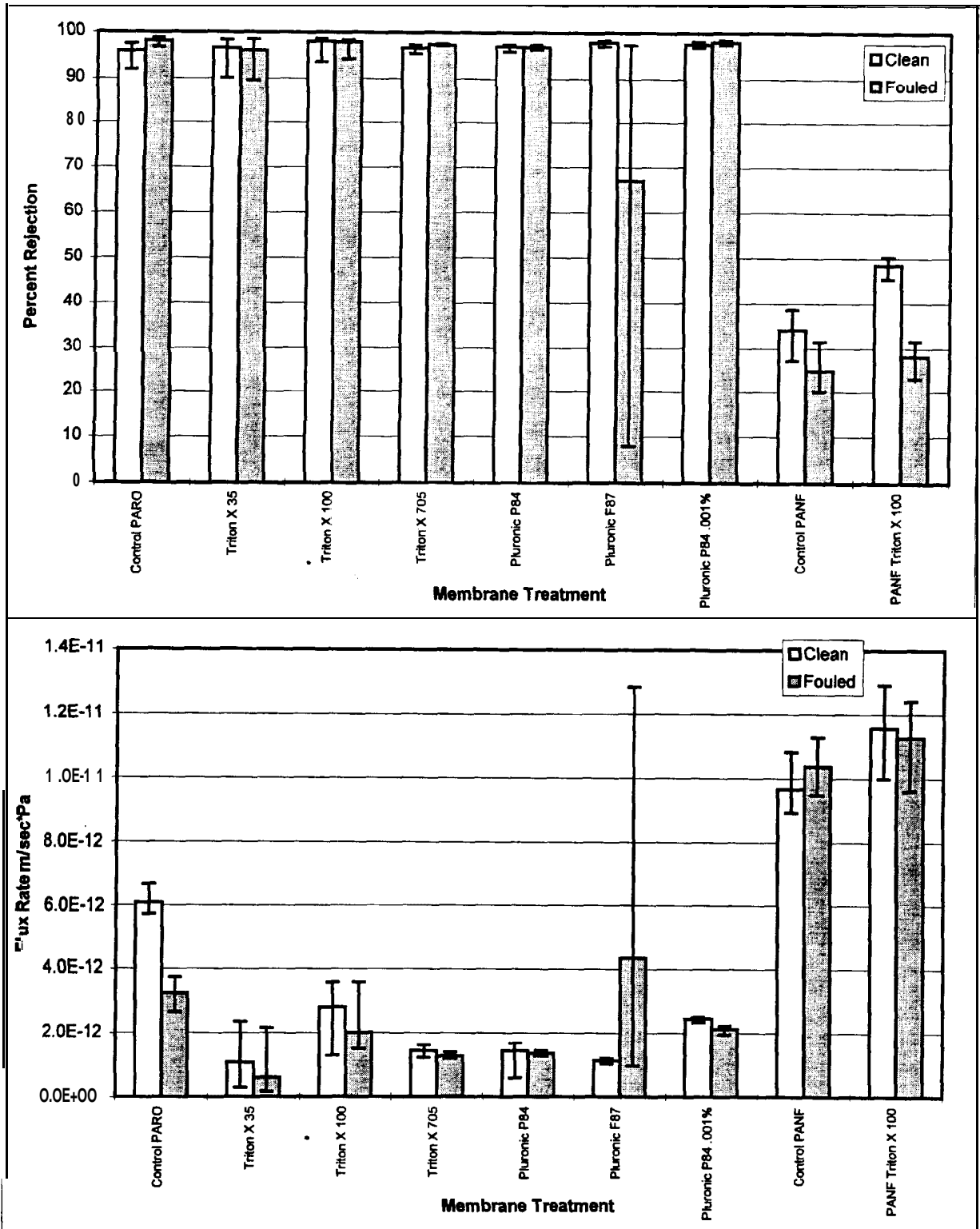
Figure 3.5.—CA membrane performance before and after fouling. Membranes were tested with 0.04 M NaCl solution. Clean membranes (open bars) have been treated as indicated. Fouled membranes (shaded bars) are the same membranes after being soaked in a fouling solution for 24 hours and retested. Bars indicate the average value of all observations; error bars represent the maximum and minimum values over test period.

Figure 3.6.—PA membrane performance before and after fouling. Membranes were tested with 0.04 M NaCl solution. Clean membranes (open bars) have been treated as indicated. Fouled membranes (shaded bars) are the same membranes after being soaked in a fouling solution for 24 hours and retested. Bars indicate the average value of all observations; error bars represent the maximum and minimum values over test period.
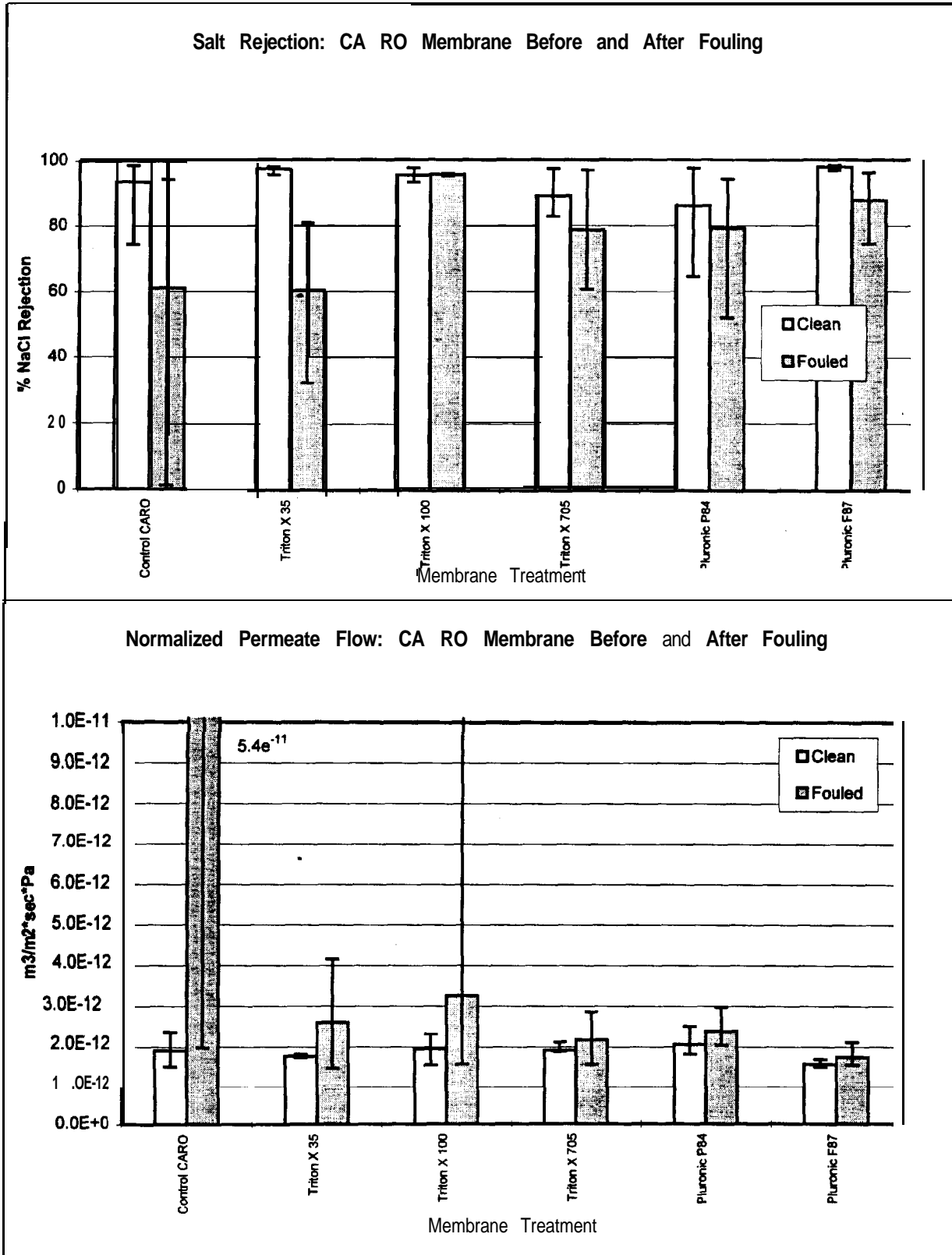
Figure **3.7.—Average** equilibrium normalized permeate flow and rejection for each set of CA RO membrane; bars are average of last data point for the three samples. Error bars represent the maximum and minimum values.
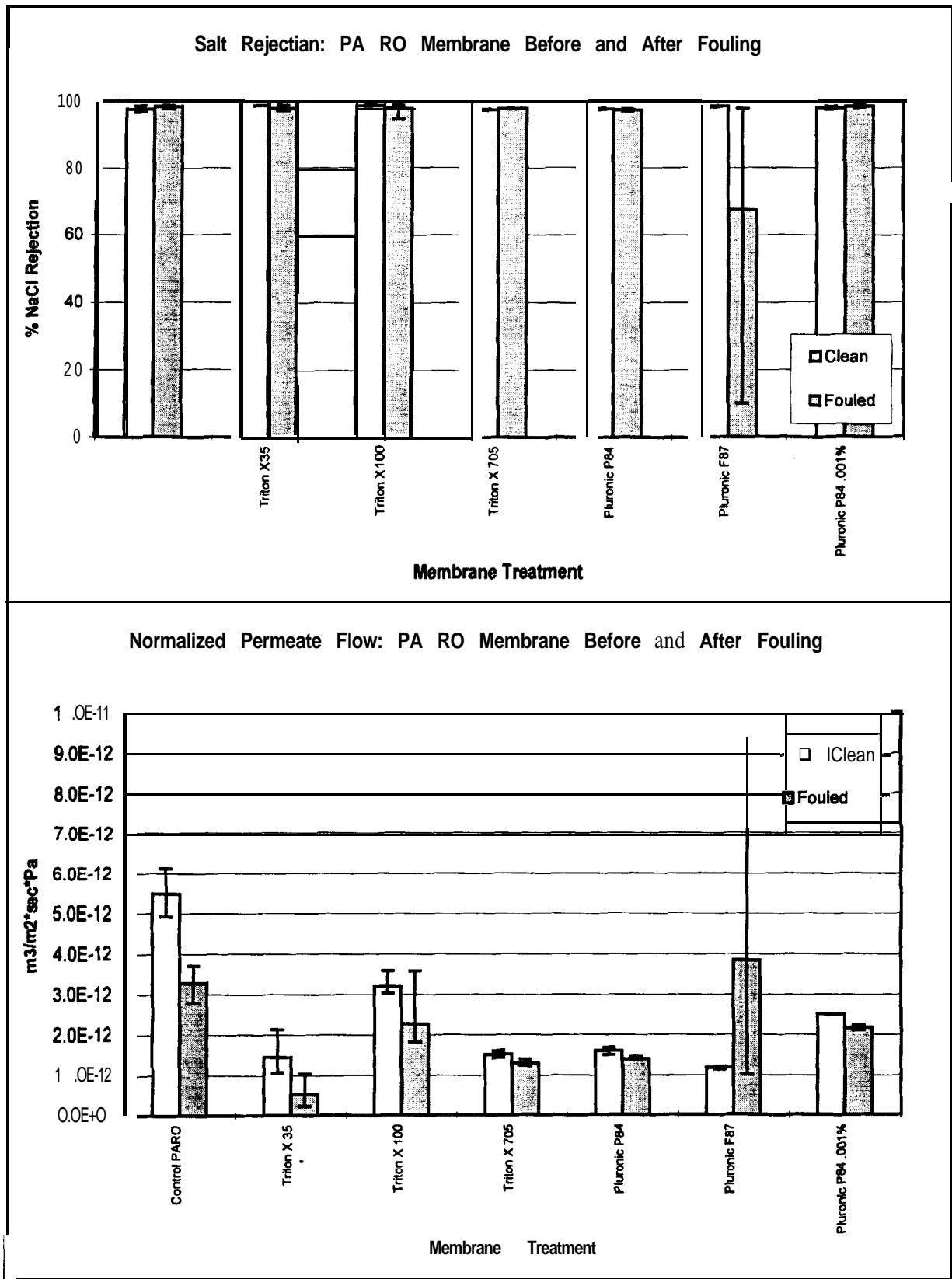
Figure **3.8.—Average** equilibrium normalized permeate flow and rejection for each set of PA RO membrane; bars are average of last data point for the three samples. Error bars represent the maximum and minimum values.

Normalized Permeate Flow: Untreated CA RO Membrane
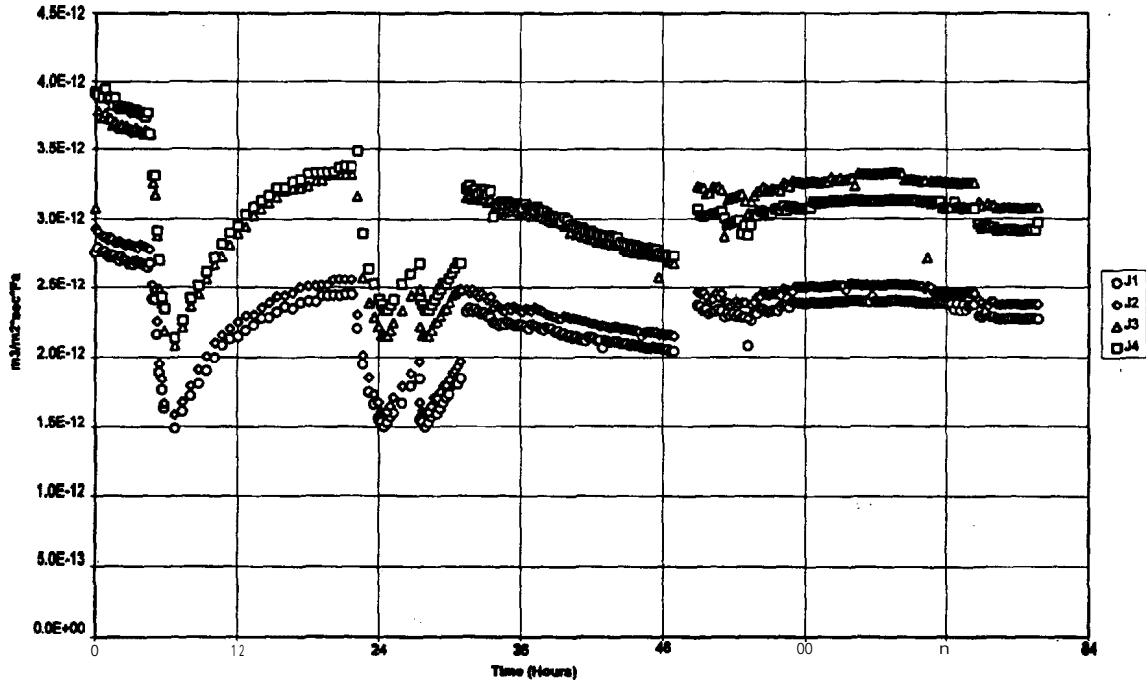
Salt Rejection: Untreated CA RO Membrane
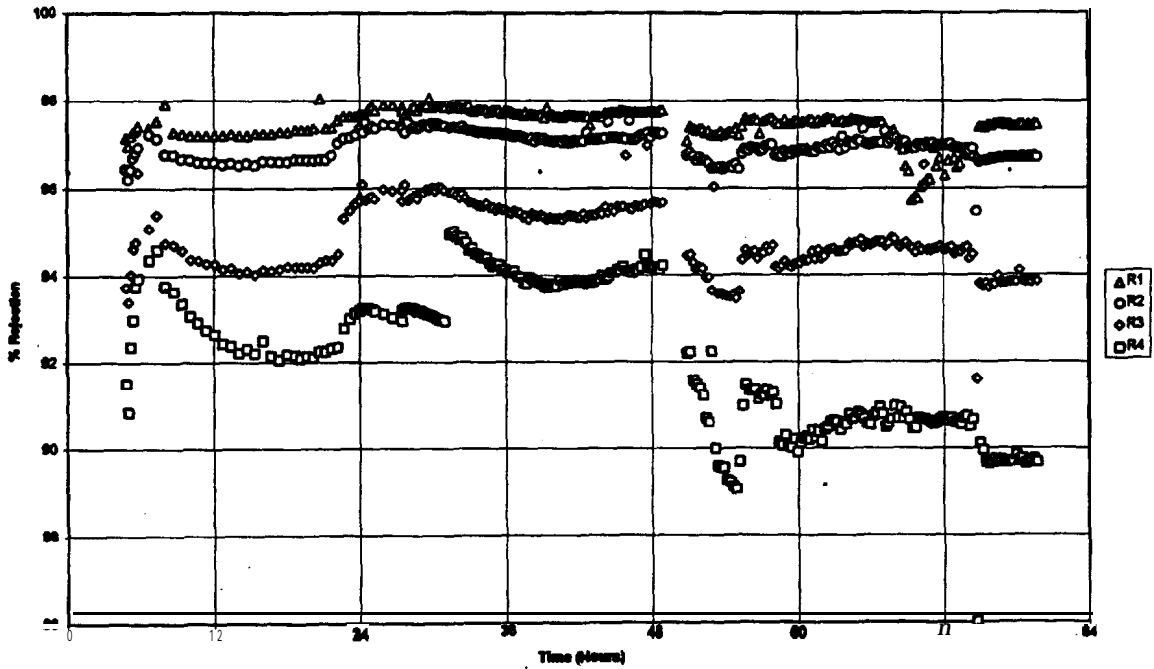
Figure 3.9.—Untreated CA RO membrane performance. NaCl was added at 4:30; fouling solution was added at 28:30; the element was rinsed from 49-51, tested with NaCl from 51 hours till end.

Normalized Permeate Flow: CA RO Membrane Treated with Triton X-100
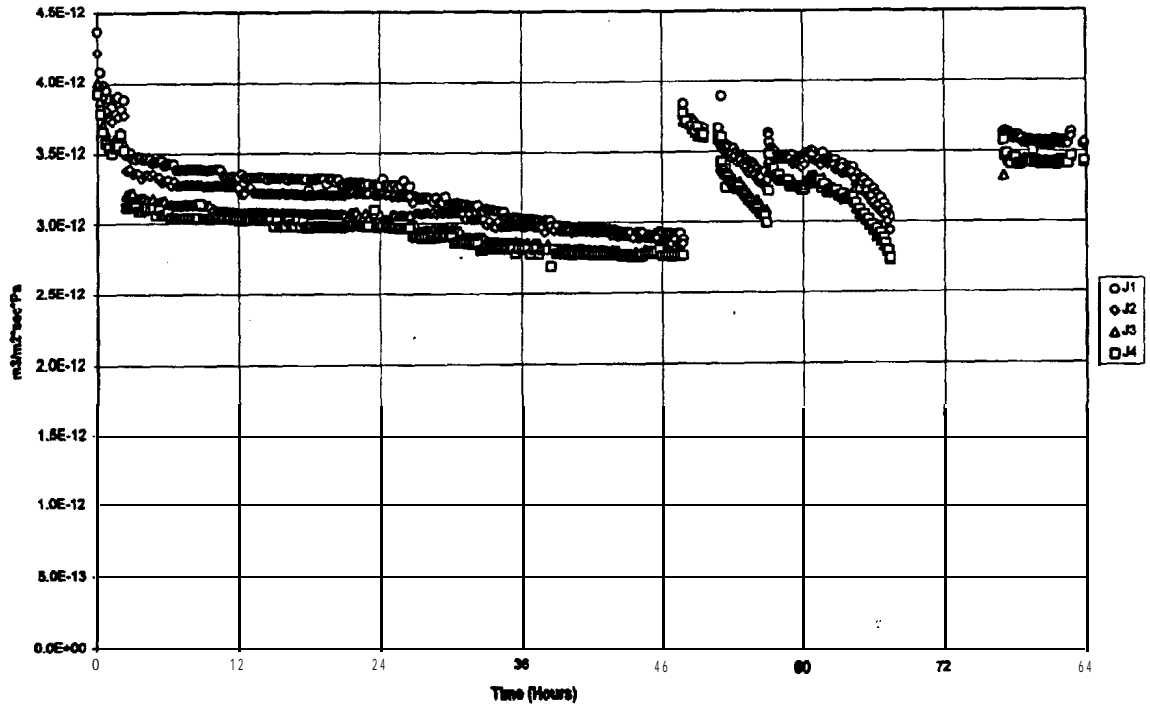
Salt Rejection: CA RO Membrane Treated with Triton X-100
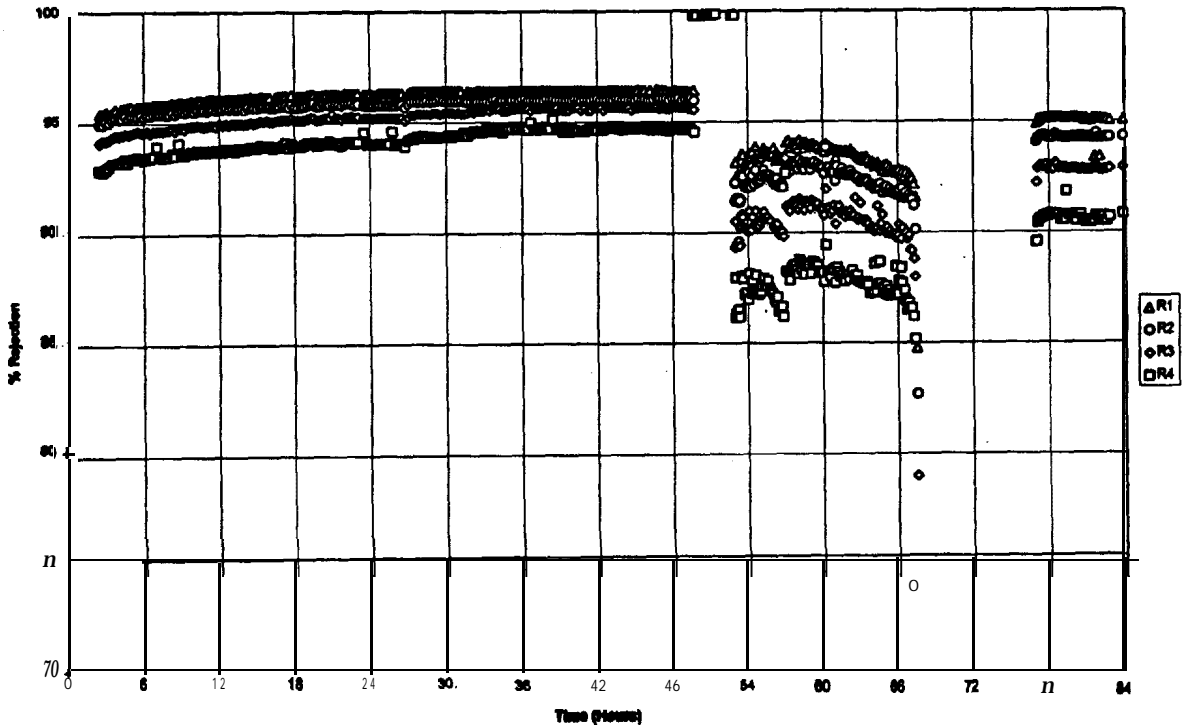
Figure 3.1 O.—Performance of CA RO membrane treated with 0.001% Triton X-I 00. NaCl was added at 2:30; fouling solution was added at 26:45; the element was rinsed from 50-53, stored for 30 days, then tested with NaCl from 53 hours till end. A valve failure caused permeate to be diverted to the Control Element tank between 70 and 78:20 hours. After that time, both sets were tested from the same NaCl solution.
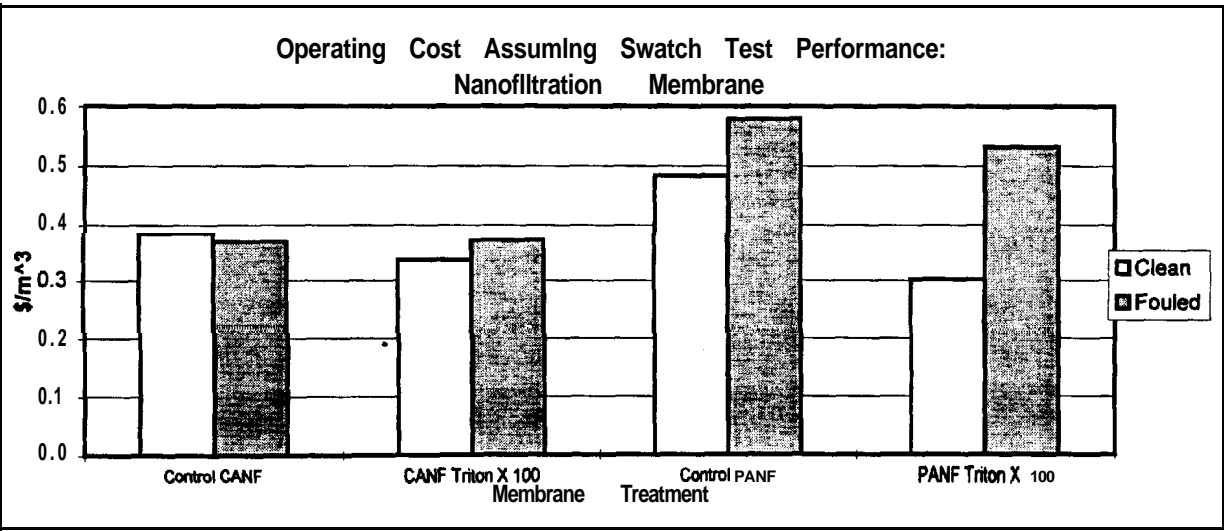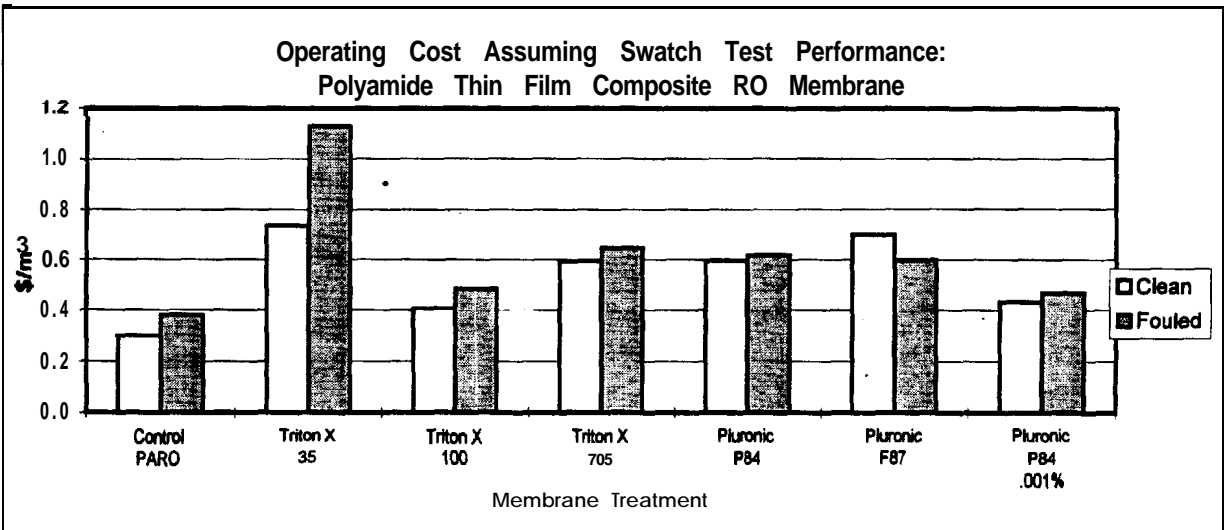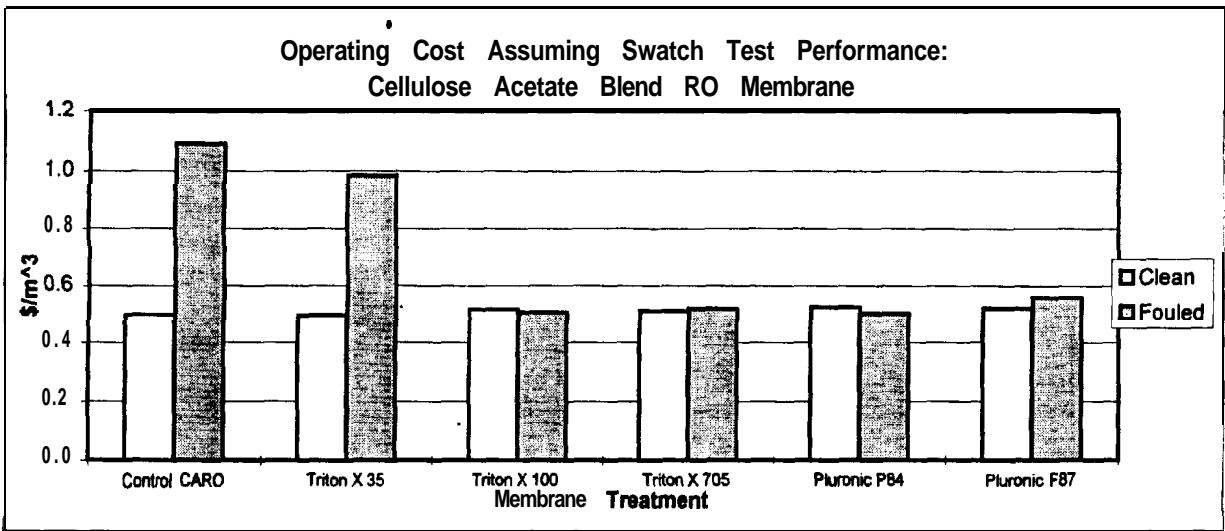
Figure 3.11 .-Estimate of operating cost changes for a plant designed according to clean control membrane performance if it should experience the performance changes observed during swatch testing.

Change In Operating Costs Assuming Element Test Performance: Cellulose Acetate Blend RO Membrane
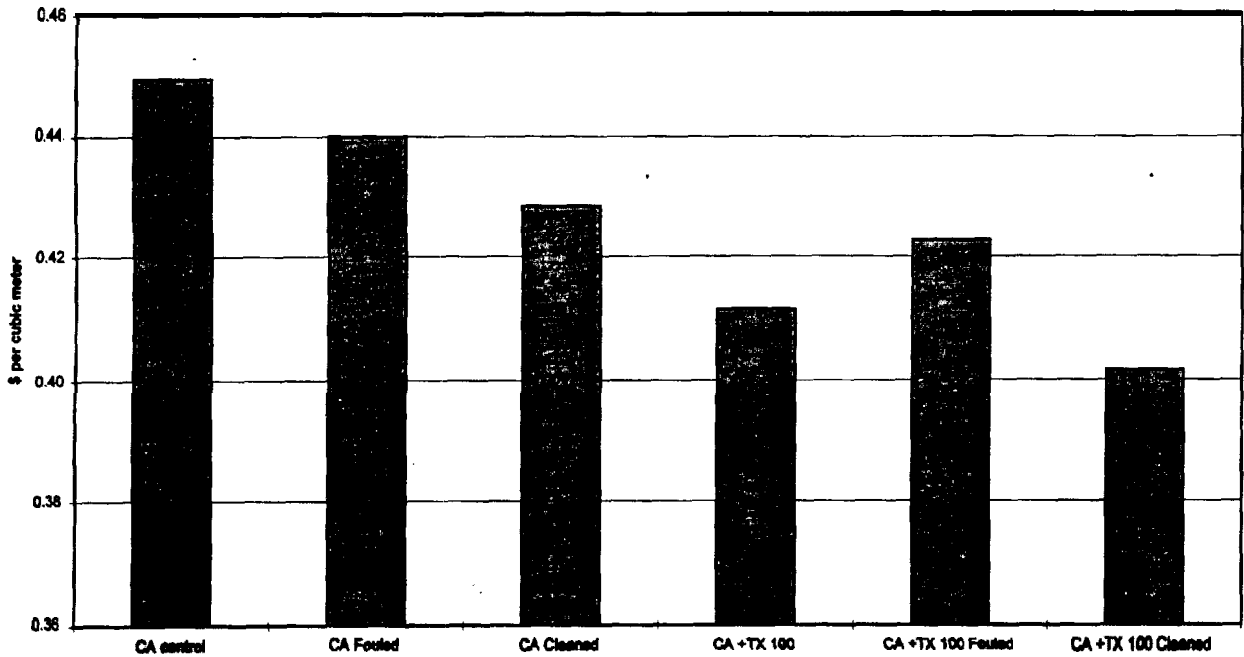

Figure 3.12.—Estimate of operating cost changes for a plant designed for clean CA RO element performance if it should experience the performance changes observed during element tests.

4. Zeta Potential Analysis

Membrane materials considered in these studies have a surface potential energy arising from ionizable groups on the surface and the polymers ability to bind ions from solution. These characteristics of the membrane polymer are partially responsible for the membranes propensity towards adsorbing fouling material from solution, other factors being surface topography, element construction, and operating conditions. One way to gain information about the surface energy is to measure the zeta potential. When the surface is exposed to an ionic solution, the potential determining ions are attracted to the charged, or high energy, sites on the surface. A layer of these ions is immobilized on the membrane surface (see figure 4.1). (Figures 4.1 through 4.16 are at the end of this chapter.) The thickness of this layer of ions, called the Stem layer, depends on the magnitude of the surface charge and the ion radius. Beyond the stem layer, is the diffuse layer, where the magnitude of the potential declines at a rate that is a function of the surface potential, valence of the potential determining ions, viscosity, and dielectric constant at the surface.

The zeta potential (ζ) is the electrical potential at the distance from the surface where particles are able to move, labeled the Surface of Shear on figure 4.1. Zeta potential is affected by electrolyte pH, conductivity, size of the potential determining ion, temperature, and the geometry of the channel through which it is measured. The pH controls the number of ionized sites on the membrane surface. An increase in ionized sites results in a higher surface potential, which in turn is reflected by a higher ζ. The pH at which ζ equals zero is defined as the isoelectric point (IP). The rate of change in ζ with pH indicates the extent to which the surface potential is due to ionizable groups. Change in ζ with increasing conductivity reflects the extent of adsorption of potential determining ions. When adsorption sites are exhausted, ζ begins to be affected by accumulation of co-ions at the surface and may either level off with increasing conductivity or even decrease in magnitude. The size of the potential determining ions dictates the number that can fit onto the membrane surface. Temperature affects the measurement of ζ through effects on viscosity, dielectric constant, and conductivity.

Change in ζ with surfactant adsorption gives information about the extent of the change in surface conditions. The anti-fouling hypothesis predicts that a lower surface potential energy is needed to minimize fouling. A lower energy surface would also have a lower ζ. There are at least three mechanisms whereby an adsorbed surfactant can result in a lower ζ.

- Excess surface energy may be lowered by interaction of surfactant molecules with charged sites on the membrane surface or with the polymers capacity to adsorb ions from solution, thereby reducing the surface potential (ψ_o) as shown in figure 4.2a.

- Potential determining ions may be adsorbed on top of the surfactant, causing the surface of shear to be extended further from the surface. In this case, there would be some drop in potential energy across the surfactant layer which would lower the value of ζ (as in figure 4.2b).

- The surfactant layer may structure the area adjacent to the membrane causing changes in viscosity and dielectric constant that affect the measurement of ζ without actually changing the surface potential (figure 4.2c).

4.1 Methods and Materials

Zeta potential measurements were performed by Professor Andrew Zydney and Terry Lohnes of the Chemical Engineering Department at the University of Colorado, Boulder. A Brookhaven-Paar Electrokinetic Analyzer, on loan from the National Institute of Standards and Technology (NIST), was used in the analysis. Figure 4.3 is a diagram of the instrument piping and data collection, and figure 4.4 shows the detail of the electrolyte circulation path. Zeta potential is calculated by the Brookhaven-Paar software from the slope of the streaming potential versus pressure curve. Thus, in taking measurements, the electrolyte solution is circulated across the membrane sample, with the pressure increasing from 0 to 200 mbar from right to left, and then again in the reverse direction. Up to 10 sets of forward and backward runs can be used to calculate the average ζ for a set of conditions.

Measurements were made to determine the relationship between ζ and solution conductivity and pH for:

- CA and PA RO membranes with and without surface treatments before and after fouling.

- CA NF membrane with and without surface treatment before and after fouling to determine if there were any differences that could be attributable to characteristics that control rejection

- CA and PA RO membranes treated with a range of surfactant concentrations

The unfouled membrane samples were prepared at the University of Colorado, Boulder. Clean dry membrane sections were cut to fit the EKA sample chamber, then soaked in a 1.0 percent (weight) solution of surfactant over night in a water bath. The surfactant solution was not buffered or circulated for the ζ analysis. Fouled membrane samples were provided from the set used for swatch testing. Due to the difficulty and expense of preparing large quantities of 1.0 percent (weight) surfactant solutions, the swatch test samples were treated with 0.1 percent (weight) solutions.

Membrane samples were loaded into the EKA and rinsed with distilled water. A series of measurements were taken on one pair of samples without removing them from the circulation chamber. Variation with conductivity would be measured by adding KC1 to the recirculating electrolyte solution with pH adjusted to 5.8 using HCI. The system would be allowed to recirculate over the membrane for 30 minutes before measurements were taken. Zeta potential, conductivity, and pH was recorded for four backward and forward flow cycles. These values were averaged to obtain one ζ for that pH and conductivity point. After the conductivity data series was complete, distilled water was added to lower the conductivity to 60 mS/m. The

system was allowed to reach equilibrium for 30 minutes, then the variation with pH series of measurements was determined in the same manner, adding HCl to decrease the pH, step-wise, to a minimum of about 3.5.

4.2 Results

4.2.1   Reproducibility and the effect of solution conductivity and pH. Figures 4.5 and 4.6 compare ζ variation with solution conductivity and pH for several CA and PA RO membrane samples analyzed on different days. The ζ increases in magnitude with solution conductivity for both types of membrane due to adsorption of Cl⁻ ions up to 60 mS/m for CA membrane and 80 mS/m for PA membrane. Zeta potential increases linearly in magnitude over the pH range tested for both membranes. From these data sets, the IP for PA membrane appears to be slightly higher than for CA membrane.

The variability in measurements is higher for CA membrane when pH is held constant and conductivity is increased, while the opposite is true for PA membrane. There are three possible causes for this variability.

- The temperature could have been slightly different on different days. Temperature was controlled, but on very hot days, it could rise a degree while measurements were being taken if the water bath was not readjusted. A one degree change in temperature results in about 5 percent error from the resulting change in viscosity.

- The time allowed for the measurements may have been different. The standard equilibration time was 30 minutes, but differences could result if measurements were interrupted. CA membrane surface conditions take longer to equilibrate when the conductivity is changed than when the pH is changed. This was not apparent until later measurements were taken to find out if ζ changed over time. The result was that, if ζ measurements were repeated for three sets of 10 flow cycles, the magnitude increased in a mannner similar to the series of points plotted at 30, 60, and 90 mS/m on figure 4.5.

- Part of the variation in ζ is due to variations in pH. Data plotted on conductivity graphs was collected with in a pH range of 5.65 to 5.8. This range in pH corresponds to a ± 3 mV error.

This variability in conductivity does not show up in figure 4.6 for PA membrane. It may be that chloride adsorption reaches equilibrium more quickly on PA membrane than on CA. PA membrane shows more variation with pH changes, especially at low pH.

Figure 4.7 compares ζ response to pH for a range of solution conductivities from 30 to 120 mS/m, or about 0.002 to 0.008 M KCl. PA membrane ζ/pH response does not change significantly with increasing solution conductivity, suggesting that ionization of amide groups on the membrane surface is the primary source of the surface charge for polyamide membrane. CA membrane, on the other hand, shows a distinctive change in ζ/pH with solution conductivity.

4.2.2   Effect of Membrane Type. Figure 4.8 illustrates the difference in ζ characteristics of CA RO and NF membrane. The NF membrane has a lower minimum ζ at 60 mS/m than the RO membrane, which could be due to a higher capacity for chloride ion adsorption. This lower minimum ζ is emphasized in the ζ versus pH graph; while the rate of change of ζ with pH is nearly the same, the NF membrane is about 5 mV lower.

4.2.3   Effect of Surfactant Adsorption. Figures 4.9 and 4.10 show the change in dependance of ζ on conductivity and pH for each membrane type with adsorption of the five test surfactants. In general, the magnitude of the ζ is decreased with adsorption of these types of surfactant. Triton X-35 on CA membrane is the one exception; ζ is more negative that the untreated sample until above about pH 4.7. Treatment with Triton X-100 has a similar effect on both CA RO and NF membrane. Both types decrease ζ by about the same magnitude. The treated NF membrane has the same ζ characteristics as the untreated RO membrane, indicating that the additional capacity for chloride ion adsorption exhibited by the NF membrane is taken up by the surfactant.

4.2.4   Effect of Surfactant Concentration. Since the unfouled membrane samples were treated with 1.0 percent weight surfactant solutions and the fouled ones were treated at 0.1 percent, it was necessary to determine the effect of surfactant concentration .on ζ. Sets of CA membrane were treated with Triton X- 100 and Pluronics F87 concentrations ranging from 0.001- 1 .O percent weight. PA membrane sets were treated with Triton X-100 and Pluronics P84. The choice of surfactant allowed determination of the effect of the hydrophobic portion and PEO chain length. Results are plotted in figures 4.12 and 4.13. In all cases, ζ magnitude is less negative for membranes treated with 1 .0 percent weight surfactant solution. For the CA membrane, lower surfactant concentrations increase ζ magnitude over that of the untreated membrane. The PA membrane exhibits a maximum increase in ζ magnitude at the CMC (0.015 percent) with Triton X-100; but with Pluronics P84, concentrations lower than 1 .O percent have little effect.

4.2.5   Effect of Protein Fouling. Figures 4.14 and 4.15 show the effect of fouling on ζ characteristics of CA and PA membrane as compared to clean untreated membrane. The membrane treated with Triton X-35 shows the only significant change in the relation between ζ and pH. The increased ionization rate shown in figure 4.10 is completely erased after fouling. If this was due to impurities, they may have been washed off or masked by the adsorbed fouling material.

 Fouling had no effect on the rate of adsorption of chloride ions onto the PA membrane, as evidenced in figure 4.15; fouling has increased the capacity for adsorption, though. While the clean PA RO membrane dζ/d Conductivity curve shows a minimum at 80 mS/m, the fouled membrane has no minimum in the conductivity range tested. Fouled CA membrane with Pluronics F87 behaves in the same way. At lower conductivities the trend is to decrease ζ magnitude. Keep in mind that figures 4.9 and 4.14 should not be directly comparable, even though they appear to be in the same range. If fouled membrane had been treated at 1 .O percent and ζ measurements followed those seen in figures 4.12 and 4.13, then the least negative values should be close to zero. One explanation for the similarity seen between the fouled samples treated at 0.1 percent and the clean samples treated at 1 .O percent could be that there is a maximum adsorption that can be made up with the excess surfactant or the fouling material. If this is true, membranes treated at 1 .O percent would be more fouling resistant than those tested in the swatch system.

4.3 Conclusions

As hypothesized, adsorption of surfactants does reduce the magnitude of the membrane zeta potential. If a more neutral ζ is desirable to protect membrane from fouling, a 1 .O percent weight solution of Pluronics P84 or F87 would be best for the CA membrane, and any of the three larger PEO chain surfactants would be best for the PA membrane. However, Pluronics F87 was shown to interact with the foulant in such a way that chloride adsorption on the CA membrane was enhanced. That leaves Pluronics P84 for CA and the three largest surfactants for the PA membrane that produced the greatest sustained decrease in ζ magnitude. Unfortunately, no judgement can be made at this point about the value of zeta potential characteristics in predicting membrane performance. The swatch tests did indicate some improvement with treatment, but they were treated at a lower concentration than that which produced the desirable change in zeta potential.

A more limited study to connect measurable zeta potential characteristics with membrane performance is warranted. Some intriguing questions brought up by the study are listed below.

- Can the zeta potential measured in low electrolyte concentration relate to performance at high concentrations? Measurements were only taken up to 180 mS/m because beyond that point the variation in zeta potential was within the error limits of the equipment.

- Do factors which control the zeta potential have anything to do with rejection and water permeation rate?

Potential

ψ_O

Adsorbed ions

$$\zeta \approx \psi_\delta - \frac{\psi_\delta}{e}$$
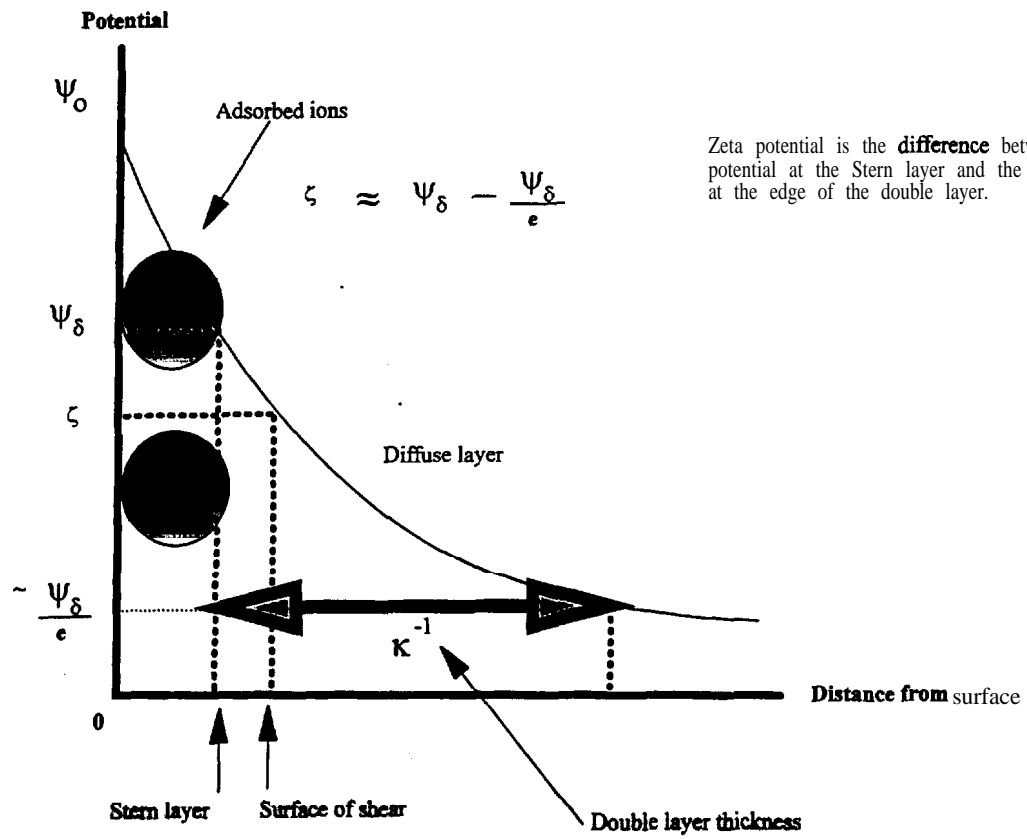
Zeta potential is the **difference** between the potential at the Stern layer and the potential at the edge of the double layer.

ψ_δ

ζ

Diffuse layer

$\sim \dfrac{\psi_\delta}{e}$

κ^{-1}

Distance from surface

0

Stem layer   Surface of shear

Double layer thickness

Figure 4.1 .-Change in surface potential with distance.

Potential

Surfactant could reduce the surface
potential

Adsorbed **surfactant** layer

ψ_0

Adsorbed ions

$\zeta \approx \psi_\delta - \psi_\delta$

ψ_δ

ζ

$\sim \dfrac{\psi_\delta}{e}$

κ^{-1}

0

Distance from surface

Stern layer   **Surface** of **shear**

Potential

A lower stem potential could **result** if
stem layer adsorption occurs **on** top of the
surfactant layer.

ψ_0

Surfactant layer

Adsorbed   ions

ψ_δ

Diffuse layer

ζ

$\sim \dfrac{\psi_\delta}{e}$

κ^{-1}

0

Distance from surface

Stern   layer'   **Surface of shear**

Poten tial

A more nuetral zeta potential could be
the result of a combination of decreased
surface potential, increasing the
thickness of the stem layer, and change
in parameters which **determine** the
potential decay rate.

ψ_0

Surfactant layer

Adsorbed ions

ψ_δ

Diffuse layer

ζ

$\sim \dfrac{\psi_\delta}{e}$

κ^{-1}

0

Distance from surface

Stern   layer   Surface   of   shear

Figure **4.2.—Probable** causes for a decrease in zeta potential.

PS: Power Supply
CU: Control Unit
STG: Pump/Valve Control
TE: Temperature
OR: Pressure
pH: pH
U/I: Current/Voltage
LF: Conductivity

Figure 4.3.—EKA block diagram.
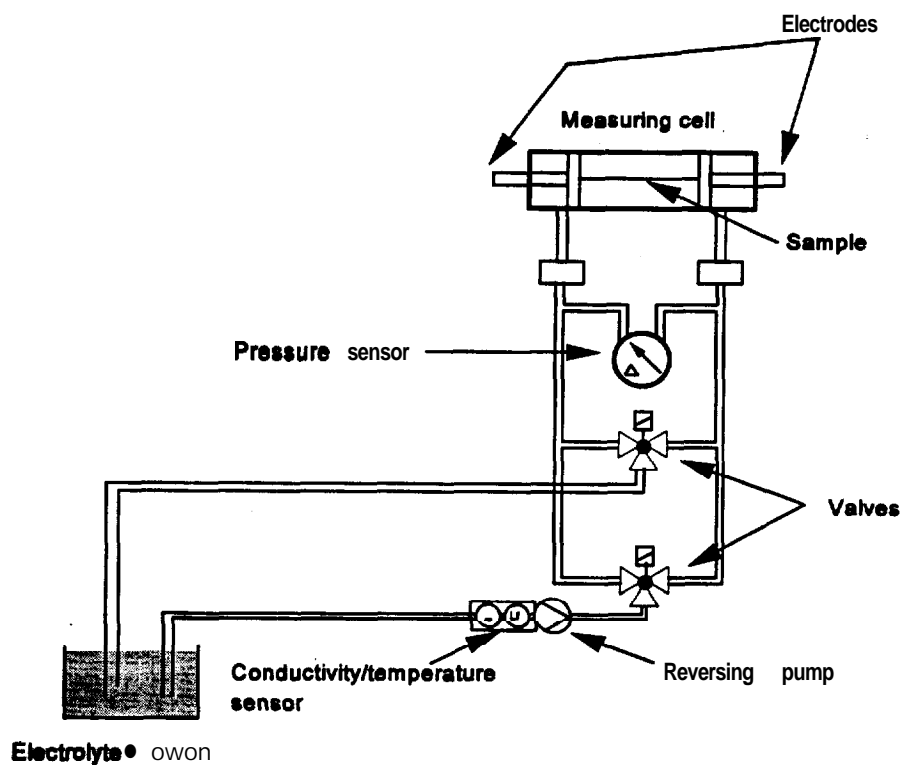
Figure 4.4.—EKA electrolyte path.

4.8

Variation in Zeta Potential with conductivity for CA RO membrane
(KCl, pH 5.8)

Variation in Zeta Potential for CA Membrane with pH
(SO mS/m KCl)
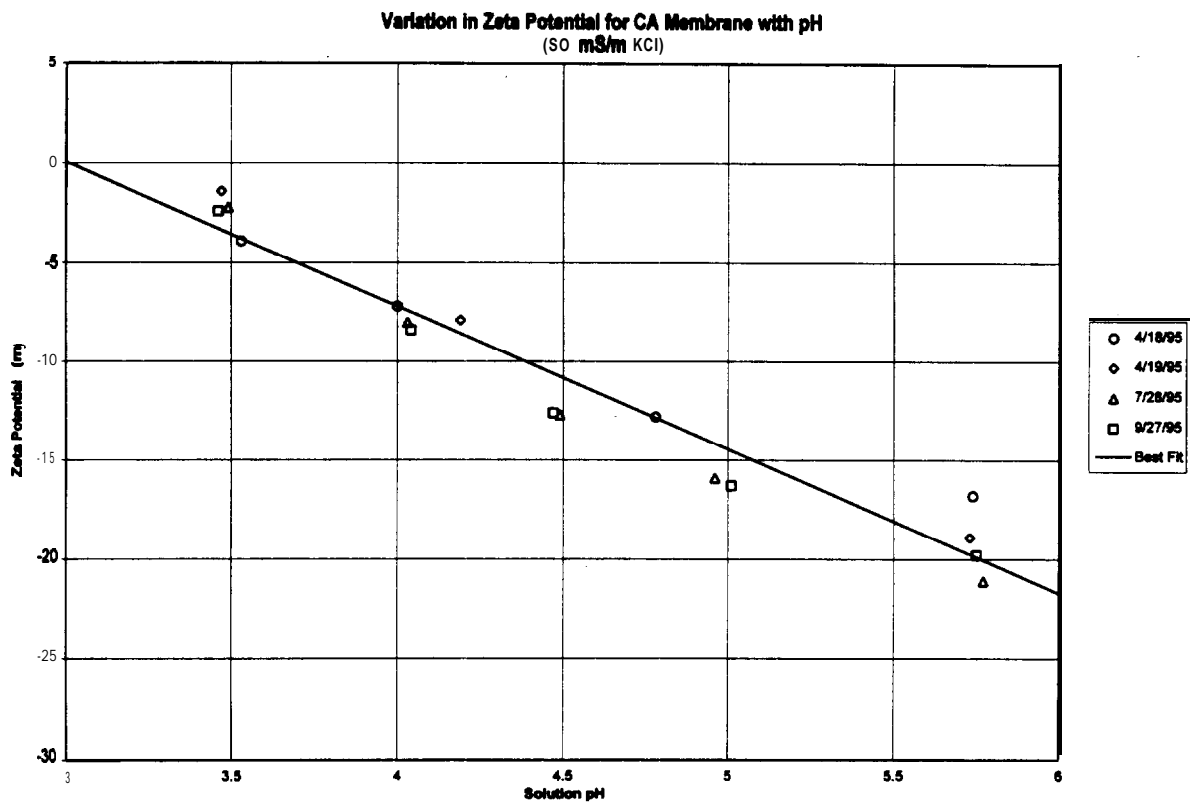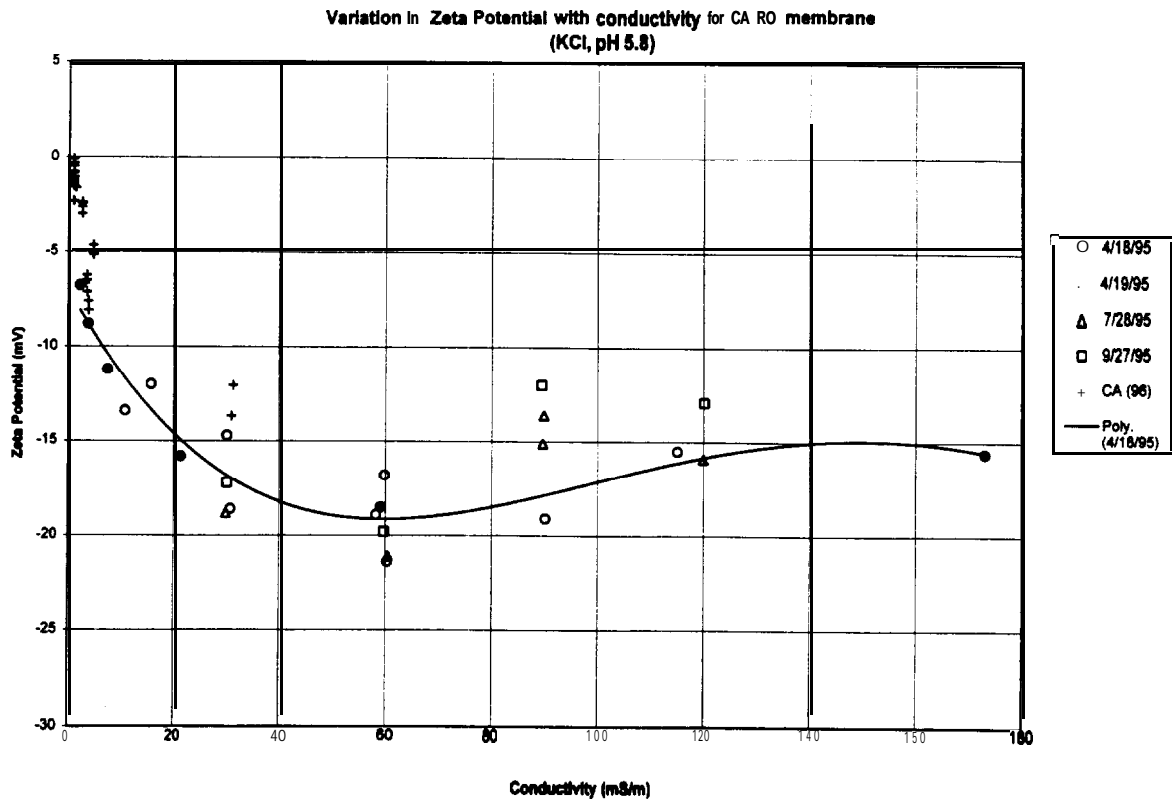
Figure 4.5.—Variation in zeta potential response to pH and conductivity with different CA RO membrane samples on different days. Each point represents the average of at least eight observations.

Variation in Zeta Potent&l with Conductivity for PA RO Membrane
(pH 5.8 KCl Solution)
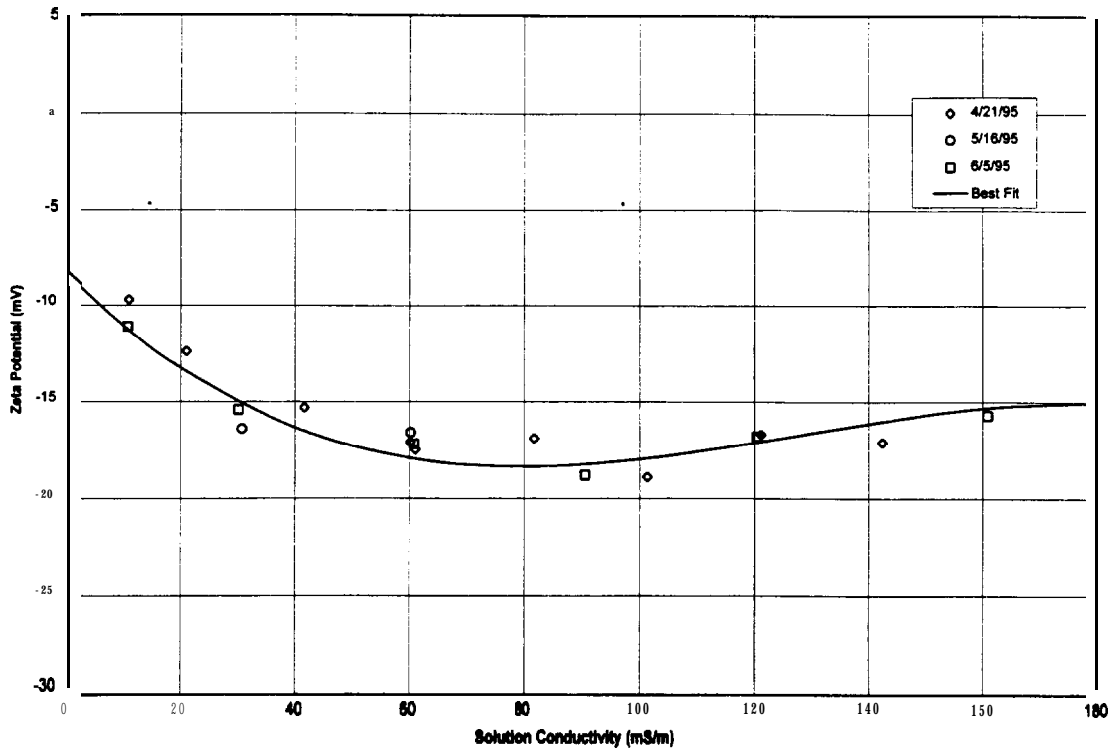
Variation in Zeta Potential with pH for PA RO Membrane
(60 mS/m KCl)
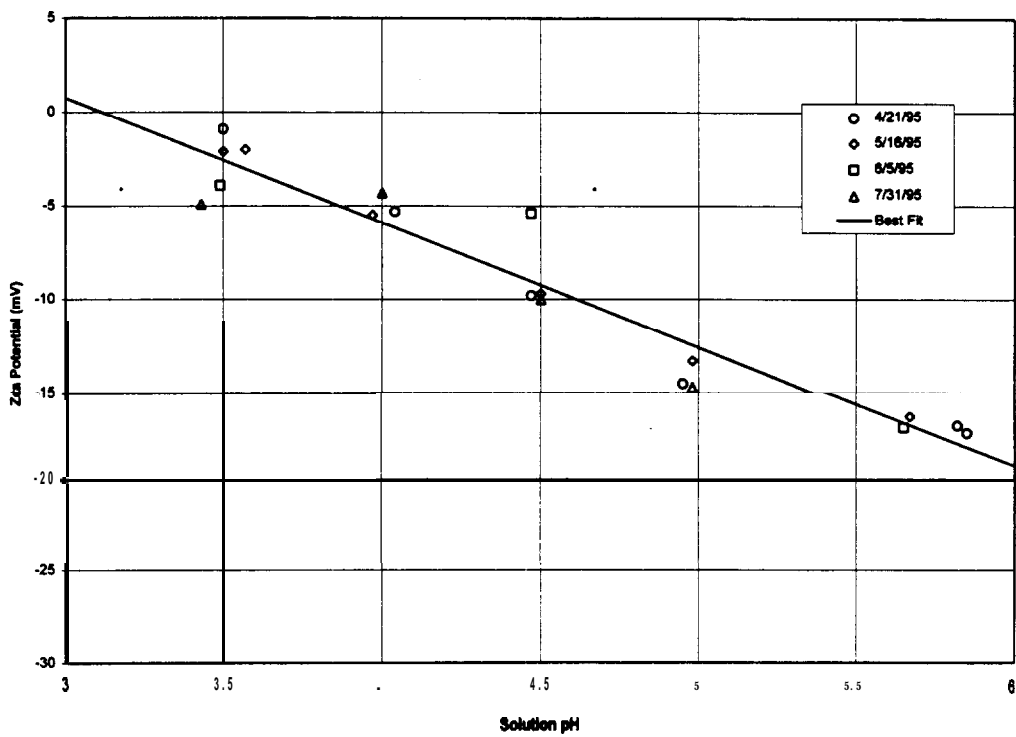
Figure 4.6.—**Variation** in zeta potential response to **pH** and conductivity with different PA RO membrane samples on different days. Each point represents the average of at least eight observations.

4.10

CA RO Membrane Zeta Potential as a Function of pH
For a Range of Solution Conductivities
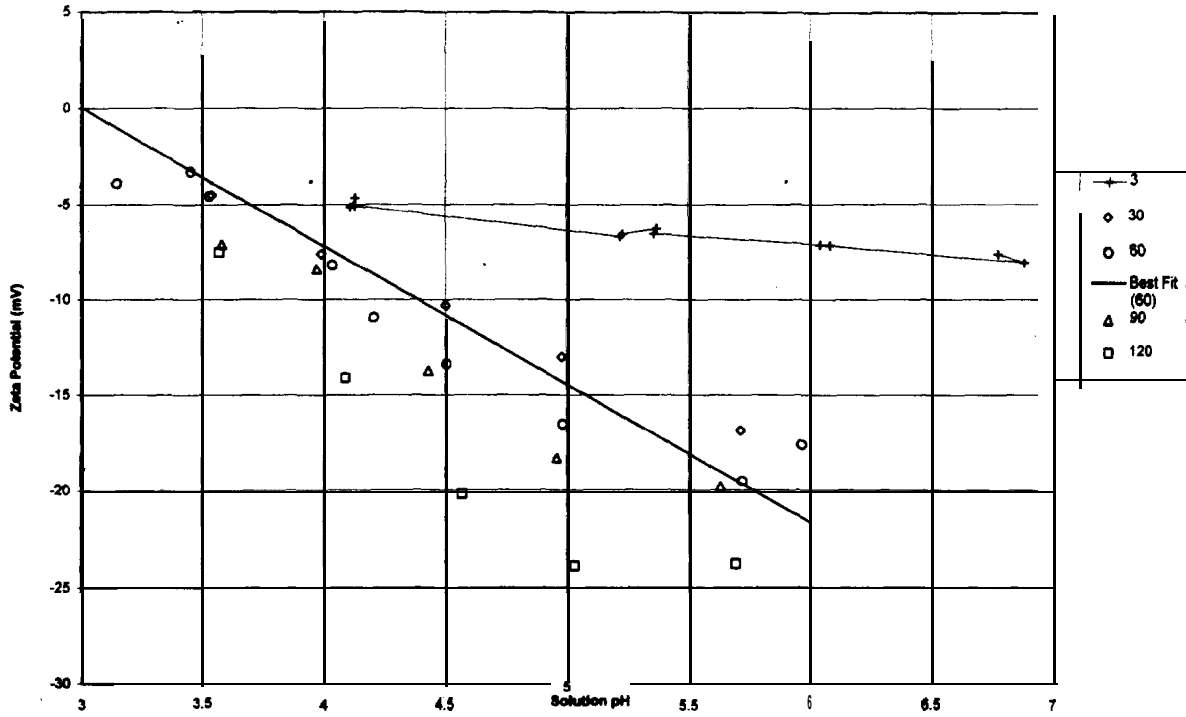
PA RO Membrane Zeta Potential as a Function of pH
For a Range of Solution Conductivities
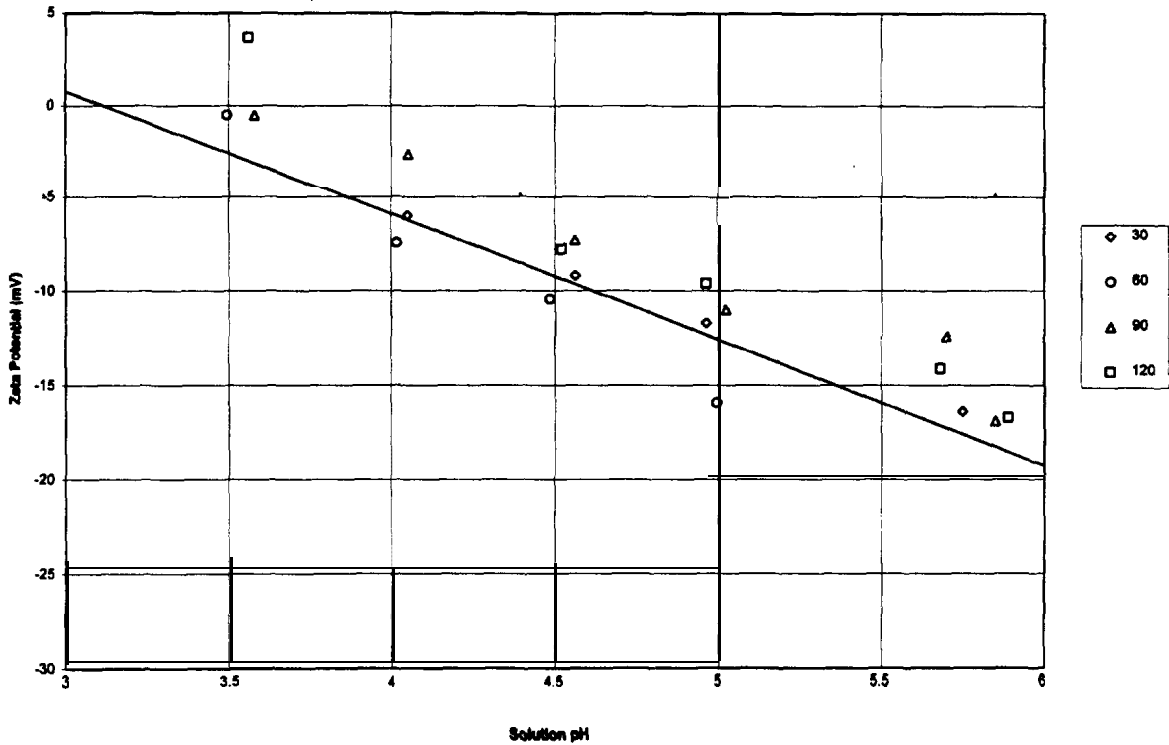
Figure 4.7.—Effect of conductivity on the ralation between zeta potential and pH. Solution pH does not have a strong effect on PA membrane's potential for adsorbing chloride ion; CA membrane capacity for adsorbing chloride ion is related to the amount available.

4.11

Comparison Between CA RO and NF Membrane
Zeta Potential Variation with Conductivity (pH 5.0)
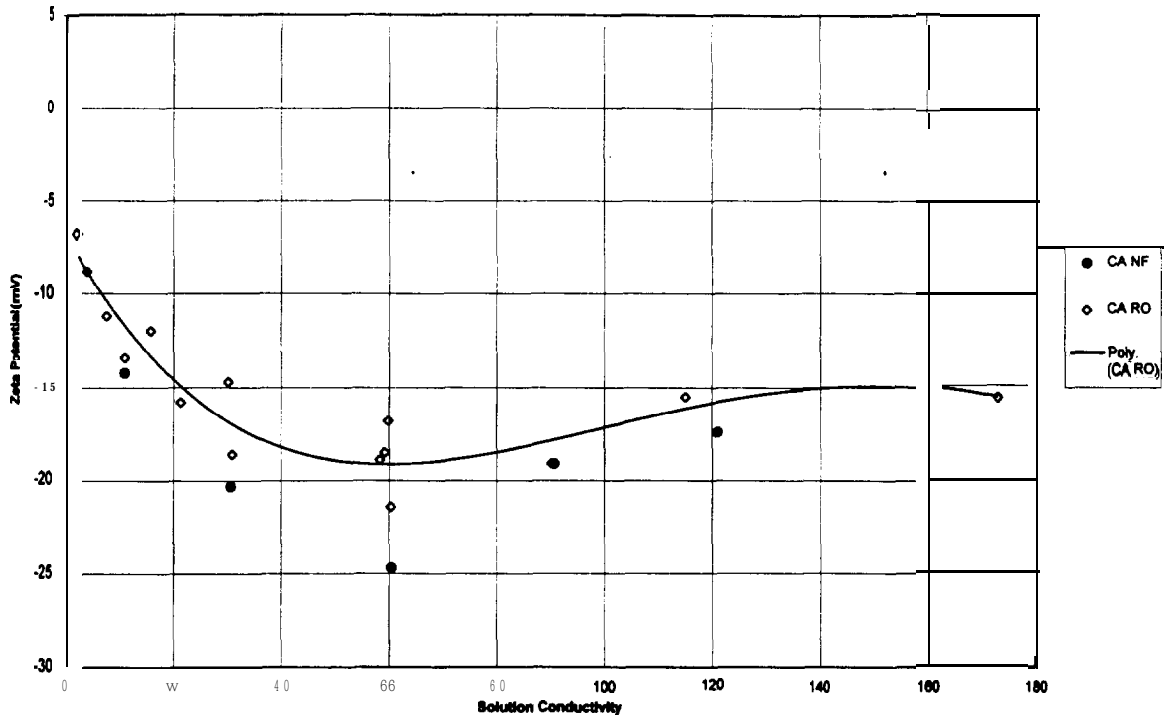
Comparison Between CA RO and NF Membrane
Zeta Potential Variation with pH
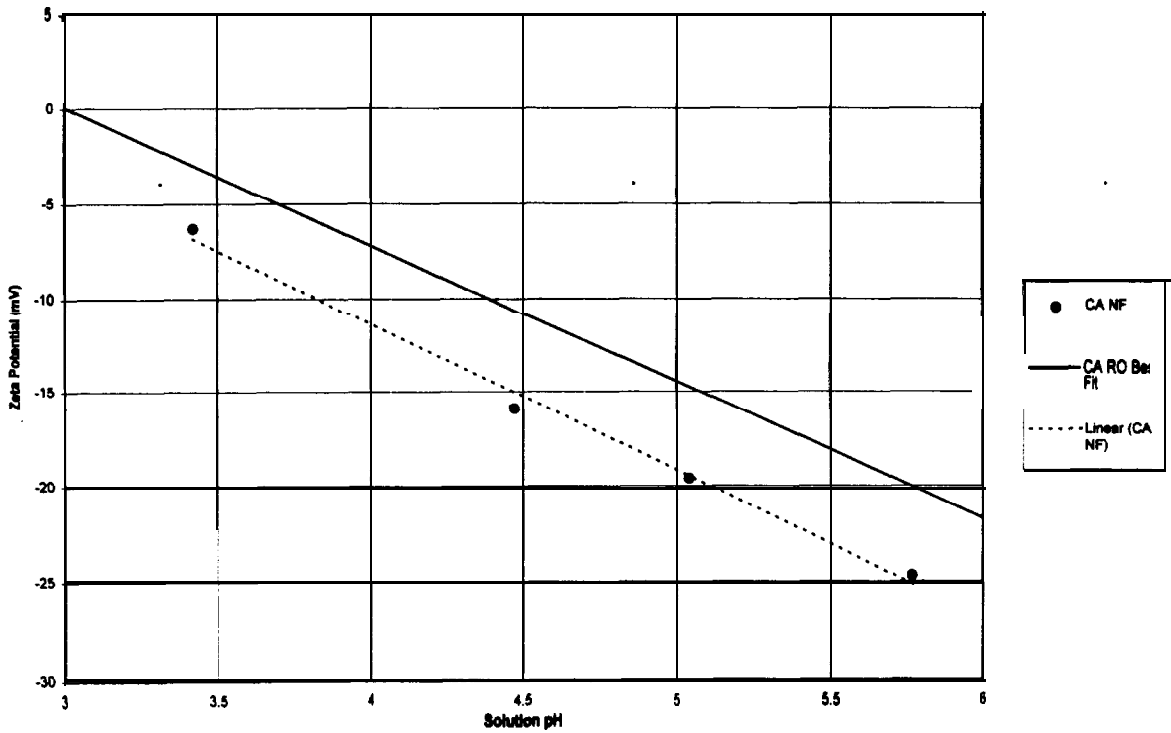
Figure 4.8.—CA RO and CA NF membrane with and without TritonX-100 surface treatment.
The maximum difference between the two membranes occurs at about 60 mS/m.
The difference in zeta potential for the two types decreases somewhat at lower pH levels.

4.12

Effect of Surfactant Adsorption on CA RO Membrane
(pH 5.8)

Effect of Surfactant Adsorption on PA RO Membrane
(pH 5.8)
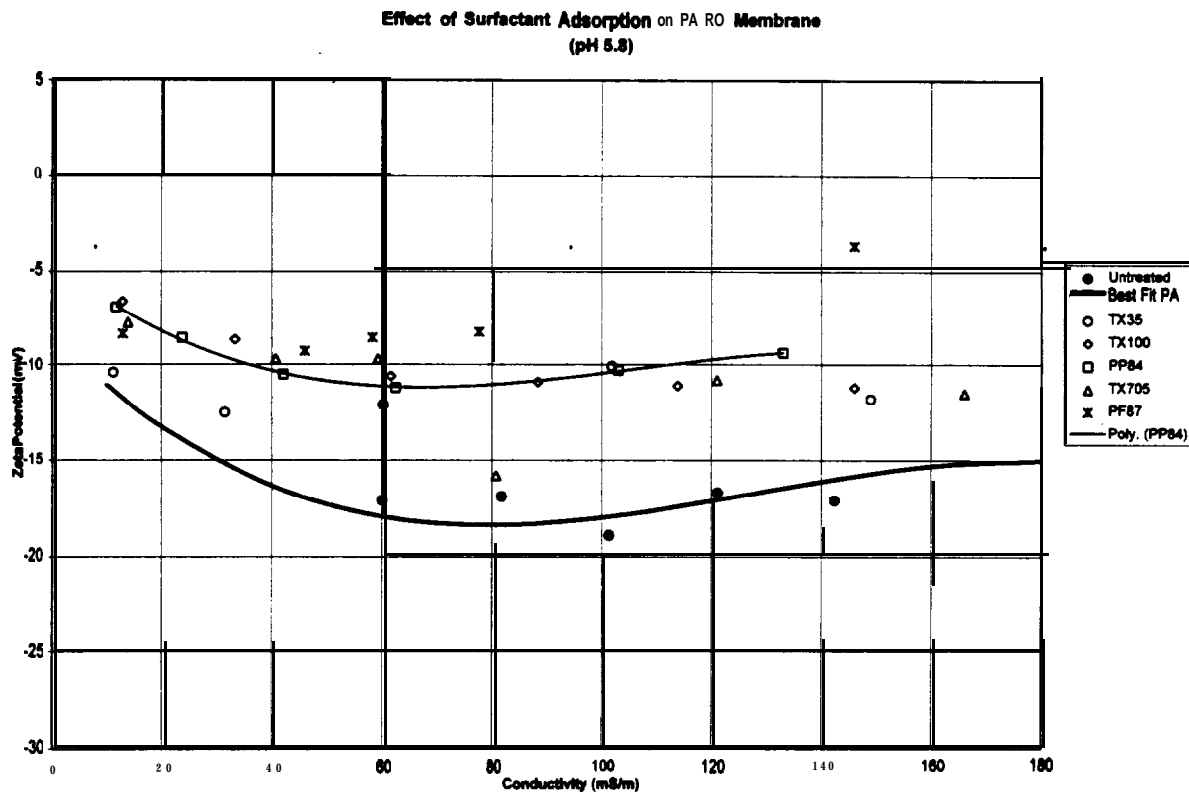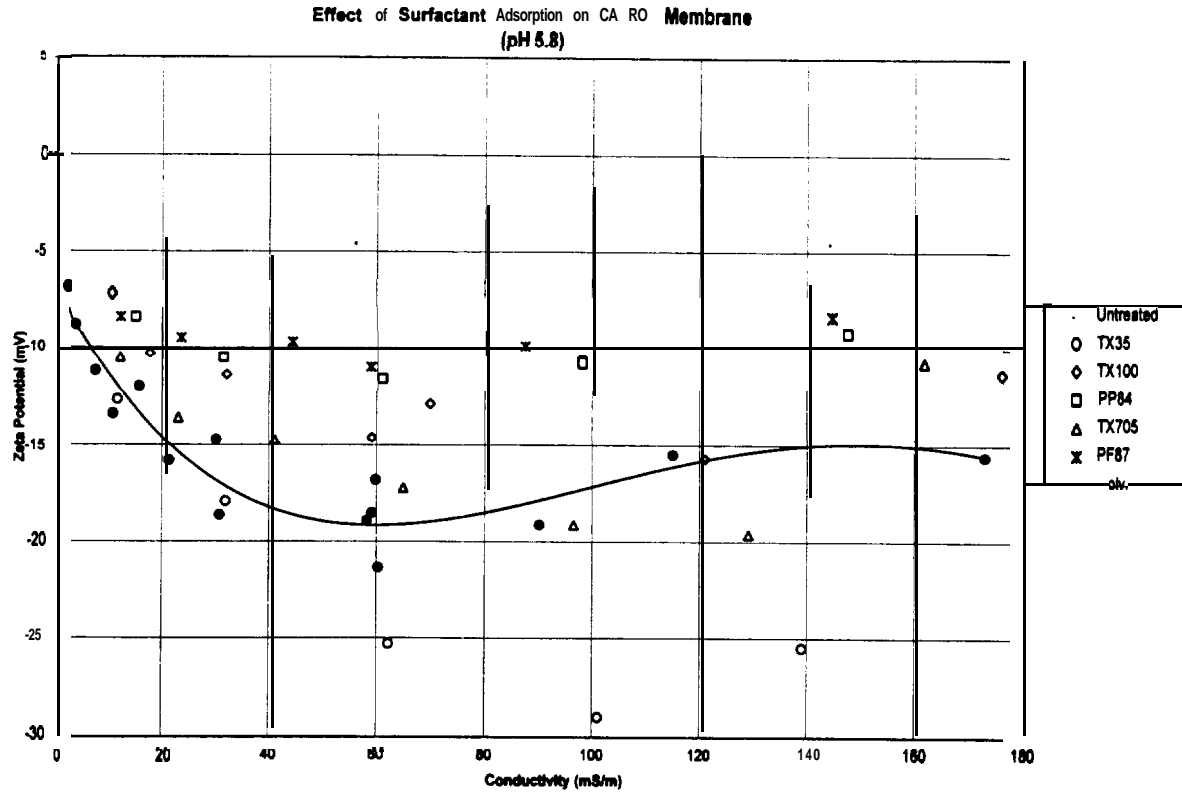
Figure 4.9.—Effect of surfactant adsorption on CA and PA membrane. All the surfactants interfered with PA membrane chloride adsorption. The larger surfactants also decreased the number of ionized groups at pH 5.8, as evidenced by the more neutral zeta potential at low conductivity. The effect of surfactant adsorption on CA membrane zeta potential varies with the PEO chain length.

4.13

Effect of Surfactant Adsorption on CA RO Membrane
(KCl, 60 mS/m)
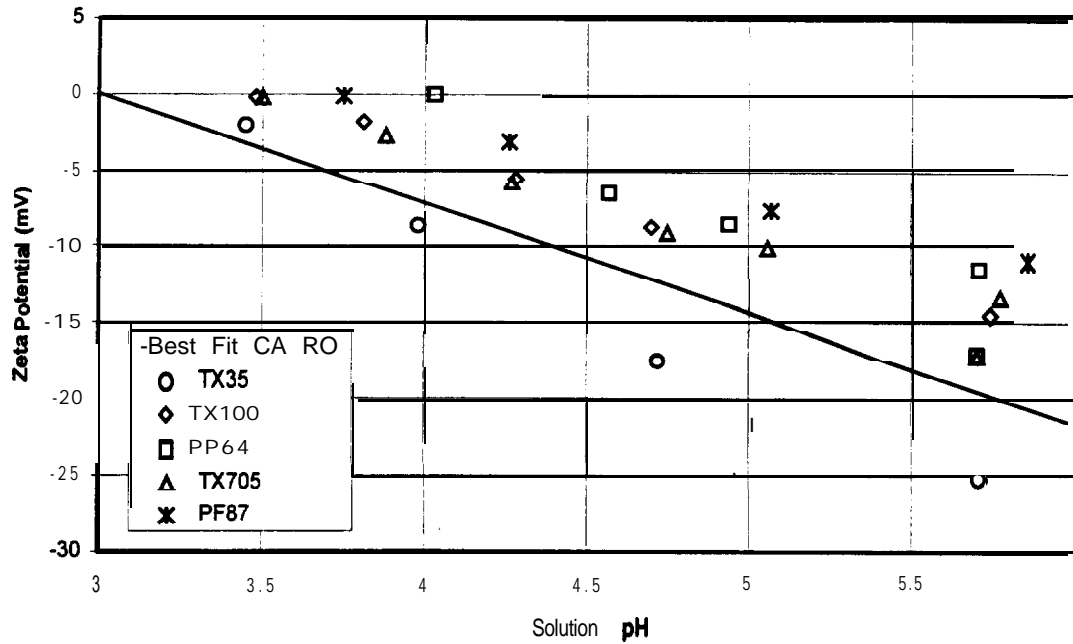
Effect of Surfactant Adsorption on PA RO Membrane
(KCl, 60 mS/m)
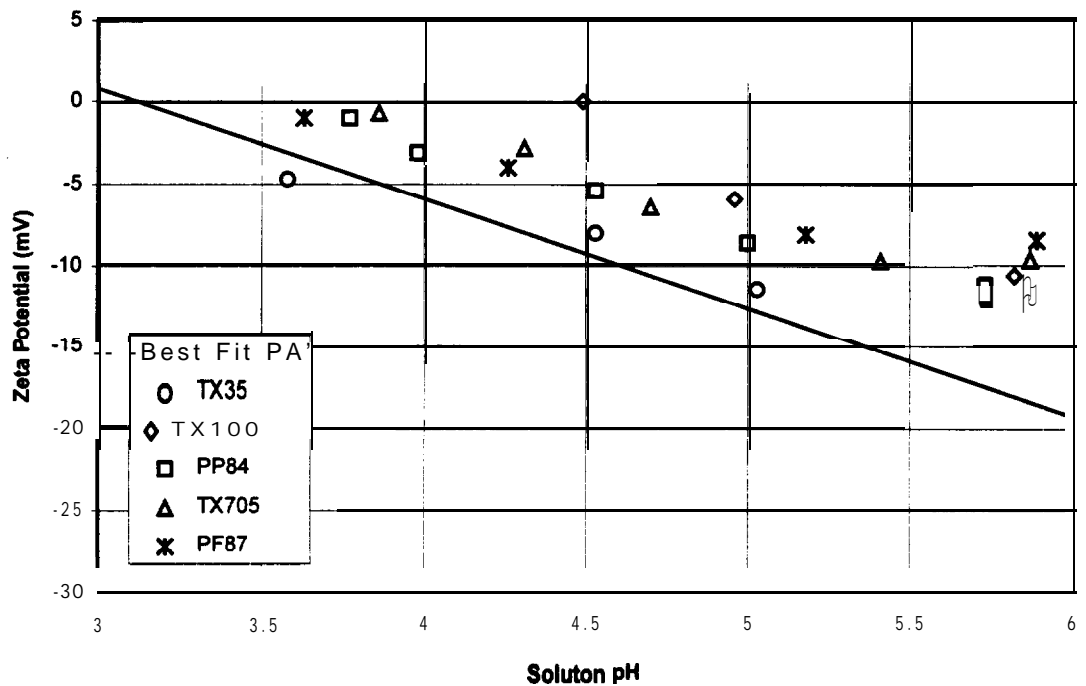
Figure 4.1 O.-Effect of surfactant adsorption on CA and PA RO membrane zeta potential change with pH.
Adsorption of surfactant reduces the ionizability of the membrane surface in all cases with both membranes with the exception of Triton X-35 on CA membrane. The Triton X-35 may include ionizable impurities.

4.14

Comparison **Between** CA RO **and** NF **Membrane Treated** With 1.0 **% Triton** X-100
Zeta Potential Variation with Conductivity at **pH** 5.8
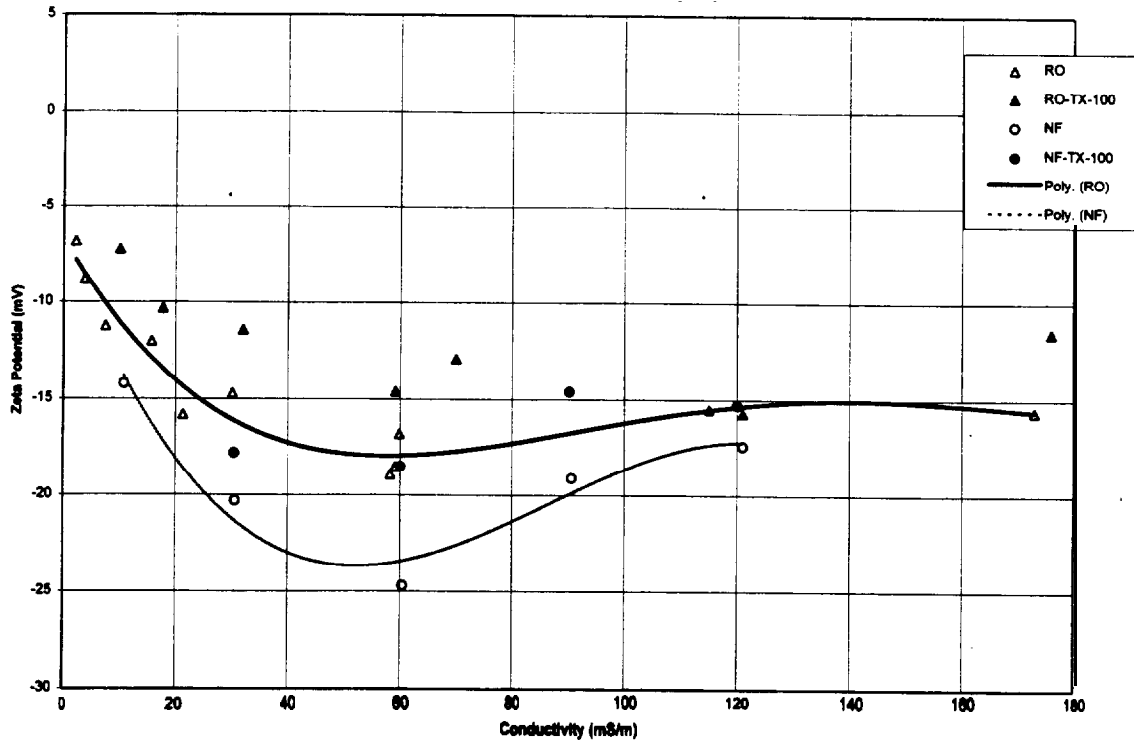
Comparison Between CA RO and NF **Membrane Treated With** 1.0 **% Triton** X-100
Zeta Potential Variation with pH at Conductivity of 60 mS/m
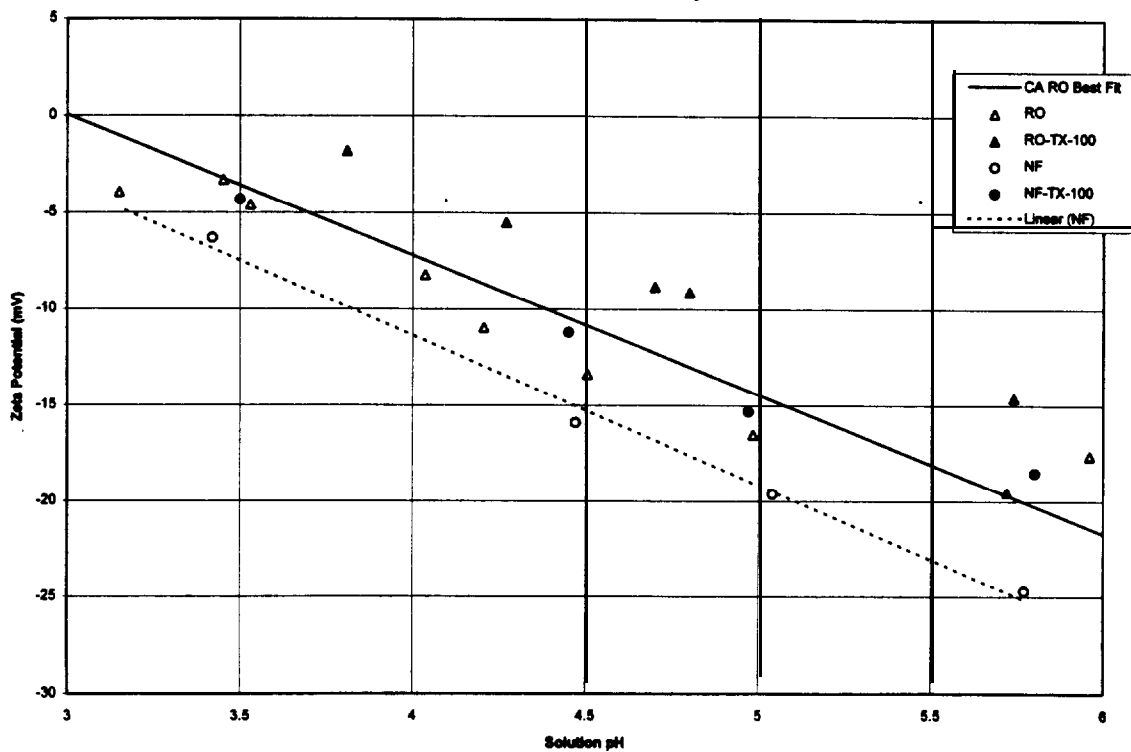
Figure 4.11 .-CA RO and NF membrane with and without treatment with a 1.0% Trition X-100 solution. Adsorption of the surfactant has the same effect on the two membrane types. The treated NF membrane has zeta potential characteristics equivalent to the untreated RO membrane.

4.15

Effect of Trtiton X-100 Treatement Concentration on Zeta Potential of Clean CA RO Membrane
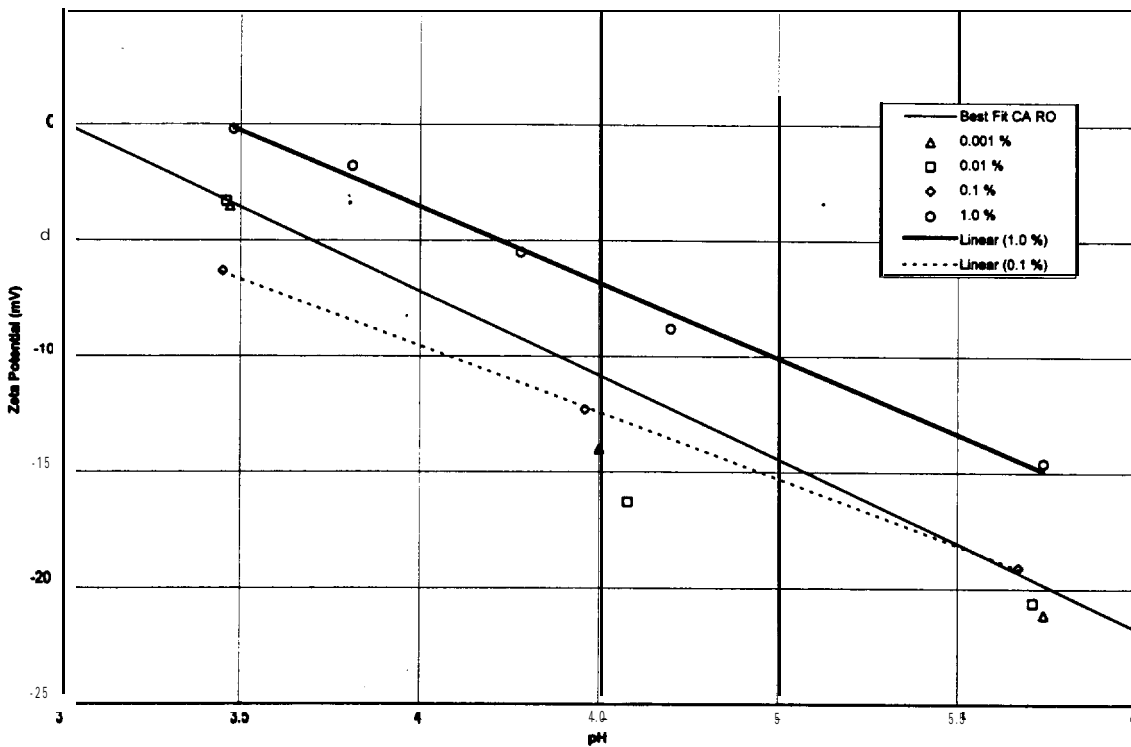
Effect of Pluronics F87 Treatement Concentration on Zeta Potential of Clean CA RO Membrane
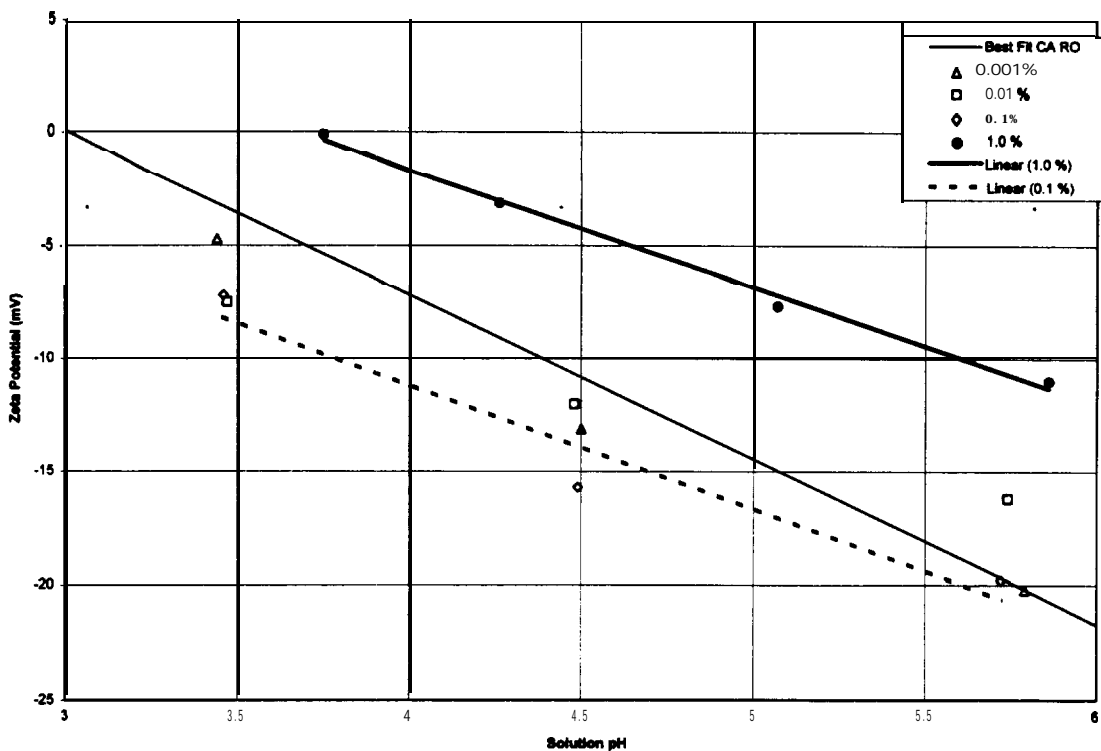
Figure 4.12.—Effect of the concentration of surfactant in treatment solution on the ionizability of CA membrane.
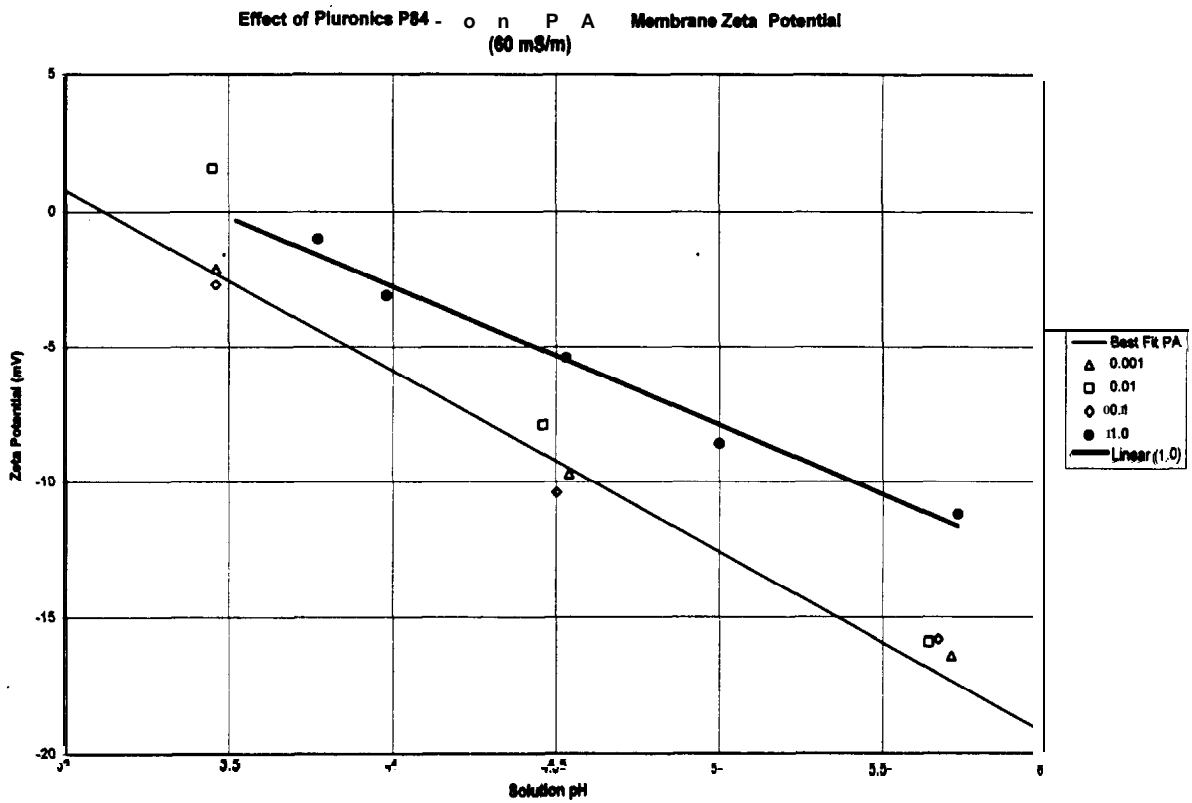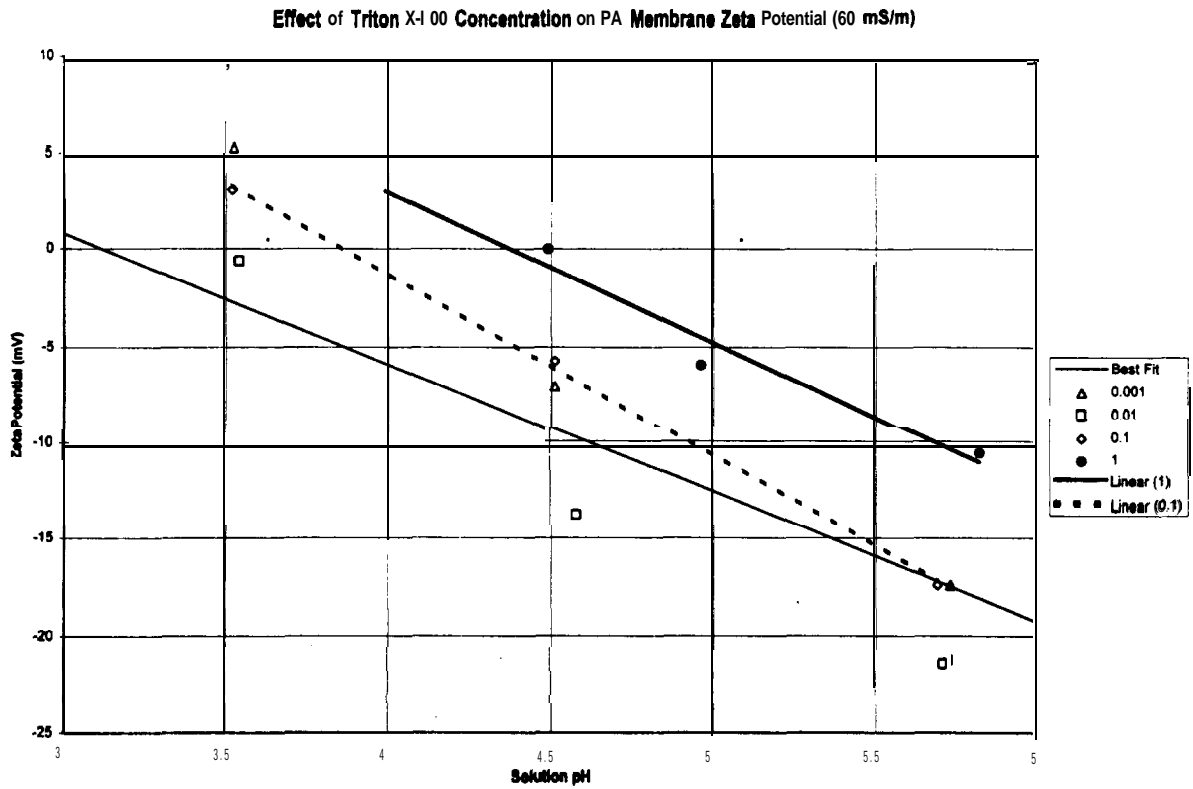
4.16

Effect of Triton X-I 00 Concentration on PA Membrane Zeta Potential (60 mS/m)

Effect of Piuronics P84 - o n P A Membrane Zeta Potential (60 mS/m)

Figure 4.13.—Effect of the concentration of surfactant in treatment solution on the ionizability of PA membrane.
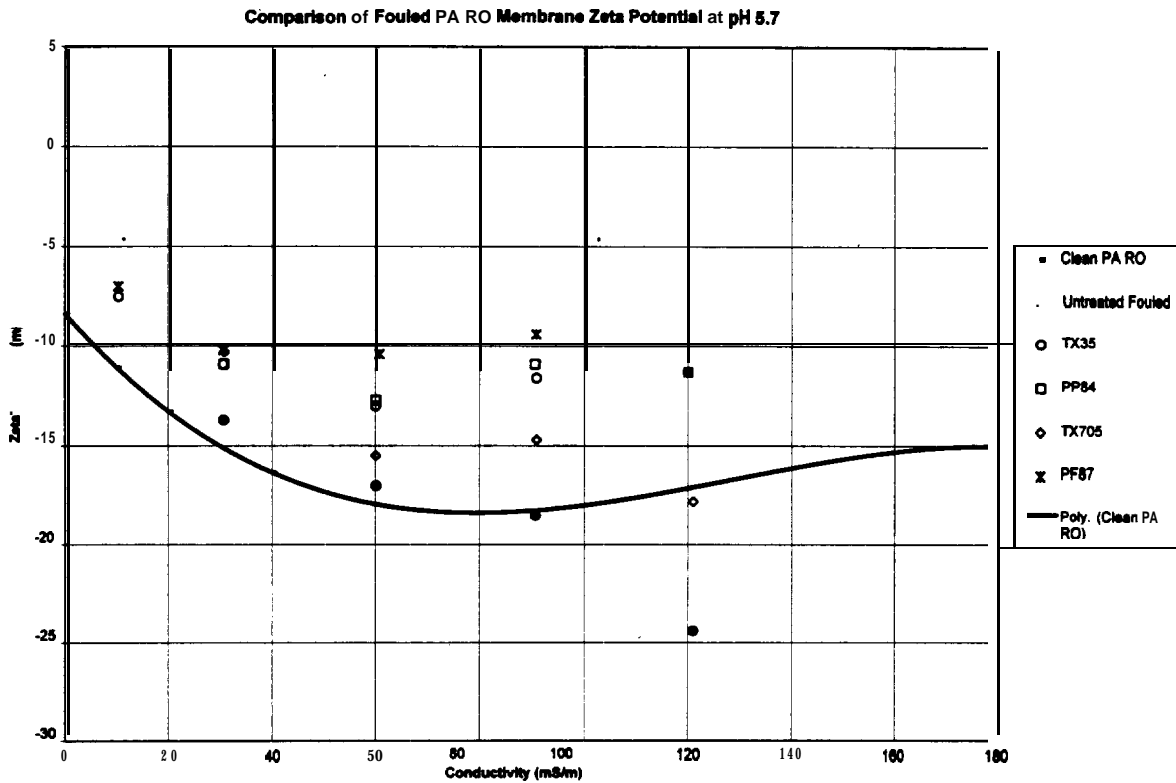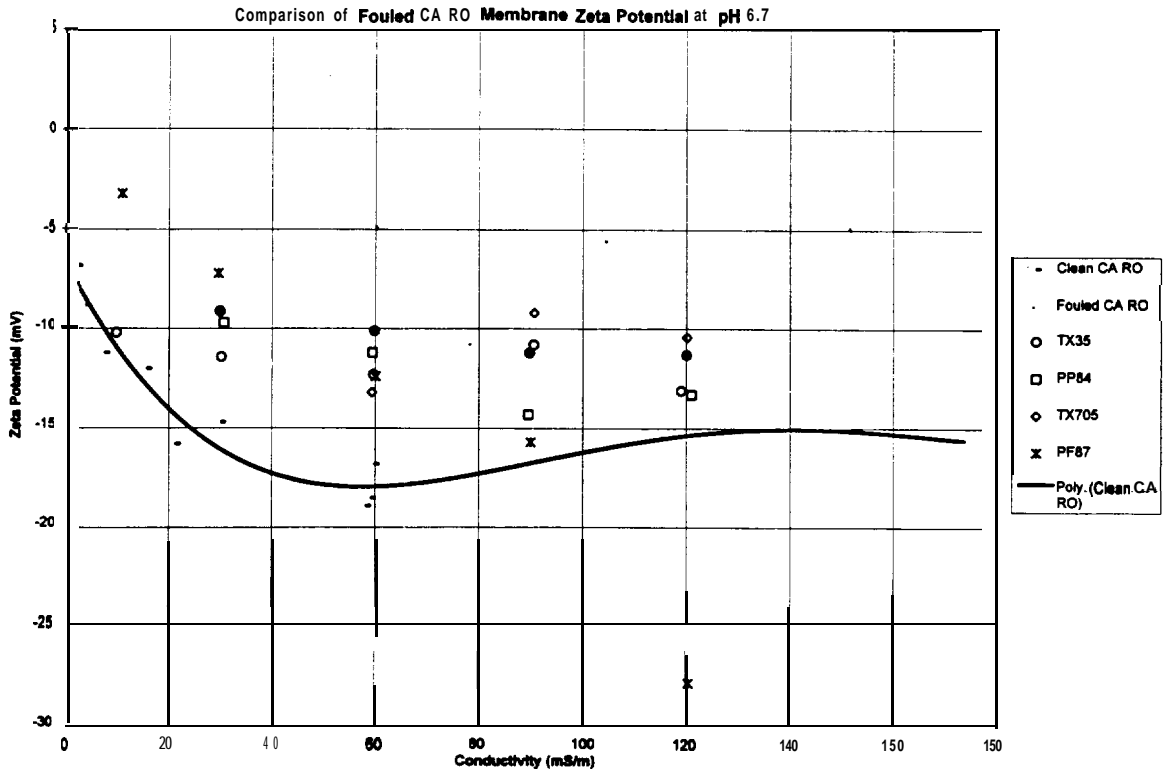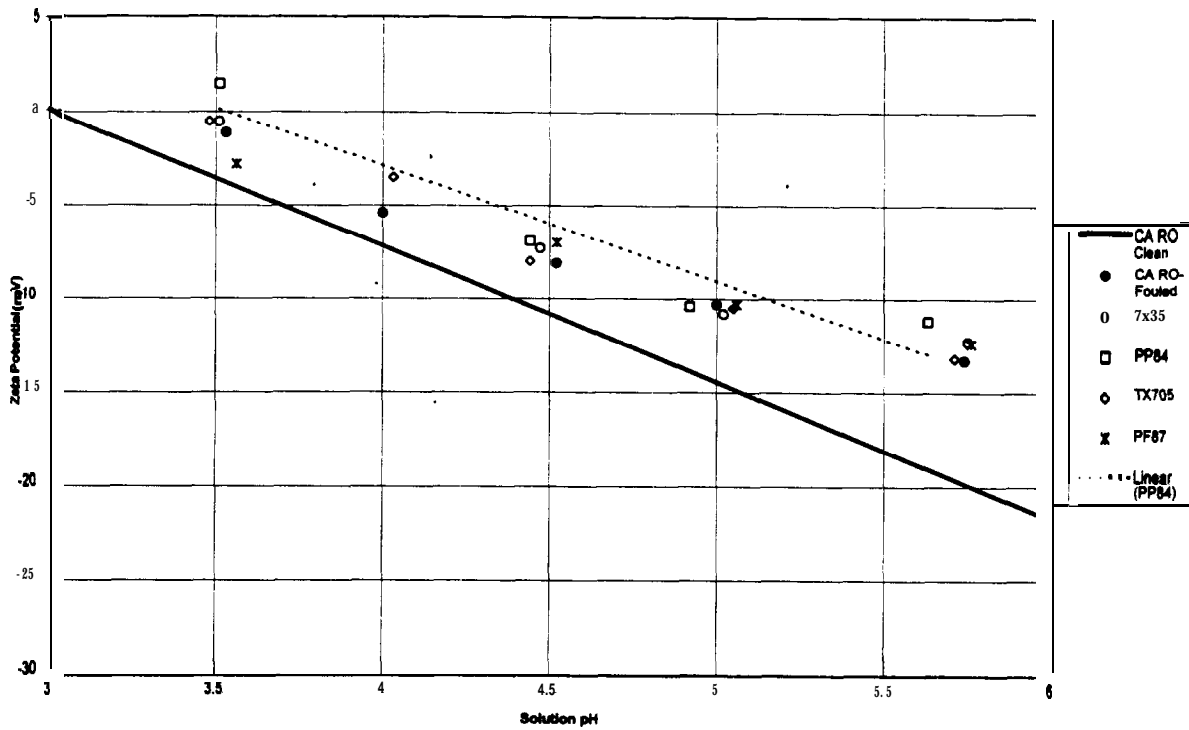
4.17

Figure 4.14.—Effect of fouling on zeta potential characteristics of PA and CA RO membranes treated with a variety of surfactants. Fouling increases the membranes capacity to adsorb chloride ion in the cases of untreated PA and CA treated with Pluronics F87. The CA membrane with Triton X-35 shows a significant decrease in zeta potential magnitude with fouling.

4.18

Comparison of Fouled CA RO Membrane Zeta Potential in 60 mS/m KCl Solution

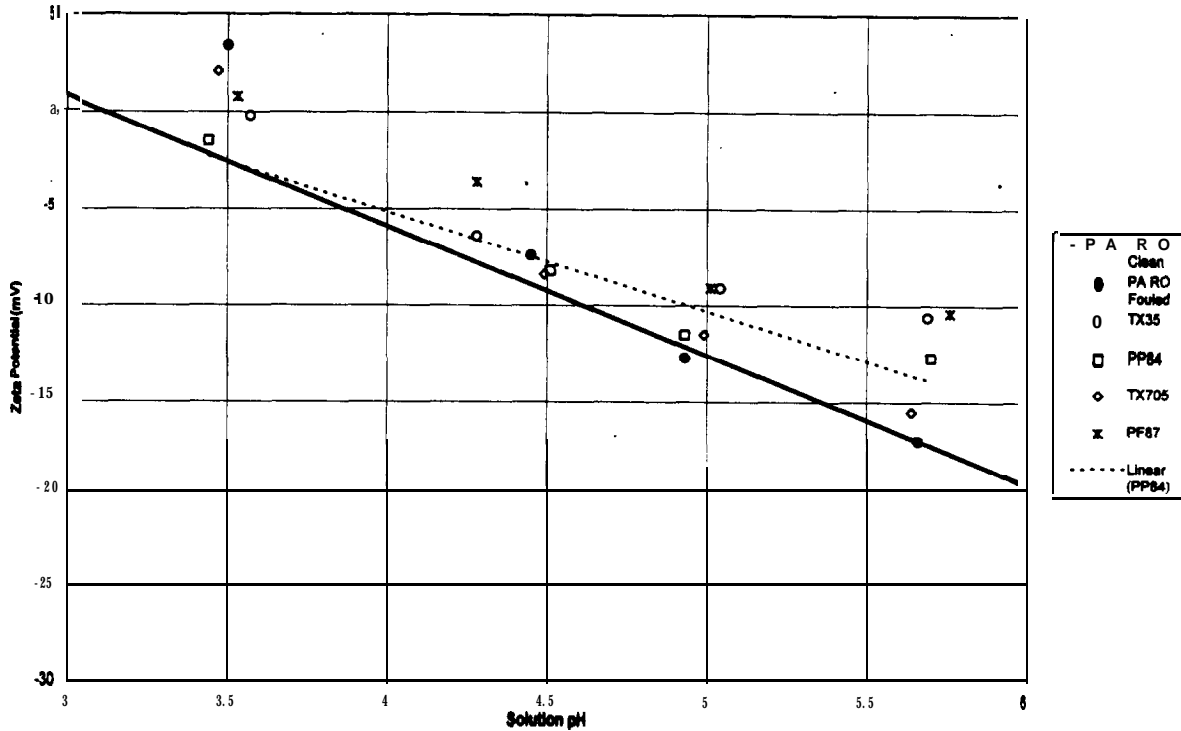Comparison of Fouled PA RO Membrane Zeta Potential
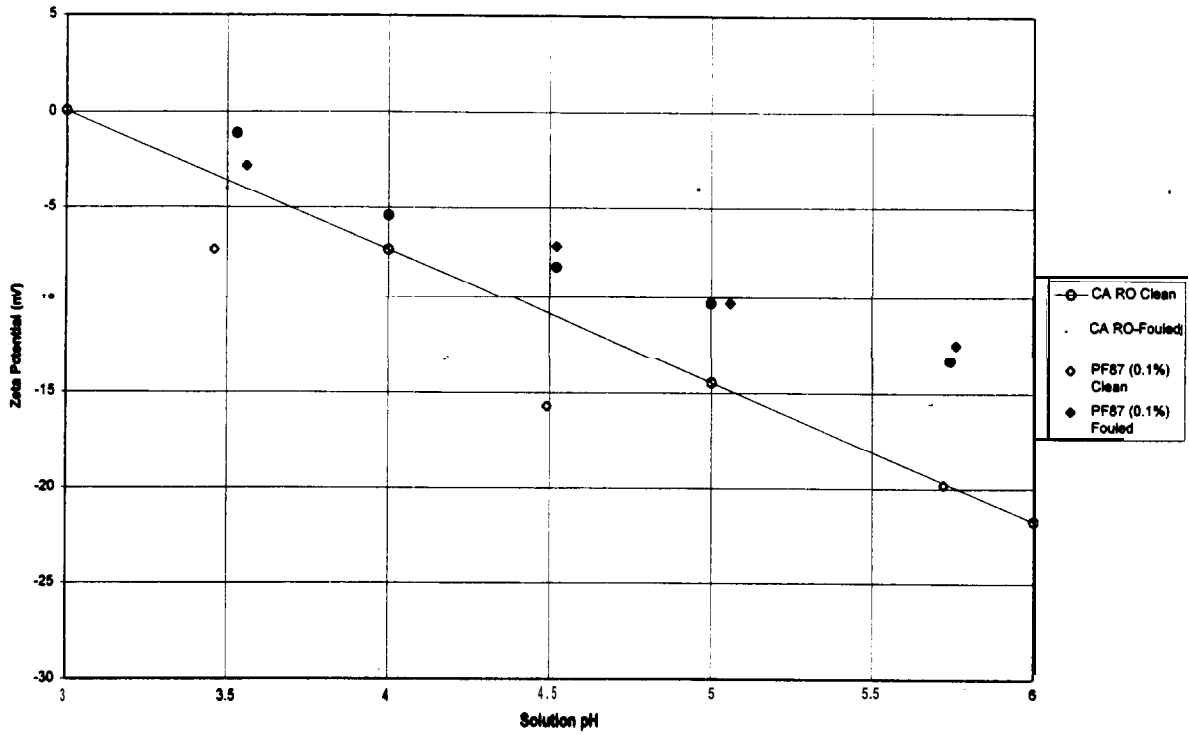in 60 mS/m KCL Solution

Figure 4.1 5.—Effect of fouling on zeta potential characteristics of PA and CA RO membranes treated
with a variety of surfactants. Fouling does not significantly change the treated CA membrane's
zeta potential response to increasing pH, with the exception, once again, of the Triton X-35 on
CA RO membrane. With fouling, zeta potential is increased only slightly in magnitude.

4.19

Comparison of Clean and Fouled CA RO Membrane With Pluronics F87
60 mS/m KCl Solution

Comparison of Clean and Fouhd PA RO Membrane With Pluronics P84
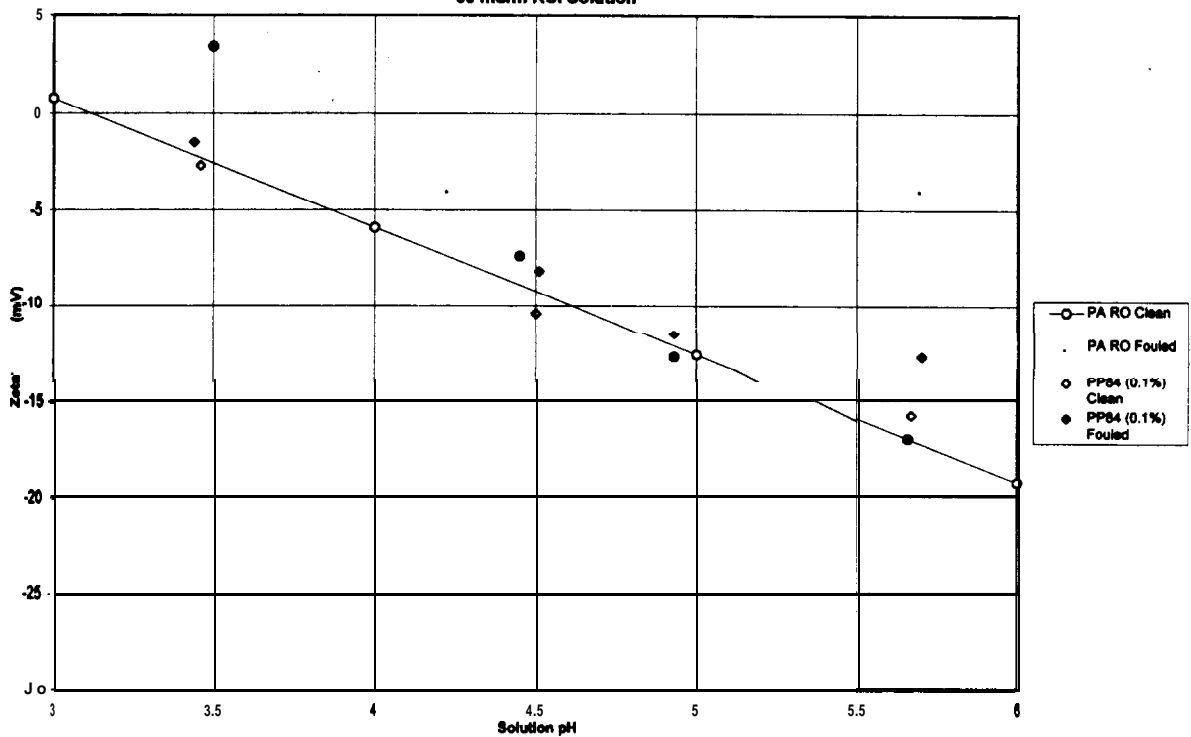60 mS/m KCl Solution

Figure **4.16.—Zeta** potential of clean and fouled membrane treated at the same surfactant concentration compared with untreated membrane. There is no difference between the treated and untreated fouled CA membrane. At pH 5.8, there is a 7 mV decrease in zeta potential magnitude with fouling, indicating an increase in foulant adsorption with increasing pH. The data for PA membrane show a similar trend for the treated membrane.

5. Atomic Force Microscopy Analysis

Atomic force microscopy (AIM) produces a topographical image of the surface based on interactions between a metallic tip and the membrane surface. (See figure 5.1. All figures for this chapter are at the end of the chapter.) Since membrane material is more delicate than hard surfaces, imaging used tapping mode rather than the normal mode where the tip is in contact with the surface at all times. With tapping mode, the tip is gently tapped over the surface and changes in resistance are recorded. AFM has the capability of vertical and horizontal resolutions on the order of 1 nm and 3 nm, respectively. Measurements can be made on materials under ambient conditions or under water. In this case, AFM was used under ambient conditions to get an image of how the surfactants change the surface topography and to find out whether the surfactant had adsorbed evenly over the surface.

5.1 Procedures

AFM imaging was performed by Ruth Thomson of the National Institute of Standards and Technology Superconductor and Magnetic Measurements Group. The first set of exploratory images was taken from parts of the membrane used in the swatch tests. However, the surface characteristics of these membranes were obscured by particles adsorbed in the swatch test system; so, a set of surfactant treated membrane samples was prepared specifically for AFM analysis. Small sections of membrane (2 cm^2) were suspended in beakers of 150 mL of 0.1 percent (weight) Triton X- 100 solution buffered to pH 6.   These were left on a magnetic stirrer overnight. After treatment, the membranes were washed with DI water and stored in separate containers under refrigeration until imaging. Fouled membrane samples were also provided, but due to the viscous nature of the foulant, it was impossible to obtain meaningful images. The extremely sensitive tip would become coated with the foulant within a very short distance. A third set of samples was prepared with a range of Triton X-100 concentrations. Sets of CA RO membrane samples were treated with 0. 1 , 0.01, and 0.001 percent solutions, and one set was treated with buffered DI water as described above.

Data from the second and third sets were processed to calculate topographical changes over the surface. Topographic analysis produces an image similar to a shaded relief map, which can be rendered into three dimensions. Aside from the images, several statistical parameters are calculated which describe the surface roughness as compared to a least squares best fit plane. The parameters of interest in this study are described below:

> **Roughness   Parameters**
>
> - **Z range:** the difference between the highest and lowest points within the image area.
>
> - **RMS:** The root mean square, or standard deviation, of the Z values within the image.

- **Surface area difference:** The percentage of the three-dimensional surface area over the two dimensional surface area produced by projecting surface onto the threshold plane. If the surface was completely flat, the surface area difference would be zero. As the surface deviates from a level plane, surface area difference increases.

- **Center line average:** Depth at which there are an equal number of pixels above and below.

5.2 Results

Figure 5.2 is a 3-D rendering of AFM images of PA and CA membrane untreated and treated with Triton-X 100. One can see from these images that the two types of membrane have quite different surface topographies. CA membrane is very smooth when compared to PA membrane. Notice the difference in Z-scale on these two images; it was chosen so as to plot the two images at the same size. The untreated CA membrane topography barely deviates form the centerline at 100 nm, while the treated sample has somewhat more relief, but not enough to warrant a smaller scale. The untreated PA membrane must have a scale of 500 nm per division to fit in the same size plot as the CA membrane. The surfactant appears to have filled in the low areas on the PA membrane, consequently the scale had to be decreased to 250 nm per division to maintain image size.

The treated CA membrane has micelles, or globules of surfactant, adsorbed onto the surface which increase the surface roughness. The PA membrane seems to be more evenly coated with surfactant. Notice how the'folds and contortions on the treated membrane seem much more rounded than in the untreated image, even though the Z-scale, or depth range, is half that of the untreated membrane. This may indicate that the indentations, which allow a higher water flux, are filled in on the treated membrane.

Average values for the roughness parameters are given in table 5.1 and graphed in figure 5.3. In both cases, the Z-range and Center line average decrease with treatment. This is to be expected if the surface is being filled in by the surfactant. There will be a smaller difference between the highest and lowest points, and the center line average will be scaled accordingly. It is also not surprising that the RMS is slightly lower for the treated membrane samples. The change in the surface area difference is also intuitive. The PA membrane has much more topographic relief than the CA membrane. As the crevices are filled in, the surface begins to flatten out somewhat, hence the lower surface area difference. The CA membrane is very flat already. The surfactant has no crevices to fill in and so builds up on the surface, increasing the surface area.

Table 5.2 and figure 5.4 present the topographic results for CA RO membrane treated with a range of Triton X-100 concentrations. The trend seen in figure 5.3 is repeated in the topographic data shown in figure 5.4. The critical micelle concentration (CMC) for Triton X-100 is approximately 0.015 weight percent. As the surfactant concentration nears the CMC, all roughness parameters increase significantly. At the CMC, the surfactant forms globules which

would adhere to the surface as such. The 0.001 weight percent treatment had the lowest RMS, indicating that the surface was more regular than any of the other samples. At such a low concentration, the surfactant molecules adsorb to the surface singly rather than in large groups.

Table 5.1 .-Comparison of roughness parameters for PA and CA membrane with (+) and without (-) Triton X-100 surface treatments. Data were collected over four 25 μm^2 areas, all on the same membrane sample. Values listed are the average of the four areas.

	PA-	PA+	CA-	CA+
Z range (nm)	530	441	132	96
Center line average (nm)	369	271	80	56
RMS (nm)	74	70	20	13
Surface area difference (%)	146	95	0.7	4.3

Table 5.2.—Comparison of roughness parameters for CA RO membrane treated with Triton X-100 in concentrations ranging from 0% to 6.1 wt % solutions. Values listed are averages from 13 - 6.25 μm^2 areas of one membrane sample.

treatment	0	0.001	0.010	0.100
Z range (nm)	32.6	35.4	44.9	53.9
Center line average (nm)	15.5	20.0	27.8	34.1
RMS (nm)	5.3	3.9	5.5	5.6
Surface area difference (%)	0.25	0.51	1.33	1.43

5.3 Conclusions

AFM is an effective tool for visualizing membrane surfaces. The differences that can be seen between PA and CA membrane make it easy to understand why PA membranes foul so easily and are so difficult to clean. Analysis of a range of surfactants with AFM was a satisfactory method for identifying the minimum concentration for effective coverage of CA membrane.

There are some problems with the analysis, however. It took 3 to 4 hours to analyze 16 different areas on a membrane sample. During this time, the membrane was exposed to air and began to dry out. Also, some of the samples became contaminated with particulates at some point and those files had to be discarded. More untreated samples need to be analyzed to assess variation in tip response. The tip is normally discarded after one analysis session. If the same membrane is then analyzed in a different area with a new tip, there is a great difference in the roughness factors. Much of the difference may be due to membrane drying, though.
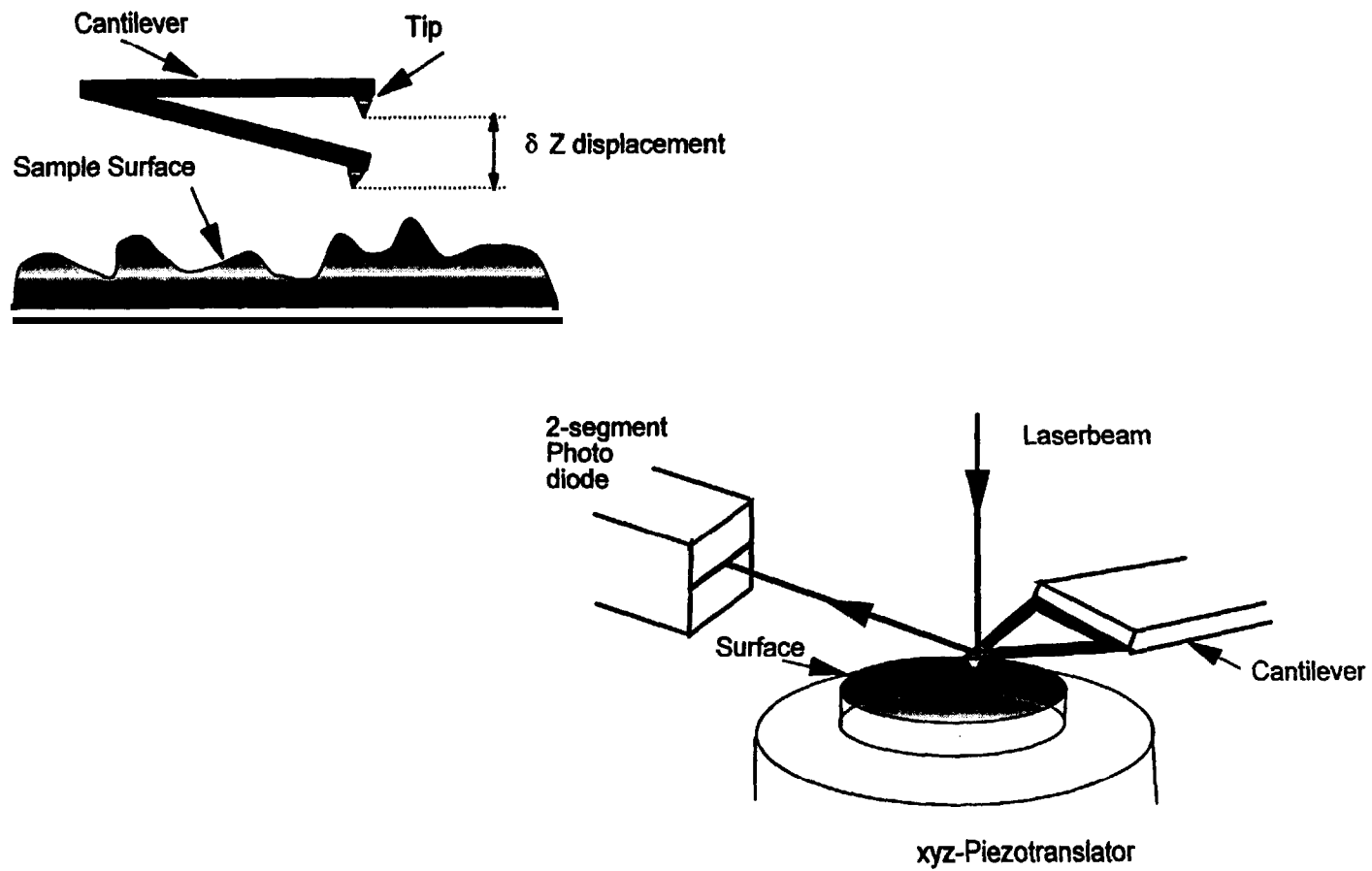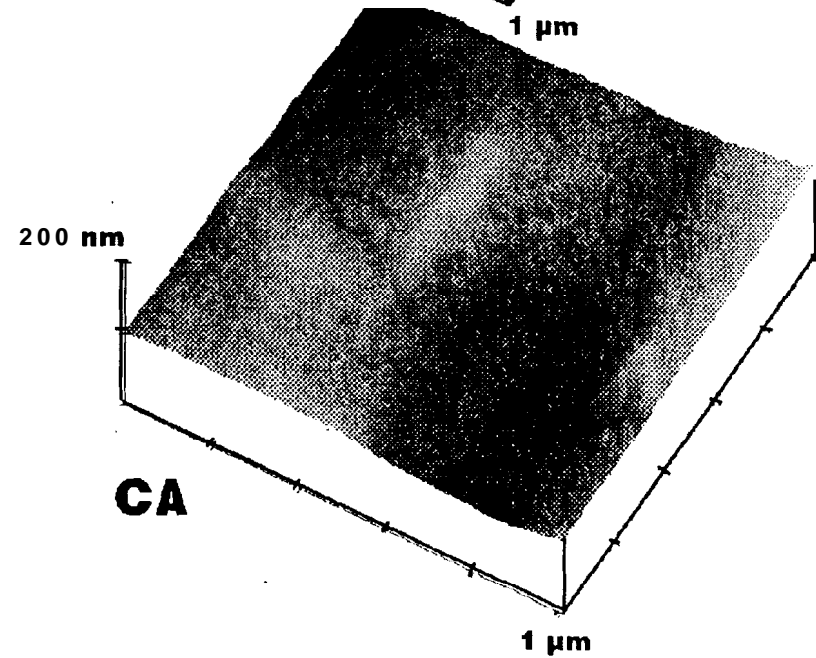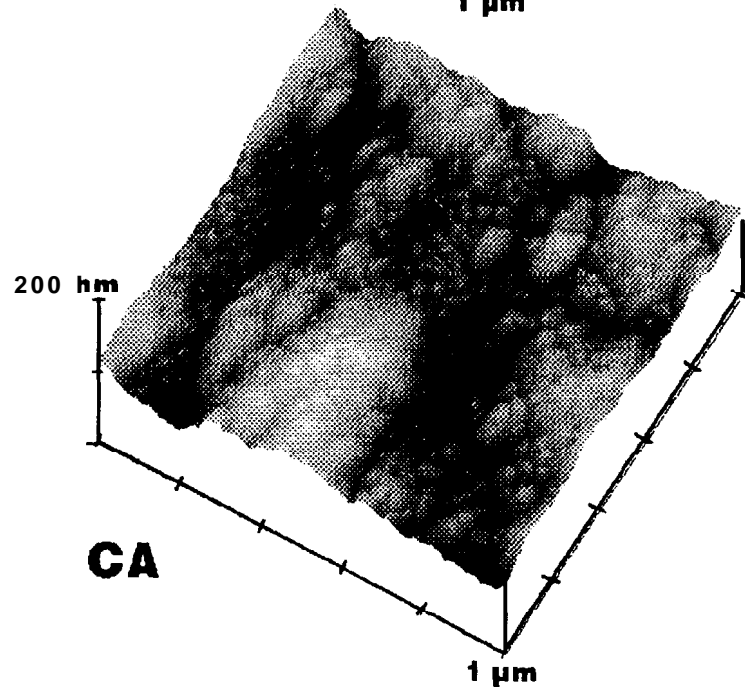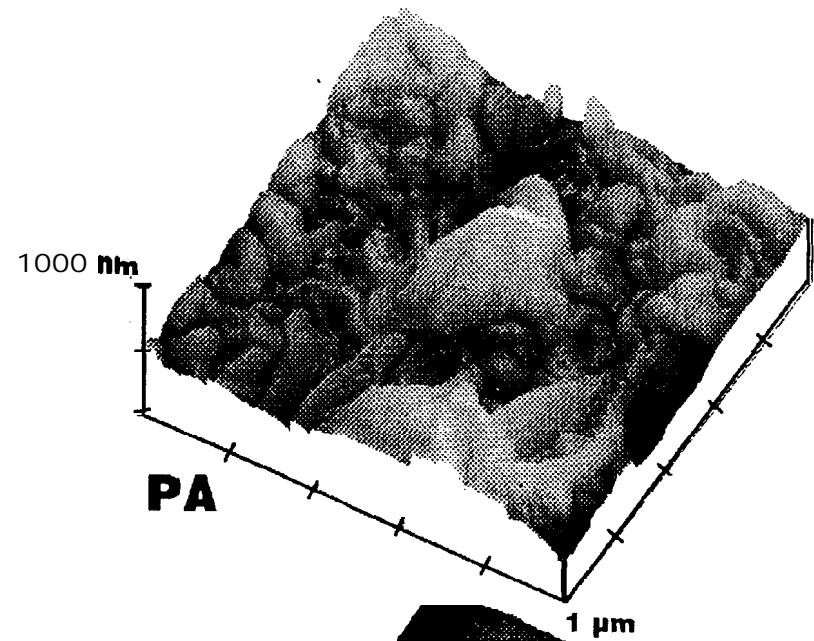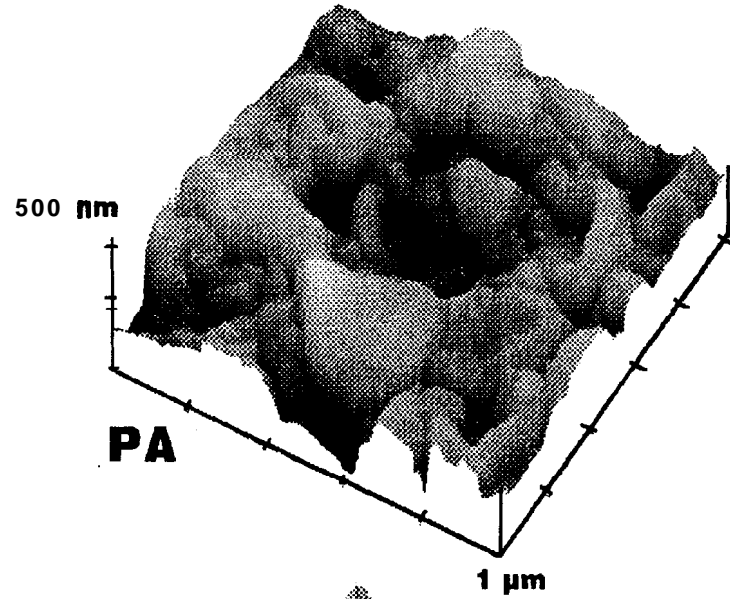
Figure 5.1 .-Atomic Force Microscopy instrumentation. As the cantilever moves the tip across the surface, a laserbeam is reflected off the cantilever into a photo diode which records displacement in the Z direction. X-Y position is a function of time.

Triton X-100 Treated

Untreated

500 nm

PA

1 µm

1000 nm

PA

1 µm

200 nm

CA

1 µm

200 nm

CA

1 µm

Figure 5.2.-Three dimensional images of treated and untreated PA and CA membrane. Images were scaled to produce equivalent sized graphics.
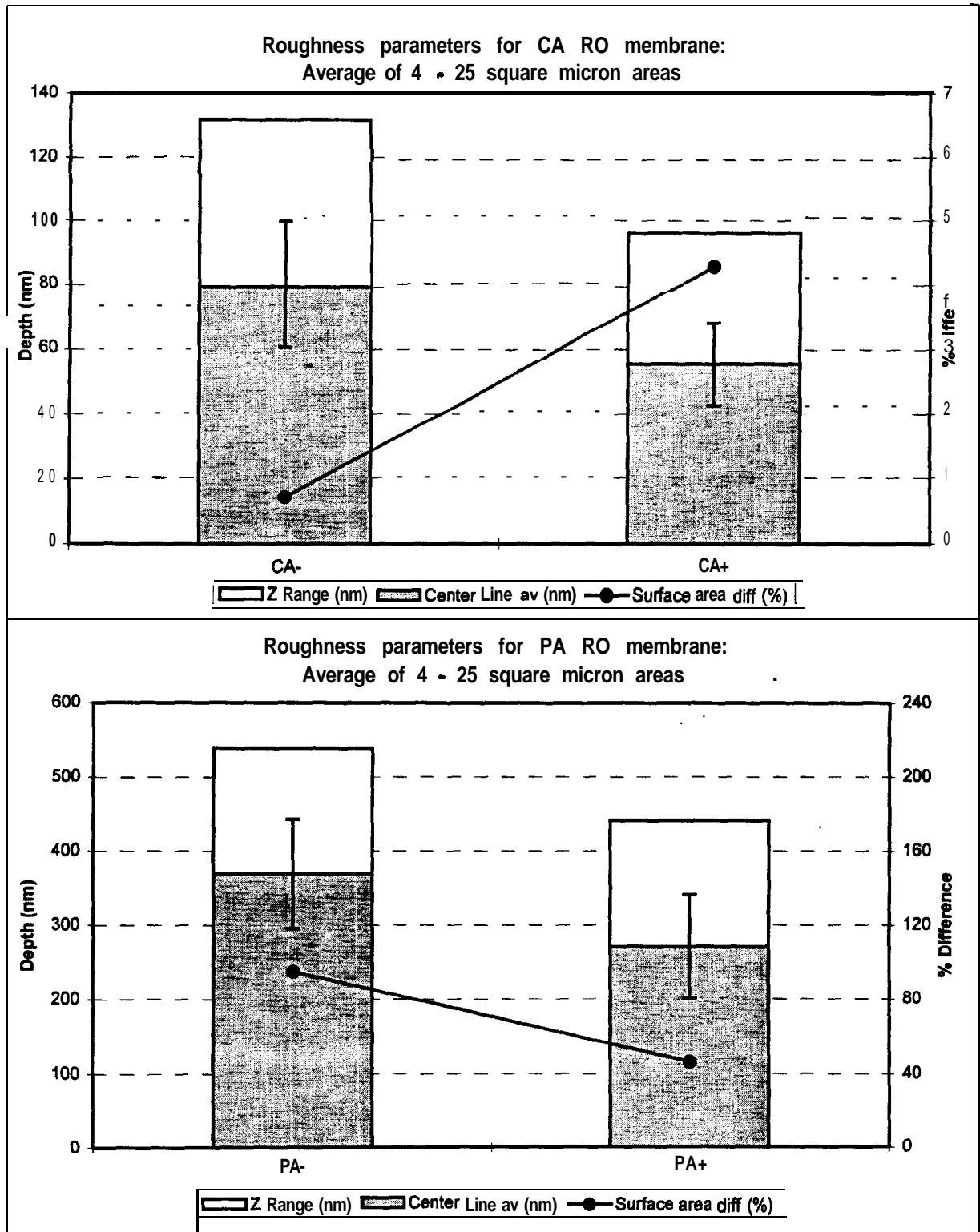
Figure 5.3.—Comparison of roughness for PA and CA RO membrane with and without Triton X-100 surface treatment. **Z** is the difference between the highest and lowest points. The center line average is the height at which there are an equal number of pixels above and below. The surface area difference is an indication of roughness. Surfaces with more peaks have a higher area difference. Error bars represent the RMS, or standard deviation, from the center line average.

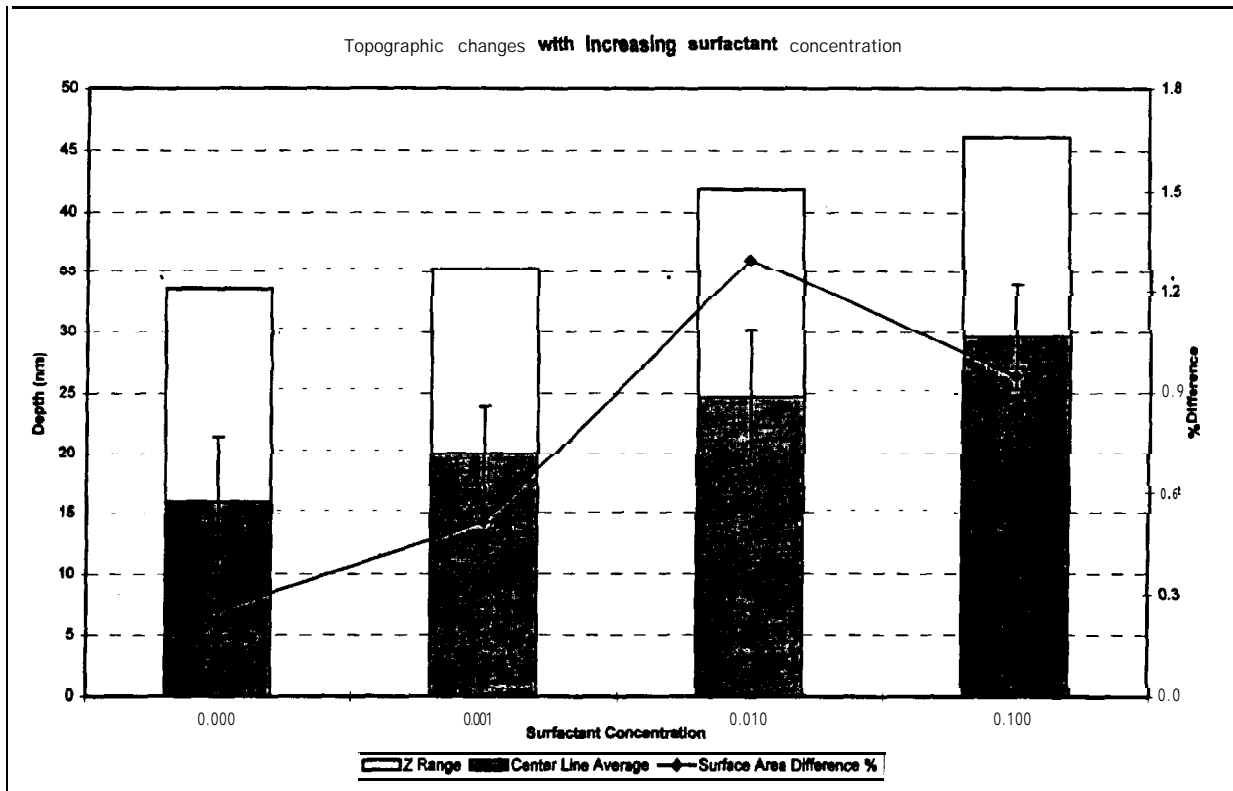Topographic changes **with increasing surfactant** concentration

Figure 5.4.—Variation in CA RO membrane roughness with surfactant concentration. Values represent averages of 13 • 6.25 square micron areas; bars represent the RMS, or standard deviation from the center line average. Higher degree of phase shift indicates higher surface frictional resistance.

6. Acoustic Time-Domain Reflectometry Characterization of Fouling

6.1 Introduction

Acoustic time-domain reflectometry (ATDR) uses the return time of sound waves bounced off a surface to characterize the interior of the substance. On a large scale, ATDR is used to probe the structure of dams to gauge their structural integrity, but it is also sensitive enough to monitor crystal development on a membrane surface. Sound waves are generated by a 50 MHz, 0.25 inch focal length, acoustic microscope lens-transducer. Sound waves are bounced off the membrane surface and the return time is monitored, processed, and if the speed of sound through the material is known, the thickness can be determined.

This process is under development at the University of Colorado, Boulder, by Dr. Leonard Bond. In previous work, his group had been able to monitor formation of calcium carbonate crystals on a membrane surface and had detected bacterial colonization of a membrane surface. They had not tried the technique to monitor organic colloidal fouling or to quantify fouling. A membrane sample fouled with the standard fouling solution was analyzed to find out if the fouling layer thickness could be determined with ATDR. Dr. Bond was able to distinguish return signals from the base plate, the membrane surface, and another surface very close to the membrane surface that could be interpreted as the surface of the fouling layer. To find out if the method could be used to quantify organic fouling, Dr. Bond's group was contracted to examine clean and fouled membrane samples used in swatch testing.

It is important in ATDR to have an accurate estimate of the speed of sound through the material of interest. The ATDR measures signal strength over time, resulting in a plot similar to figure 6.1. Thickness is calculated from the time lag between strong signals generated by the tops of distinct layers. For instance, a signal is received from the bottom of the platform the membrane is resting on, the membrane surface, and the fouling layer surface. The thickness of the membrane is related to the time lag between the signal from the platform and that of the membrane surface and the speed of sound as it travels through the membrane. The thickness of the fouling layer is calculated in the same way, using the signal from the membrane surface, the fouling layer surface, and ideally, the speed of sound through the fouling material.

After performance evaluation of fouled membrane samples in the swatch test unit, one sample of each set was delivered to the University of Colorado, Boulder, for ATDR analysis of the thickness of the fouling layer. Independent membrane thickness measurements were made with SEM to assist in estimating the speed of sound through membrane material. The fouling layer could not be seen in the SEM.

6.2 Materials and Methods

The various membrane samples provided by Reclamation were refrigerated in sealed polymer bags with distilled water before analysis. The acoustic measurements were made by placing the

membrane or a section of the sample in an immersion tank about 30 cm square and 10 cm deep, which contained about 2.5 cm of distilled water. The samples were set on a glass sheet and held in place using either small weights or clips. In all cases, the membrane was held firmly against the glass plate.

The 50 MHz, 0.63 cm focal length, acoustic microscope lens-transducer was moved over the samples in a standardized pattern. The surface was set in the focal plane of the transducer, which illuminated a spot of about 250 microns in diameter with acoustic energy. The pulse-echo (RF) response showing pressure/voltage as a function of time was recorded using a digital oscillo-scope. Data were initially recorded at a series of points starting close to the membrane center and moving outward along a line parallel to one side. This scan pattern was subsequently modified so that measurements were again taken starting near the membrane sample center and the transducer scanned in the XY plane. The transducer was first moved north, then east, then south, and then west, to return close to the starting point. The second scan pattern was employed on all samples and the dimensions of the measurement "box" were in all cases a few millimeters. The RF output was observed as the transducer was scanned and typical data were recorded. In addition, the pulse-echo response from the thickest region of fouling seen was recorded and measured. Notes were made to record the nature of the fouling/surface response seen during each scan.

In the majority of the data recorded and presented in this report, single-shot data are shown, with no signal averaging being employed. The only exceptions are the data shown in figure D.9, for which averaging was employed.
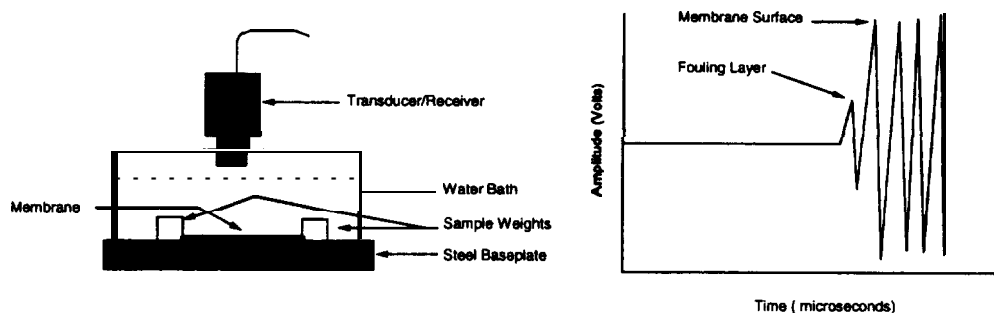

Figure 6.1 .-Schematic showing ATDR apparatus and representative acoustic signal for a fouled membrane.

6.3 Results and Discussion

The pulse-echo RF data for each point measurement were recorded and transferred to computer disc. Each waveform was given a unique identifier/filename. The data were subsequently

reviewed and selected data plotted. The fouling thickness measurements and other characteristics seen are summarized in table 6.1 for the CA membrane and table 6.2 for the PA membrane. In addition, the examples of RF data are shown in the series of figures numbered D. l-D.25 in appendix D. For each fouling thickness, two estimates are provided: one with an assumed velocity close to that of saltwater (1,500 m/sec) and the second with a velocity more typical of polymers and many biological tissue and cell-mass systems (2,000 m/sec).

The current measurement system at the University of Colorado, Boulder, employs a digital oscilloscope with a 5 nanosecond step. Therefore, for an assumed fouling velocity of 2,000 m/sec, a layer with a thickness of 5 microns or greater can be detected and measured. The wavelength at 50 MHz is 30 microns. A shift of about one tenth of a wavelength can be measured using a pulse-echo system without resorting to more complex signal processing. Therefore, the current system can reasonably be considered to have a minimum thickness resolution of about 3 microns. For a layer 100 microns thick, the measurement accuracy would be ±3 microns.

There is a distinctive difference in surface response between a "clean" and a fouled membrane, which can be seen clearly when the data from figures D. l-D.25 are compared. Even a thin layer of fouling can be detected by changes in the initial part of the time-domain signature. There is, therefore, a "fouling detection" capability which has been demonstrated at 50 MHz to detect the presence of thin fouling layers less than one micron in thickness.

Despite the detection capabilities, this demonstration has not shown that ATDR signatures taken at a point, or even on a scan line, can be useful in monitoring performance changes. Figure 6.2 compares the fouled membrane normalized permeate flow rate with the ATDR determined fouling layer thickness. There is no correlation. The problem is that the ATDR measurements are characteristic of one 250 μm diameter circle. Water permeation would be related to the thickness of a fouling layer, but the measured permeation rate is a function of the mode of the layer thickness. With the exception of the clean control membrane, all of the samples submitted for ATDR were fouled in the same manner. They were all visibly fouled when delivered, yet several of the spots chosen for analysis were "clean." Apparently, the membranes became clean sitting in DI water for a long period of time. If ATDR were to have any usefulness in experiments of this sort, membrane samples would have to be analyzed soon after or during fouling. A large population of measurements need to be taken so as to determine the mode of fouling layer thickness. An on-line instrument measuring ATDR would have to scan the membrane surface rather than monitor one point.

Table 6.1 .-ATDR results for CA membrane (see appendix D)

Membrane	Comments	Figure D.#	Assumed Velocity 1,500 m/sec	2,000 m/sec
CA -clean	1) Clean	1	No fouling	No fouling
	2) Light fouling	2	< 5 µm	N/A
CA RO + Triton X-35	Some fouling, mostly thin with clumps	3 4 clump	Clean V. thin 60-80 µm	Clean 80-100 µm
CA RO + Triton X-l 00	1) Small patches of fouling, mostly clean	5	Clean	Clean
	2) Light yellow fouling, most thin, some clumps	6 7 clump	60 µm 147 µm	80 µm 196 µm
CA RO + Triton X-705	Light fouling, thickness varies	8 9 line	48 pm, (hard layer) 45-60 pm	64 µm 60-80 pm
CA RO + Pluronics F87	Some fouling, mostly very light	1 0	Clean	Clean
CA RO + Pluronics P84	1) Yellow light fouling, clumps	11 1 2	27 µm 100 µm	36 µm 133 µm
	2) Appears graded across the membrane	13 14	15 µm 27 pm	20 pm 38 pm
CANF + Triton X-l 00	Light fouling, no clumps	15	6 µm	8 µm

6.4

Table 6.2.—ATDR results for PA membrane (see appendix D)

| Membrane	Observations	Figure D.#	Assumed Velocity	
			1,500 m/sec	2,000 m/sec
PA • unfouled	No fouling seen	16	Clean	
PA - fouled	Some fouling, thin clump	17 18	Clean 159 pm	212 μm
PA + Triton X-35	Some small yellow strips ½" long, few mm wide, thin	19	140 μm much of the surface is clean	187 μm
PA + Triton X-100	1) Few thin patches	20	47 μm	63 pm
PA + Triton X-705	Mostly looks clean, few small thin areas of fouling	21	Very thin layer in a few places, could be surface condition.	
PA + Pluronics F87	Some small thin patches of fouling, very thin	22	4 μm or less	6 μm
PA + Pluronics P84	Minimal fouling, soft and hard layers	23	Soft: 40 μm Hard: 3 μm	53 μm 4 μm
PA + Triton X- 100 0.001%	No fouling seen, or very thin	24	Clean	
PA NF + Triton X-100	Few very thin patches	25	30 μm	40 μm
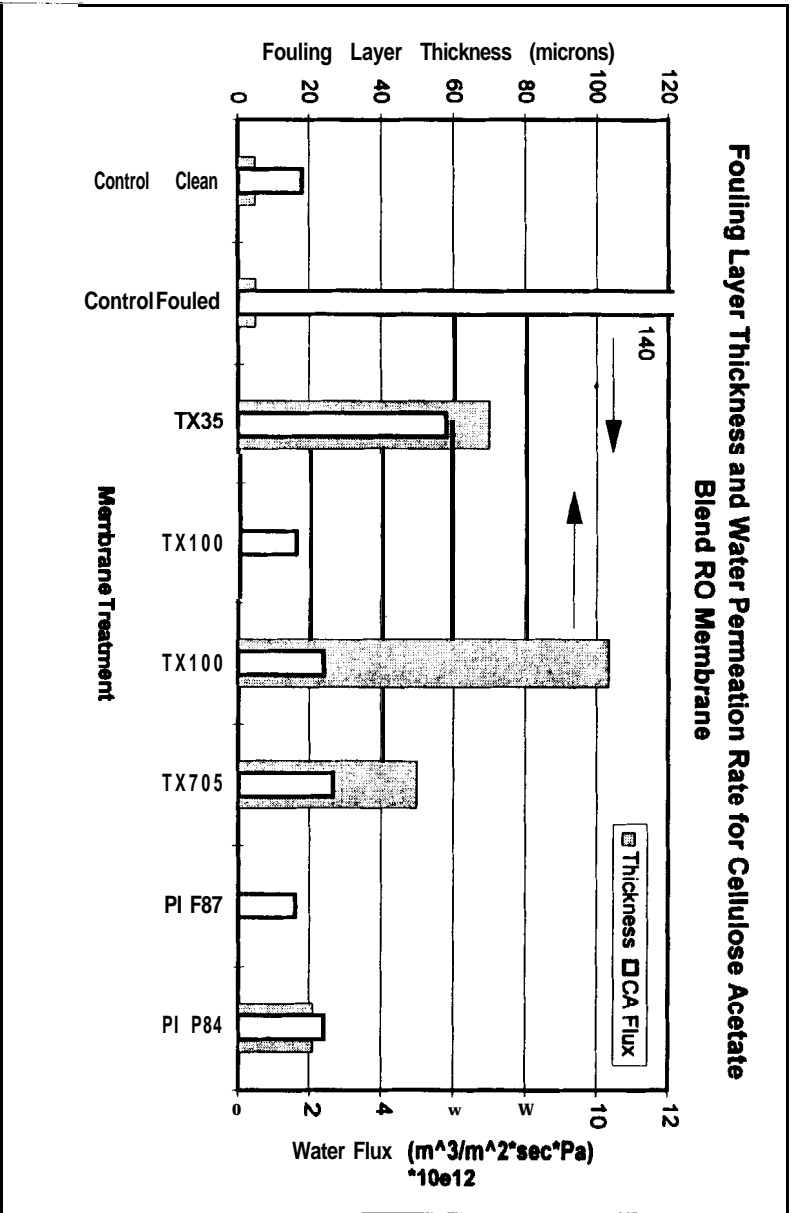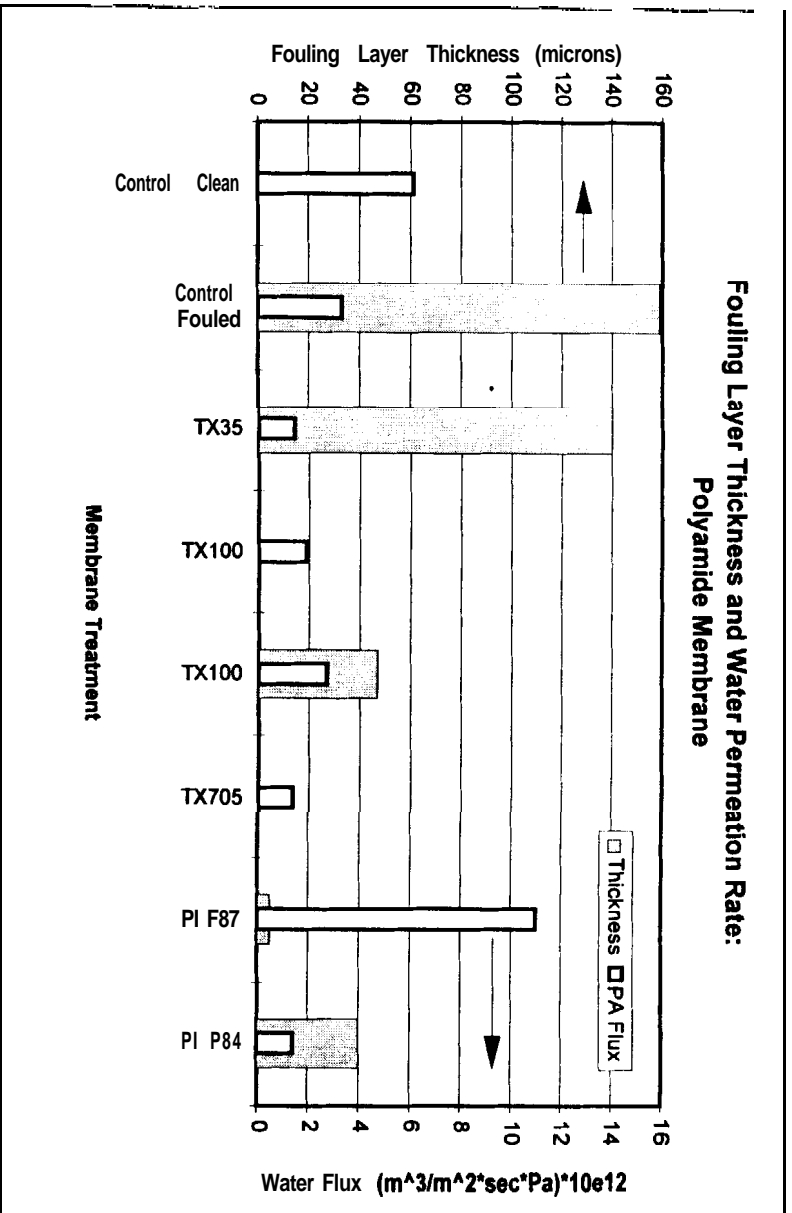
Figure 6.2.—Comparison of ATDR fouling layer thickness results with the last observed normalized permeate flow for the fouled membrane samples subsequently analyzed with ATDR.

7. Conclusions

7.1 The State of Membrane Maintenance

Two contradictory messages were clearly stated by the Membrane Cleaning survey respondents:

1. Membrane maintenance is not a problem.

2. It is extremely difficult to find the best way to clean membranes.

Both of these statements are true. If a membrane plant has good quality water, the system can be maintained with periodic cleaning using generic chemicals or no chemicals at all. However, if the feedwater is of poor quality, cleaning is an extreme and tedious process straining the limits of membrane pH and temperature tolerance as well as the operators economic tolerance. It is recognized that improved monitoring, pretreatment, and operator training would provide immediate relief to many of the problems experienced in membrane treatment plants. However, there are still several areas of research that could provide information needed to improve membrane element design and system operation to minimize fouling and scaling. Many of these have been the focus of new research projects in the past 2 years.

- Develop optical sensors with the capability of monitoring conditions at the membrane surface.

- Model solubility of sightly soluble salts at high pressure and ionic strength.

- Collect data on the transport of microorganisms through the pretreatment and membrane system.

- Study the affinity of bacterial species to different membrane polymers.

- Determine the effect of using an oscillating pump with membrane systems.

Hopefully, results from studies in these areas will result in improvements to membrane materials and systems operation.

7.2 Efficacy of Surfactant Adsorption in Improving Fouling Resistance

In this study, adsorbed PEO based surfactants were found to enhance fouling resistance and protect against degradation when adsorbed to cellulose acetate and polyamide thin film composite membrane. CA RO membrane maintained high performance with surfactant adsorption while the water permeation rate of PA RO membrane declined severely. A possible reason for this behavior was revealed in the AFM images of treated and untreated membrane. The rough surface PA membrane tends to fill in with adsorbed surfactant. The CA membrane is

very smooth, resulting in a much thinner coating of surfactant. The increased resistance to water permeation through the treated PA membrane is due to the very thick layer of surfactant in the nooks and crannies of the surface.

Surfactant adsorption had an intriguing effect on PA NF membrane that is worthy of further study. The PA NF membrane treated with Triton X-100 had an increase in rejection and water permeation rate over the untreated samples. It is not clear whether the improvement is due to spatial variation in membrane samples cut from the same sheet or to real improvement caused by the surfactant layer. Treatment had very little effect on the CA NF membrane.

7.3   Evaluation of Membrane Characterization Techniques

Five different methods were used to evaluate changes in membrane performance with treatment and fouling: swatch testing, element testing, zeta potential, atomic force microscopy, and acoustic time-domain reflectometry.

7.3.1   Swatch testing. Swatch testing is an adequate method for measuring performance of small samples of membrane one time only. Since membrane material is variable, several samples of each type need to be tested to get a measure of the population variance.   Then the performance of a small number of experimental samples can be compared to the average population performance with confidence. The samples can only be tested one time with confidence, though. Compression in the test cell causes minute tears near the O-ring, so that if the membrane is not placed in exactly the same position the second time, there will be a decline in performance due entirely to the test method. In this study, the membrane samples were padded with a thin layer of open cell polyurethane foam to protect them from O-ring damage and water carrier damage. The samples were punched with four registration holes to ensure that they were placed in the same position the second time. Even with these precautions, in some cases there was a high degree of variability between samples that had been treated in the same way and had performed similarly in the original test.

Another problem is that the duration of swatch testing was not adequate to achieve equilibrium performance. The system was not robust enough to be left operating over night. It needed to be watched continuously to keep the pressure from creeping up and activating high pressure cut off systems. This was especially troublesome when testing the CA RO membranes at 2,757 kPa.

Swatch testing is labor intensive. Permeate samples are collected by hand with a beaker and stopwatch. The samples are weighed and then transferred to a constant temperature water bath before the conductivity is measured. The sample may have been collected at a different temperature, though, so the calculated performance is not tied to actual operating conditions.

The good aspects of swatch testing are that three samples are tested at one time, and the results are directly related to element performance.

7.3.2   Element testing. Performance tests on membrane elements are preferable to tests on membrane swatches for several reasons.

- Performance is averaged over a larger area than swatch test data.

- The membrane is tested under the same conditions as full sized units.

- More samples can be tested at one time.

- The system is robust enough to run overnight or even for a few days.

- Automatic data acquisition available on the RO Test System reduces error caused by temperature and flow changes during sampling.

7.3.3 Zeta Potential Analysis. As hypothesized, adsorption of surfactants does reduce the magnitude of the membrane zeta potential. However, it is still not clear if there is a link between zeta potential characteristics and membrane performance. Some intriguing questions brought up by the study are listed below.

- Can the zeta potential measured in low electrolyte concentration relate to performance at high concentrations ? Measurements were taken up to only 180 mS/m because beyond that point the variation in zeta potential was within the error limits of the equipment.

- Do factors which control the zeta potential relate to salt rejection and water permeation rate?

If these questions can be answered, zeta potential could be very useful for screening membrane treatments and/or polymers.

7.3.4   **Atomic Force Microscopy. AFM** is an effective tool for visualizing membrane surfaces. The differences that can be seen between PA and CA membrane make it easy to understand why PA membranes foul so easily and are so difficult to clean. Analysis of a range of surfactants with AFM was a satisfactory method for identifying the minimum concentration for effective coverage of CA membrane.

There are some problems with the analysis, however. It took 3 to 4 hours to analyze 16 different areas on a membrane sample. During this time, the membrane was exposed to air and began to dry out. Also, some of the samples became contaminated with **particulates** at some point and the data had to be discarded. More untreated samples need to be analyzed to assess variation in tip response. The tip is normally discarded after one analysis session. If the same membrane is then analyzed in a different area with a new tip, there is a great difference in the roughness factors, but much of the difference may be due to membrane drying.

7.3.5   Acoustic Time-Domain Reflectometry. This demonstration has not shown that ATDR signatures taken at a point, or even on a scan line, can be useful in monitoring performance changes. The problem is that the ATDR measurements are characteristic of one 250 μm diameter circle. Water permeation is related to the thickness of a fouling layer, but the measured permeation rate is a function of the mode of the layer thickness ▪ not the average thickness or the thickness at a single point. If ATDR is to have any usefulness as a fouling monitor, a large population of measurements need to be taken to determine changes in the predominant fouling layer thickness.

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APPENDIX A

Membrane Cleaning Survey

Appendix A: Membrane Cleaning Survey

Survey of Membrane Cleaning Processes, Problems, and Solutions

Plant Data

Plant Name: Address:	Plant Type	Year of startup	Name of Equip. Mfg.& Contractor
Telephone: FAX Respondent: Title:	Brackish RO Seawater RO EDR Softening Groundwater Enhancement		

Process Data- Please send a copy of a recent water analysis.

' Rated Capacity (GPD)	Intake Well or Surface	Pretreatment Processes	TDS Feed/Product	Recovery %

Membrane Data

Make   Model Number   Number in system   Number replaced/year

Does this plant have shutdown periods?

Regular_____   Intermittent _____
Average **Length**_____   **Average Length**_____
Purpose_____   **Purpose**_____

What membrane fouling or scaling problems do you have?

Type   Symptoms
Biological?
Silicate?
Metals?
other?

Please briefly describe your element cleaning process.
  what cleaning products do you use?

  How often: **Temperature**:   Concentration: **pH**:

  Flow rate of cleaning solution:

Please characterize the effectiveness of this cleaning process.
Post-cleaning productivity: Post-cleaning permeate quality:
  100% of nominal productivity   100% of **nominal** rejection
  99-93%   **99-93%**
  93-87%   **93-87%**
  87-83%   **87-83%**
  83-75%   **83-75%**
  less than 75%   less than **75%**

Have you tried or considered mechanical cleaning process aids such as pulsed flow or reverse flow?

APPENDIX B

Listing of Chemical Manufacturers

Appendix B: Listing of Chemical Manufacturers

Company	Telephone	Address	Comment	Chemical	pH
Ashland Chem., Inc.	614 889 3514	P.O. Box 2219 Columbus, OH. 43216		Ammonium Hydroxide	
				Citric Acid	
				Sulfamic Acid	
				Sodium Hydroxide	
				Phosphoric Acid	
			Versene (R), Photo chelate	Ferric Ammonium EDTA	
AAKASH Chem and Dry Stuffs, Inc.	708 543 0810	447 Vista Ave. Addison, IL 60101		Sulfamic Acid	
Alconox, Inc.	212 532 4040	9 E. 40th St. #200 New York, NY 10016-0402	Aniiic: Sodium linear alkylaryl-sulfonate Alcohol sulfate Phosphates & carbonates	Alconox	9.5
			Alconox w/ Protease enzyme	Terg-A-Zyme	9.5
			Anionic & Non-ionic: Phosphate free	Liqui-Nox	8.5
			Acid detergent	Citri-nox	2.5
			Alconox w/ effervescense	A h tabls	6.5
			Phosphate free	Detergent 8	11
			Sequesterant	Det-O-Jet	13
Alloy Chemical, Inc	212644 1510	6OOMdinAve. New York, NY 10022		Sulfamic Acid	
Atlas Powder Co.		15301 Dallas Pkwy. Ste. 1200 Dallas. TX 75248		Ammonium Hydroxide	
BASF Corp	201-316-3000	100 Cherry Hill Rd. Parsippany, NY 07054	Non-ionic Surfactant	Pluronics P-84	6
Brown Chemical co. Inc.	201337 0900	P.O.B. 440 302 West Oakland Ave. Oakland, NY 07436		Ammonium Hydroxide	
				Nitric Acid	
				Sulfamic Acid	
				Sodium Hydroxide	
				Phosphoric Acid	

Company	Telephone	Address	Comment	Chemical	pH
Cardinal Chemical Div. of Alexander Corp.	708 257 9330	P.O.B. 248 Lemont, IL 60439		Ammonium Hydroxide	
Corco Chemical Corp.	215 295 5006	451 Tybum Rd. Fairless Hills, PA 19030		Ammonium Hydroxide	
				Nitric Acid	
				Phosphoric Acid	
Coyne Chemical Co.	800 523 1230 215 785 3000	3015 State Rd. Craydon, PA 19020		Ammonium Hydroxide	
				Nitric Acid	
				Sulfamic Acid	
				Phosphoric Acid	
Drew Industrial Division Ashland Chemical	201263 7600	One Drew Plaza Boonton, NJ 07005	Non-ionic: Butoxy-Polyethylene-Polypropylene glycol: 10-25% Polydimethylsiloxane: 1-10%	Drewsperse 738 Anitfoulant	
Du Pont Chem. Co.	800 4417515	1007 Market St. Wilmington. DE 19898		Nitric Acid	
Electronic Space Products International	818 9916724	5310 Derry Ave. Agaura Hills CA 91301-4509	Non-toxic. biodegradable general purpose cleansing agent	DeContam	
FMC Corp. ltd. Process Additives Div.	800 545 6532 215 299 6000	1735 Market St. Philadelphia, PA 19103	For inorganics, contains organic acids, detergent builders and chelating agents	Floclean (R) 403	
			For organics and particulates. Contains detergent buiders, chelating agents and pH buffer.	Floclean (R) 4 1 l	
Henkle Corp. Emery Grp. Cospha/CD	800 955 1456	1301 Jefferson St. Hoboken, NJ 07030	Alkyl PolyGlycoside: 50%	Plantaren 1200	
			Sodium Lauryl sulfate: 29% Water: 70% 5 00ppm formaldehyde	Standapol WAQ SP.	
Hill Brothers Co.	714 998 8800	1675 N. Main St. Orange, CA 92667		Ammonium Hydroxide	

Company	Telephone	Address	Comment	Chemical	pH
Houseman Ltd.	(0628) 604488	The Priory, Burnaham, Slough, SL1 7LS	Sequestrant : Na • EDTA	PermaClean 33	10 . 10.5
			Disinfcnctant	PermaClean 44	2-4
			SDS: colloidal & organic fouling	PermaClean 66	12
			Ammonium Citrate: Iron fouling	PeramClean 77	3.6
			HCI: Aldaline scale & hydroxids	PeramClean 88	2-3
			NaOH+surfactant & builders: Alkaline cleaning for organic and bio-fouling at 30 deg C.	PeramClean 99	11
Kaltron Rettibone	708 350 1116	1241 Ellis St. Bensenville, IL 60106		Sulfamic Acid	3
LaRouche Industries Inc.	404 85 10300	1100 Johnston Ferry Rd. Atlanta, GA 30342		Ammonium Hydroxide	10
				Nitric Acid	
Mays chemical co.	404 6% 6711	5544 Oakland Rd. Smyrna, GA 30082		Ammonium Hydroxide	pH < 2 for acid pH 10-11 for salts
				Nibic Acid	
Mobay Corp. Inorganic Chem. Div.	412 777 2000	Mobay Rd. Pittsburgh, PA 15205-9741		Nitric Acid	
Monsanto	3 14 694 1000	800 N. Lindbergh Blvd St. Louis, MO 63 167	Sequesterant, chelate, and dispersant Available as Acid or sodium salts	Dequest Phosphonates	
				Dequest 2010	
Occidental Chem. Corp.	214 404 3300	5005 LBJ Fwy. Occidental Tower Dallas. TX		Ammonium Acid	
Peridot Chem. Inc.	201 696 9000	1680 Rt. 23 N. Wayne, NJ 07470		Nitric Acid	
Rhone Polence Inc.	609 395 8300	Prospect Plaines Rd. Cmnbury. NJ 085 12		Lauryl Sulfate	
				Jaguar • HP Series (sludge)?	
Ruger Chemical Co. Inc.	201926 033 I	83 Cordier St. Irvington, NJ 04-0711 I		Ammonium Hydroxide	
				Nitric Acid	7
				EDTA	

Company	Telephone	Address	Comment	Chemical	pH
Shell Chemical Co.	714 9919200 800 872 7435	51 I N. Brookhurst St Anaheim, CA 92801	Diethylene Glycol Monobutyl Ether: 2-(2-Butoxyethoxy) Ethanol	Butyl Dioxitol (R) Glycol Ether (BuDiox)	
			Ethylenen Glycol Monobutyl ether: 2-Butoxy Ethanol	Butyl Oxitol (R) Glycol Ether (BuOx)	
Spectrum Chemical Mfg. Corp.	213 516 8000	14422 S. San Pedro St. Gardena, CA 90248-9985		Ammonium Hydroxide	
				Citric Acid	
Union Carbide Chemical	203-794-5300	39 Old Ridgebury Rd. Danbury, CT 06817-0001	Non-ionic Surfactants	Triton X-100, 705	7
Unocal Chemical Div. Union Oil Co. of CA	708 619 2589	1700 E. Golf Rd. Schamumburg, IL 60173		Ammonium Hydroxide	
Van Waters & Rogers Inc.	2% 447 5967	801 2nd Ave. Ste. 1600 Seattle, WA 90104		Sulfamic Acid	
				Phosphoric Acid	

APPENDIX C

Swatch Test Data
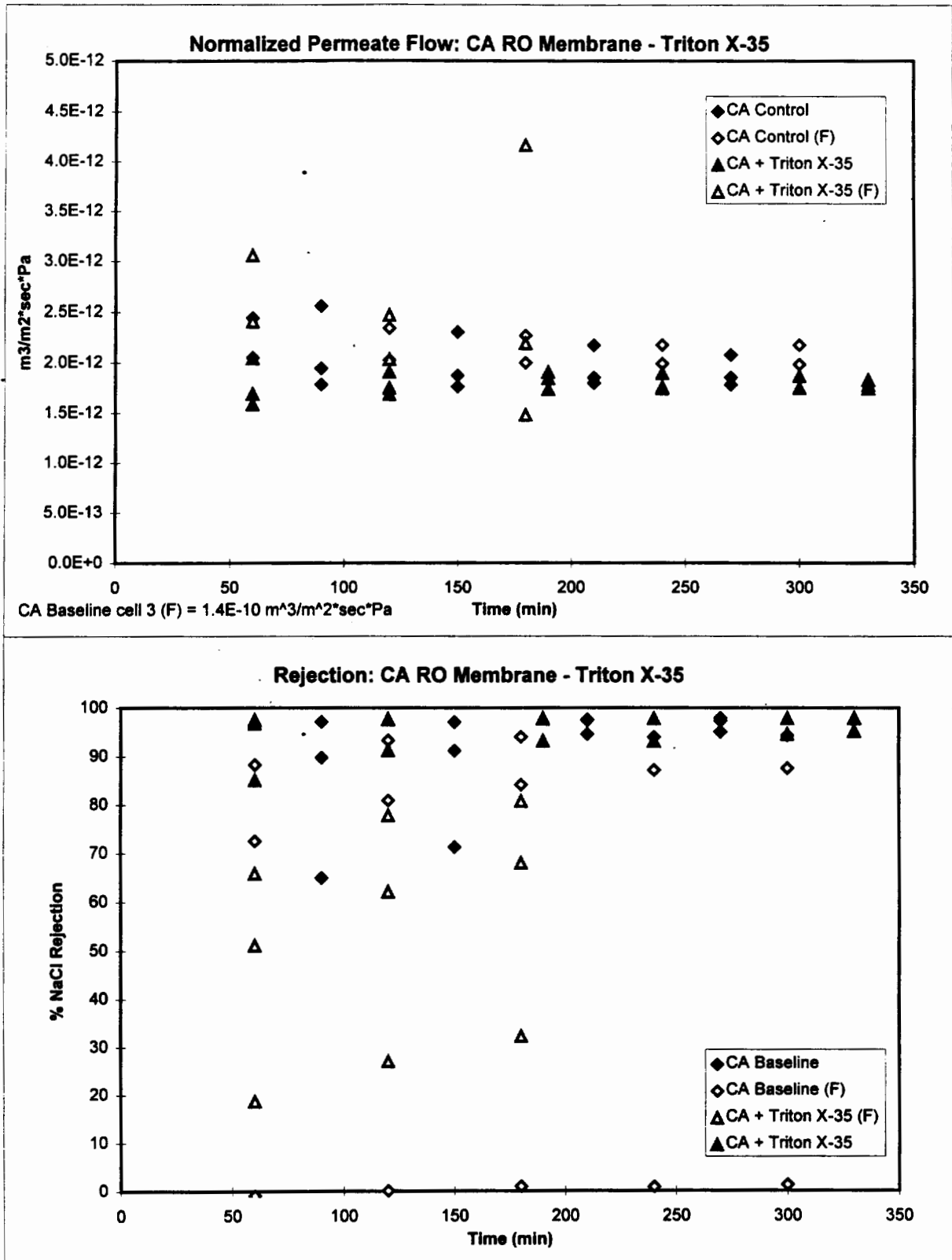
Figure C.1 Comparison of normalized permeate flow and rejection for untreated and Triton X-35 treated CA RO membrane. All observations are shown - solid symbols represent clean membrane performance, open symbols represent performance after fouling.
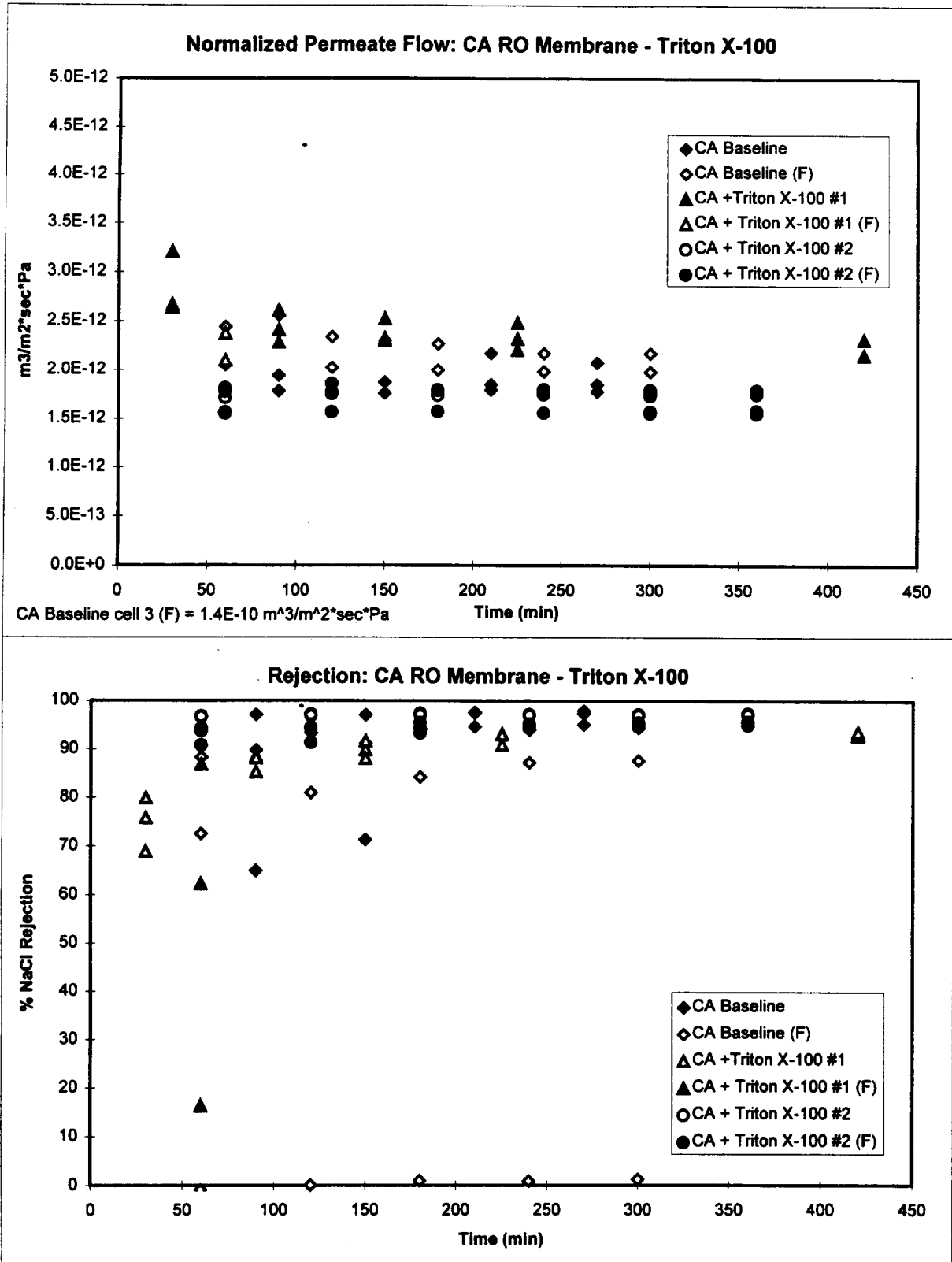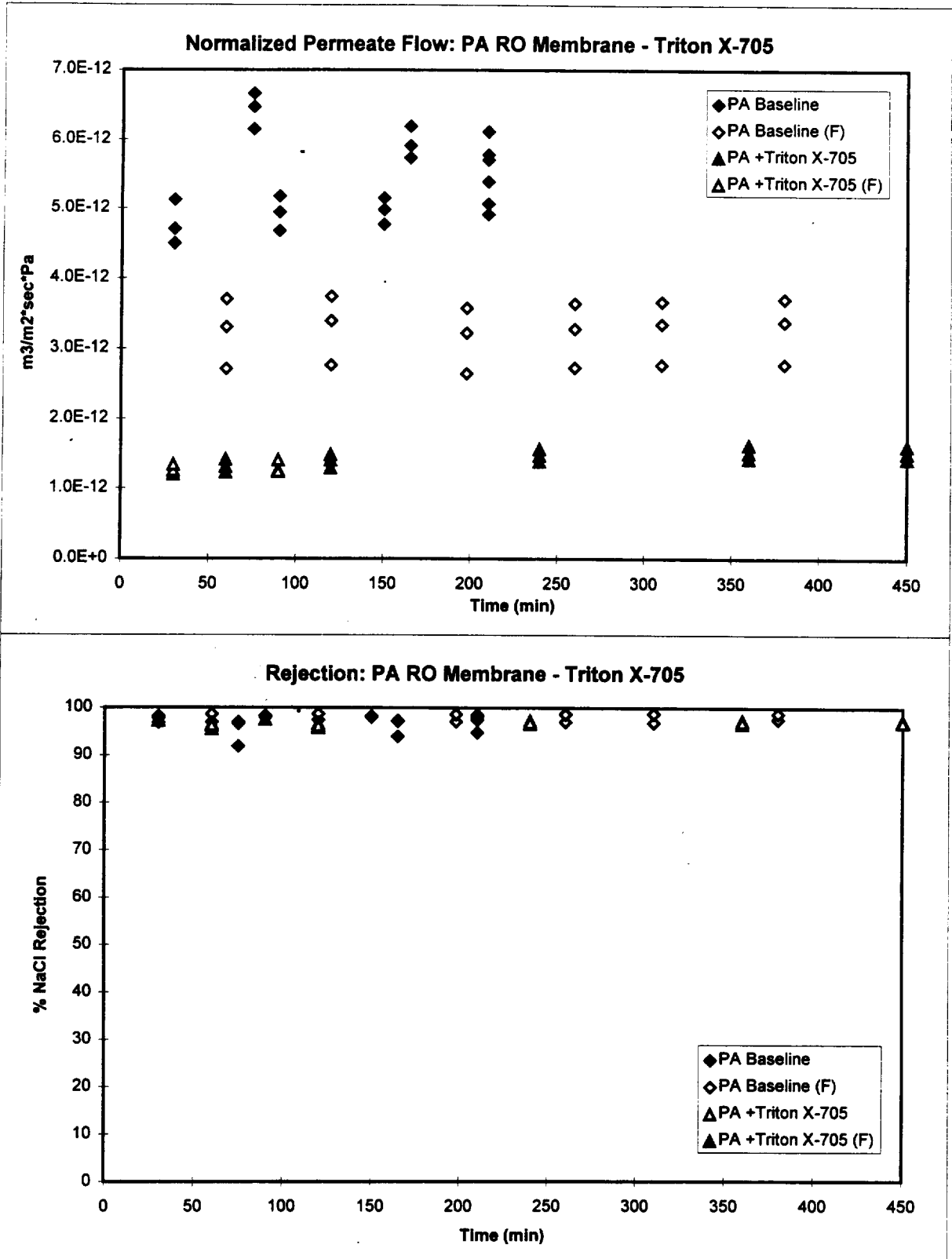
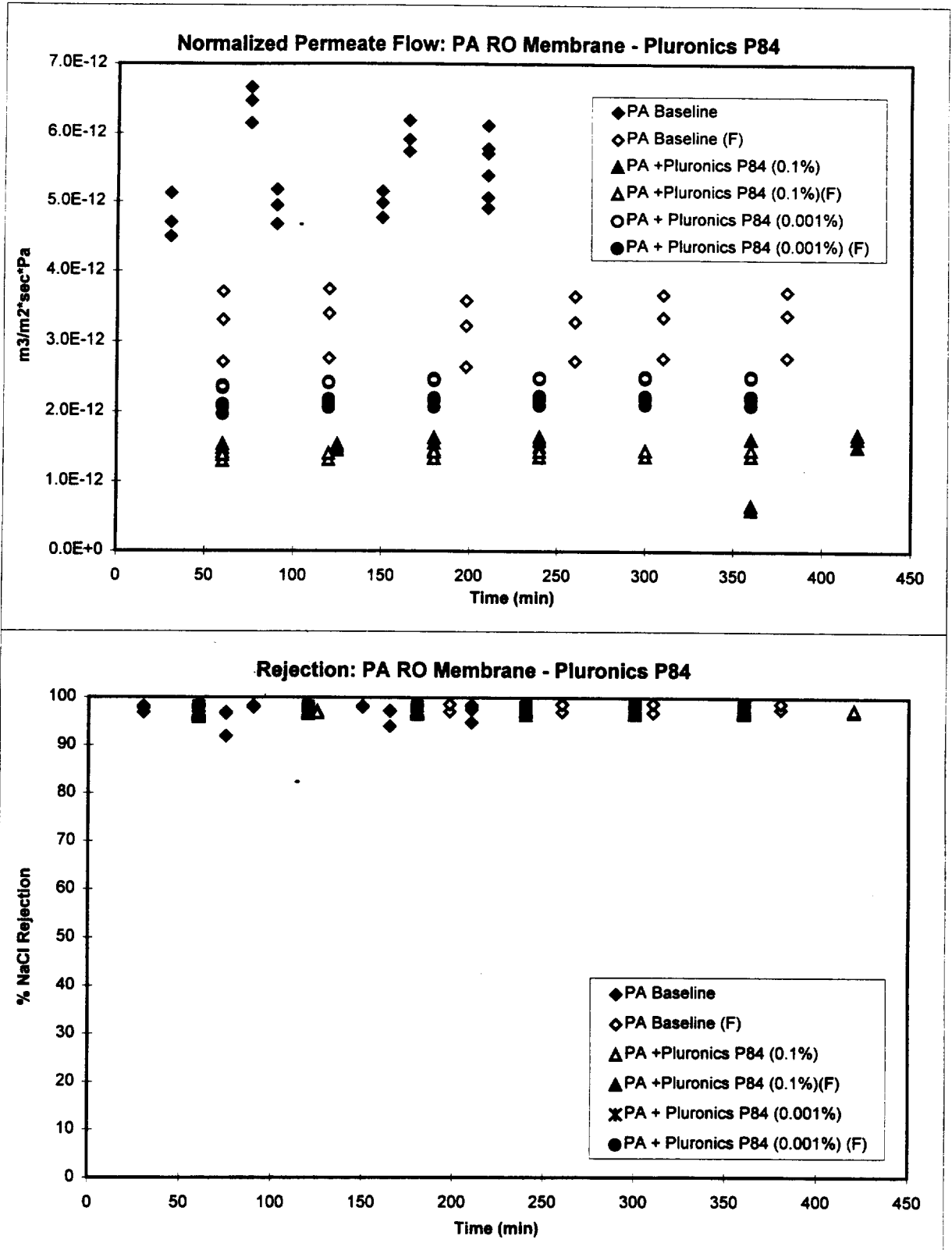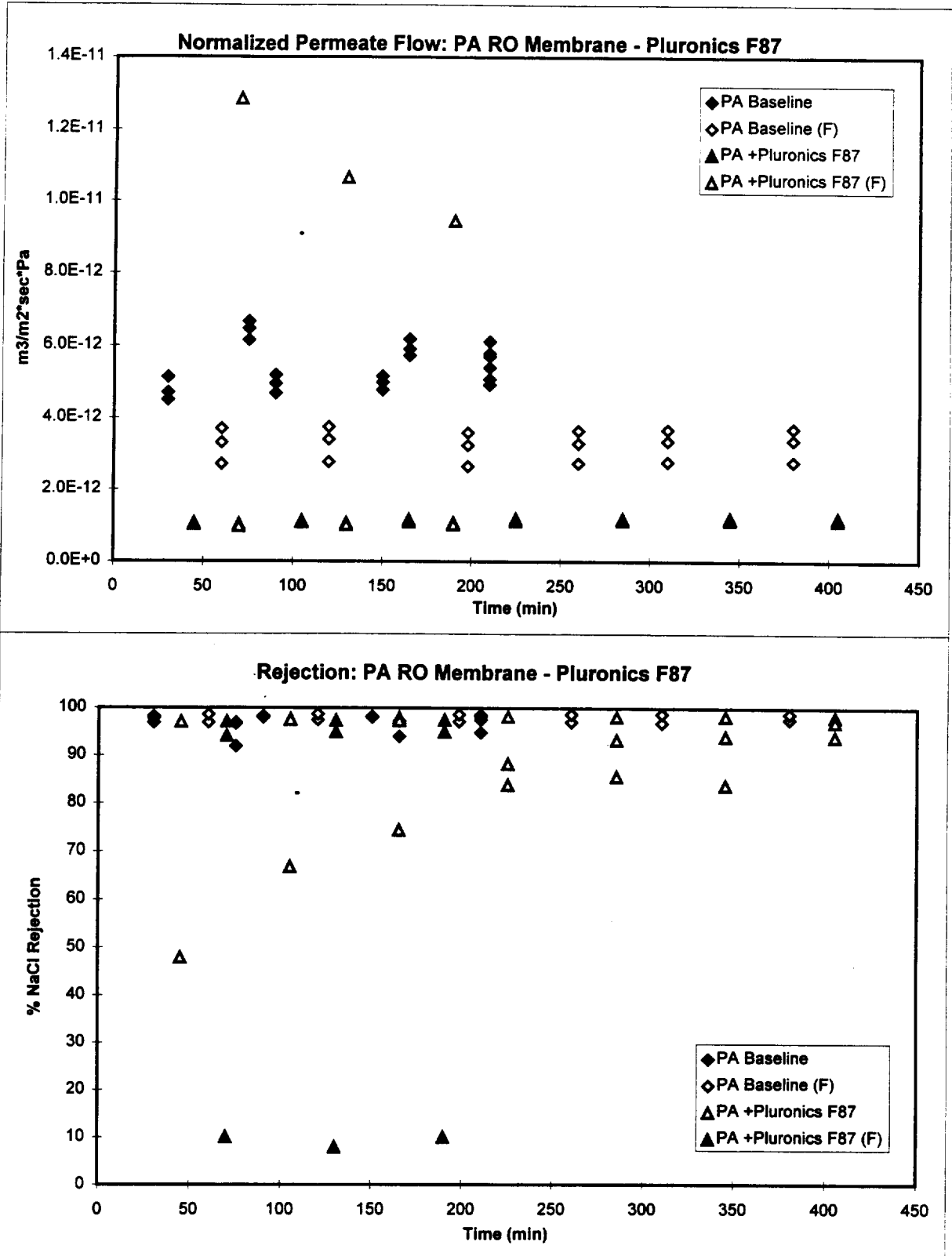Figure C.2 Comparison of normalized permeate flow and rejection for untreated and Triton X-100 treated CA RO membrane. All observations are shown - solid symbols represent clean membrane performance, open symbols represent performance after fouling.
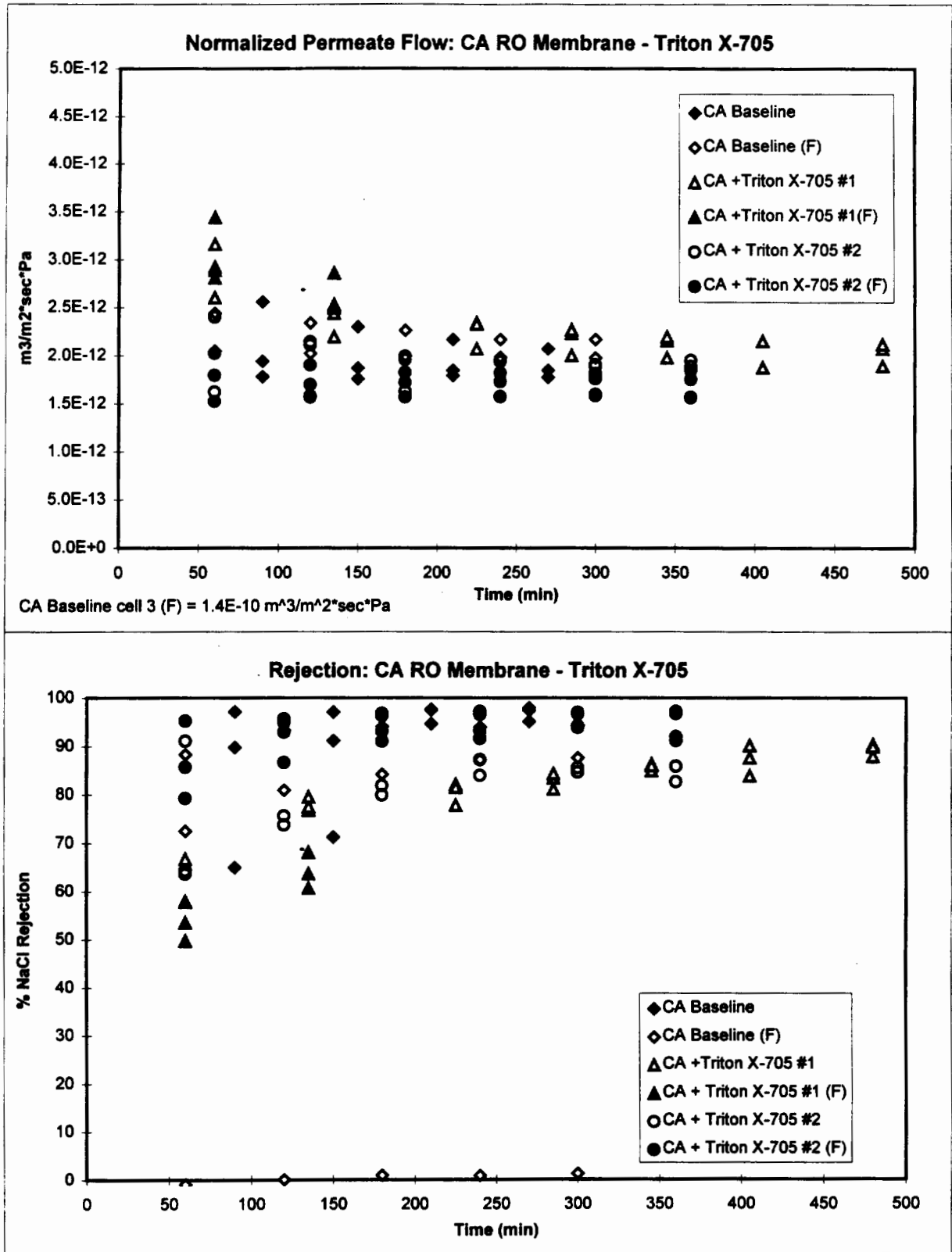
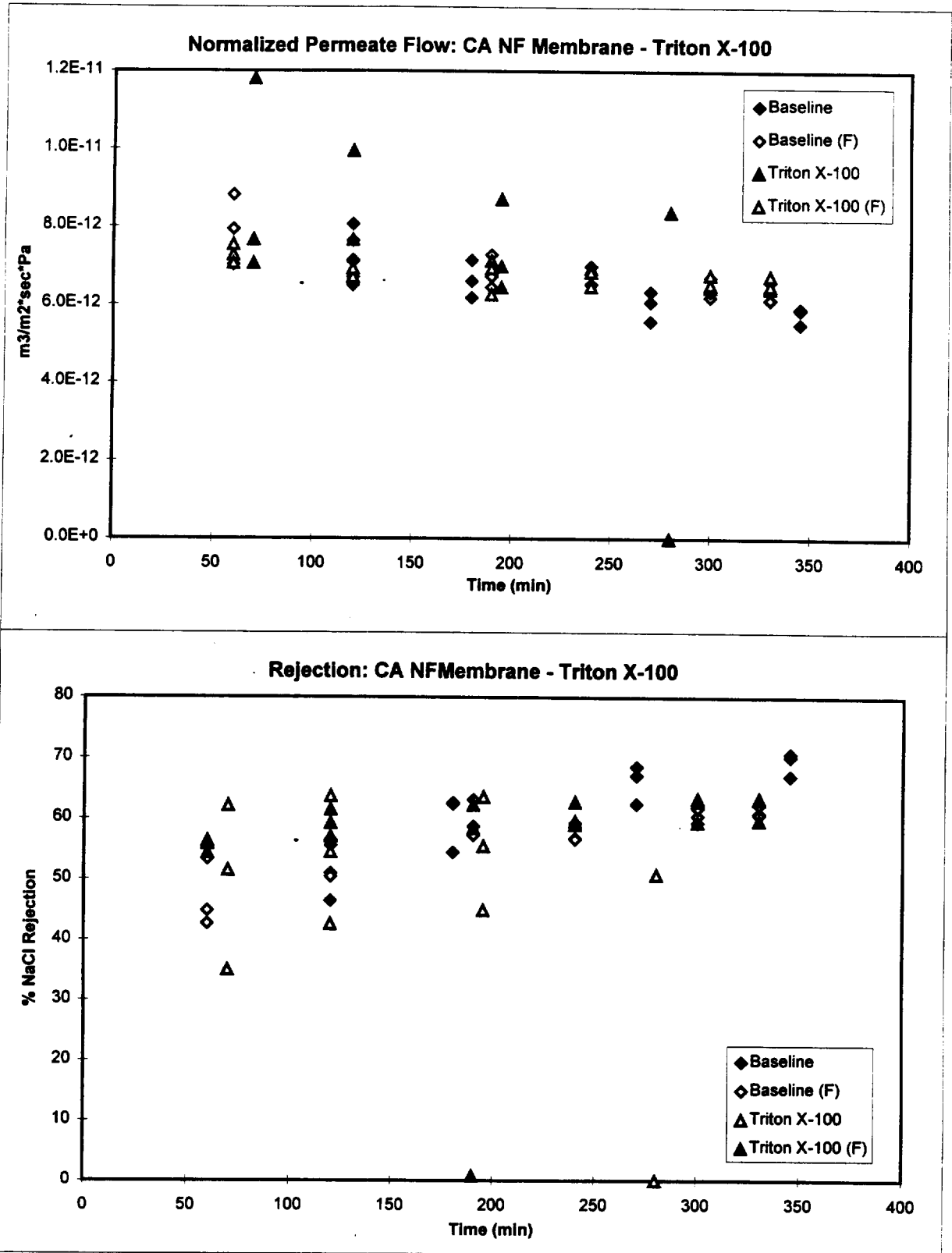**Figure C.3** Comparison of normalized permeate flow and rejection for untreated and Triton X-705 treated CA RO membrane. All observations are shown - solid symbols represent clean membrane performance, open symbols represent performance after fouling.
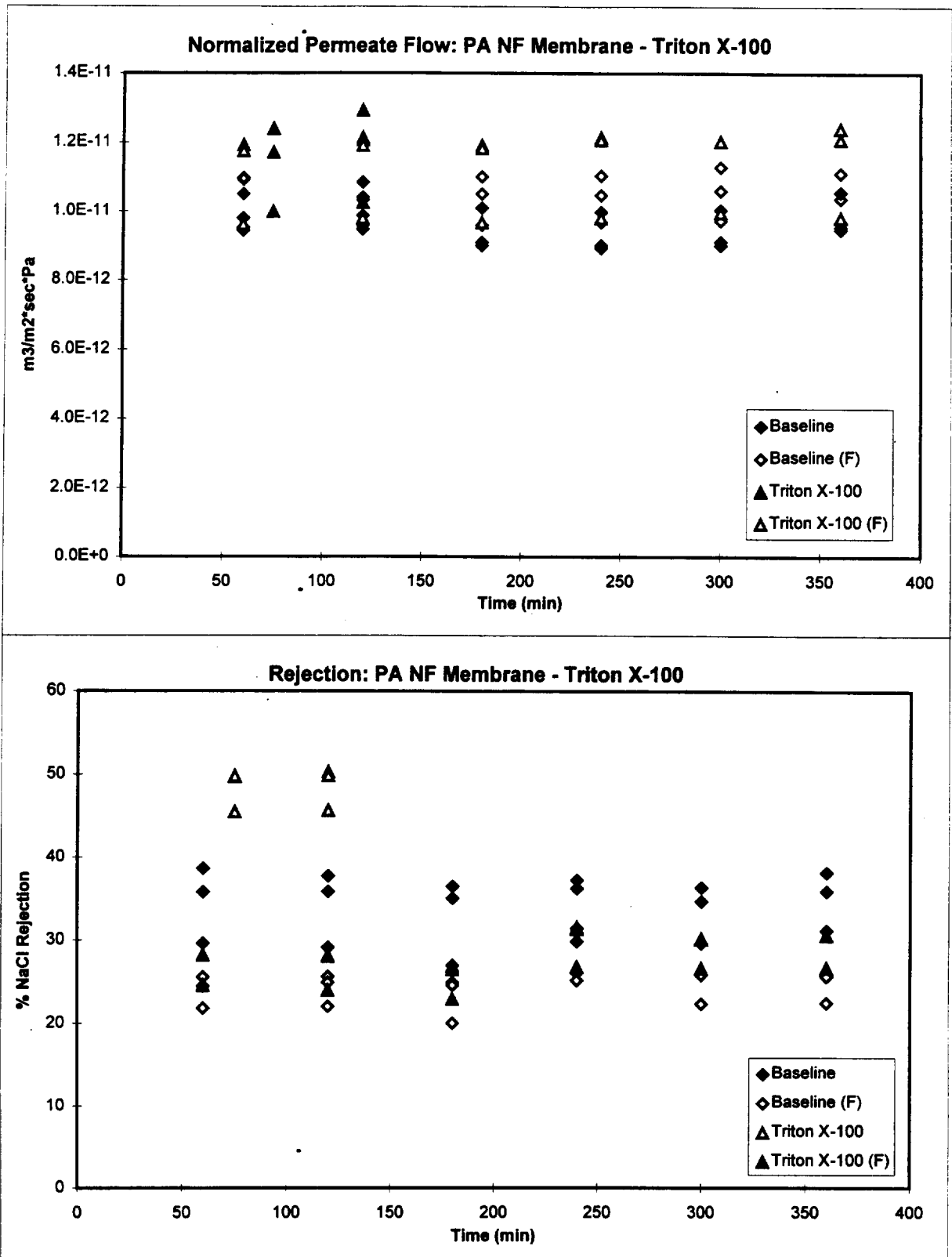
Normalized Permeate Flow: CA RO Membrane - Pluronics P84

y-axis: m3/m2*sec*Pa

Legend:
◆ CA Baseline
◇ CA Baseline (F)
▲ CA + Pluronics P84
△ CA + Pluronics P84 (F)

CA Baseline cell 3 (F) = 1.4E-10 m^3/m^2*sec*Pa

x-axis: Time (min)

Rejection: CA RO Membrane - Pluronics P84

y-axis: % NaCl Rejection

Legend:
◆ CA Baseline
◇ CA Baseline (F)
△ CA + Pluronics P84
▲ CA + Pluronics P84 (F)

x-axis: Time (min)
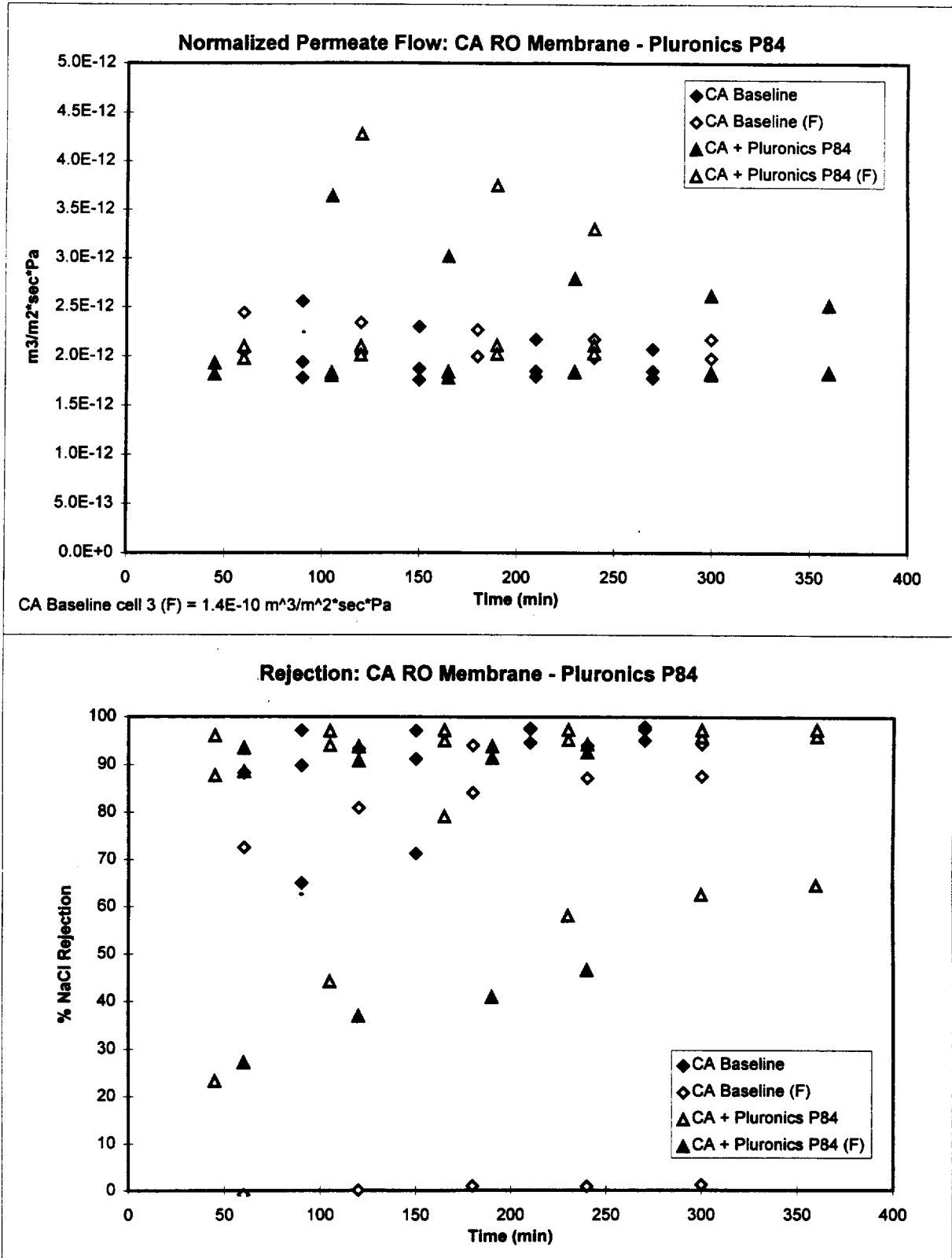
Figure C.4 Comparison of normalized permeate flow and rejection for untreated and Pluronics P84 treated CA RO membrane. All observations are shown - solid symbols represent clean membrane performance, open symbols represent performance after fouling.

Normalized Permeate Flow: CA RO Membrane - Pluronics F87

Legend:
- ◆ CA Baseline
- ◇ CA Baseline (F)
- ▲ CA + Pluronics F87
- △ CA + Pluronics F87 (F)

y-axis: m3/m2*sec*Pa
x-axis: Time (min)

CA Baseline cell 3 (F) = 1.4E-10 m^3/m^2*sec*Pa

Rejection: CA RO Membrane - Pluronics F87

Legend:
- ◆ CA Baseline
- ◇ CA Baseline (F)
- ▲ CA + Pluronics F87
- △ CA + Pluronics F87 (F)

y-axis: % NaCl Rejection
x-axis: Time (min)
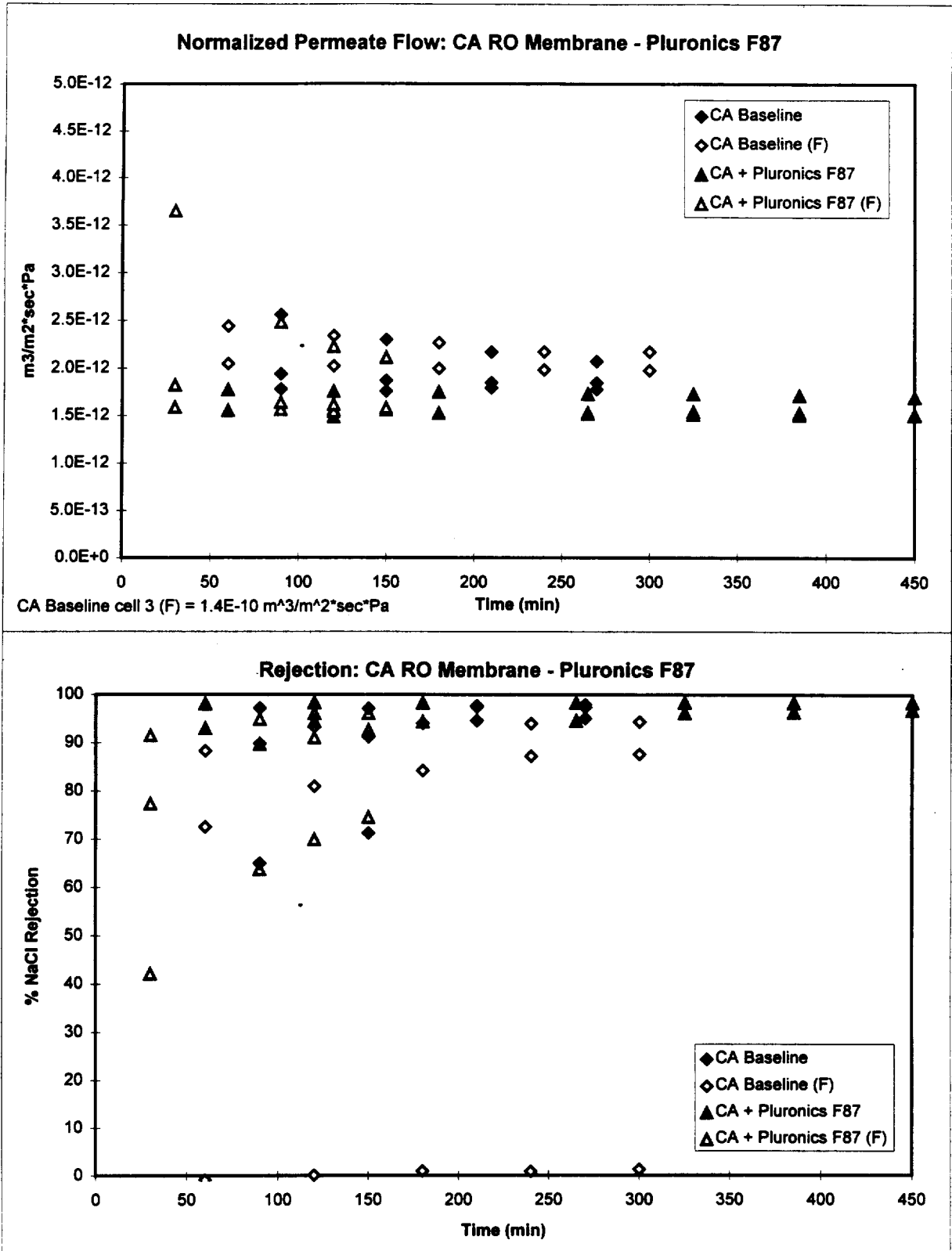
Figure C.5   Comparison of normalized permeate flow and rejection for untreated and Pluronic F87 treated CA RO membrane. All observations are shown - solid symbols represent clean membrane performance, open symbols represent performance after fouling.
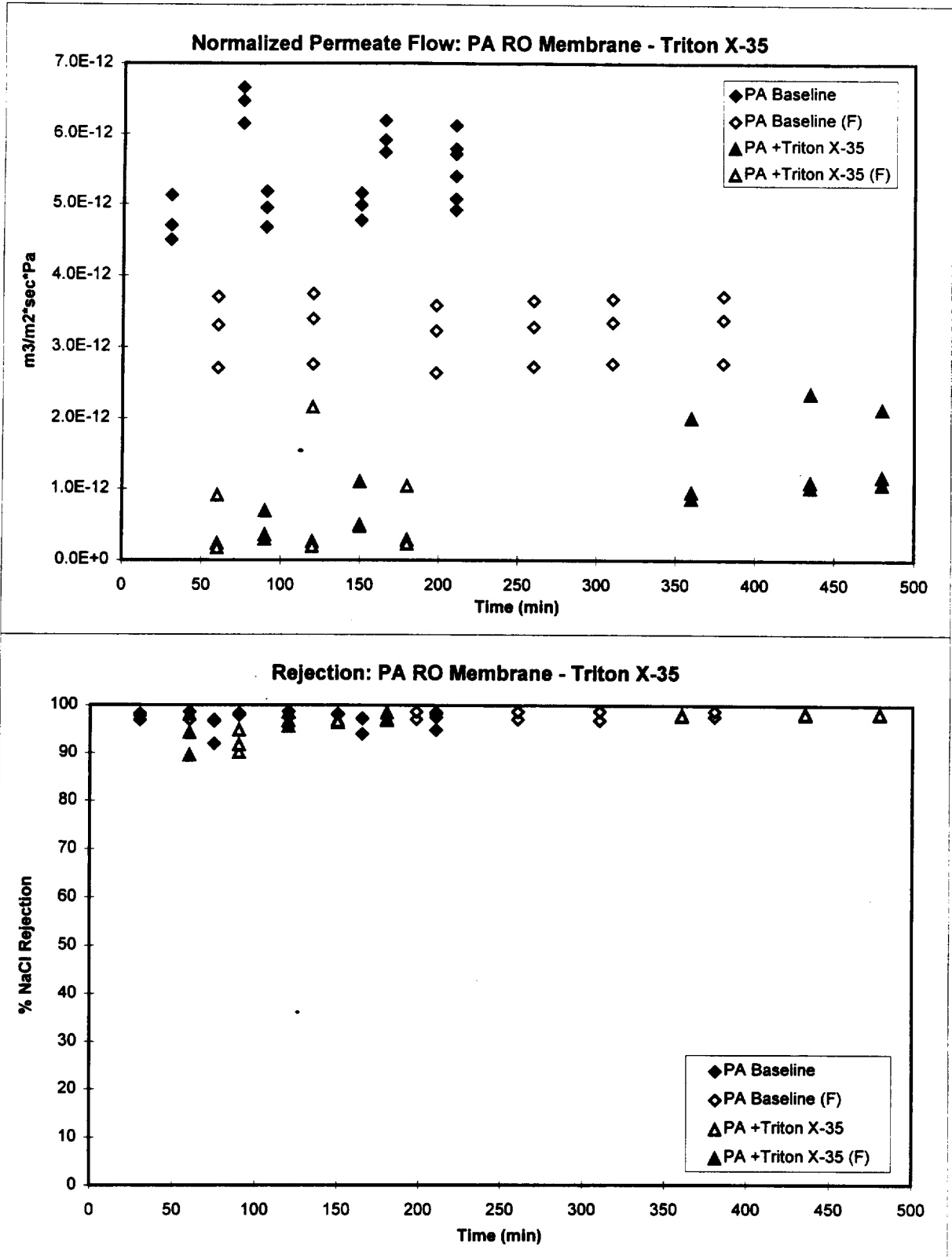
Figure C.6   Comparison of normalized permeate flow and rejection for untreated and Triton X-35 treated PA RO membrane. All observations are shown - solid symbols represent clean membrane performance, open symbols represent performance after fouling.
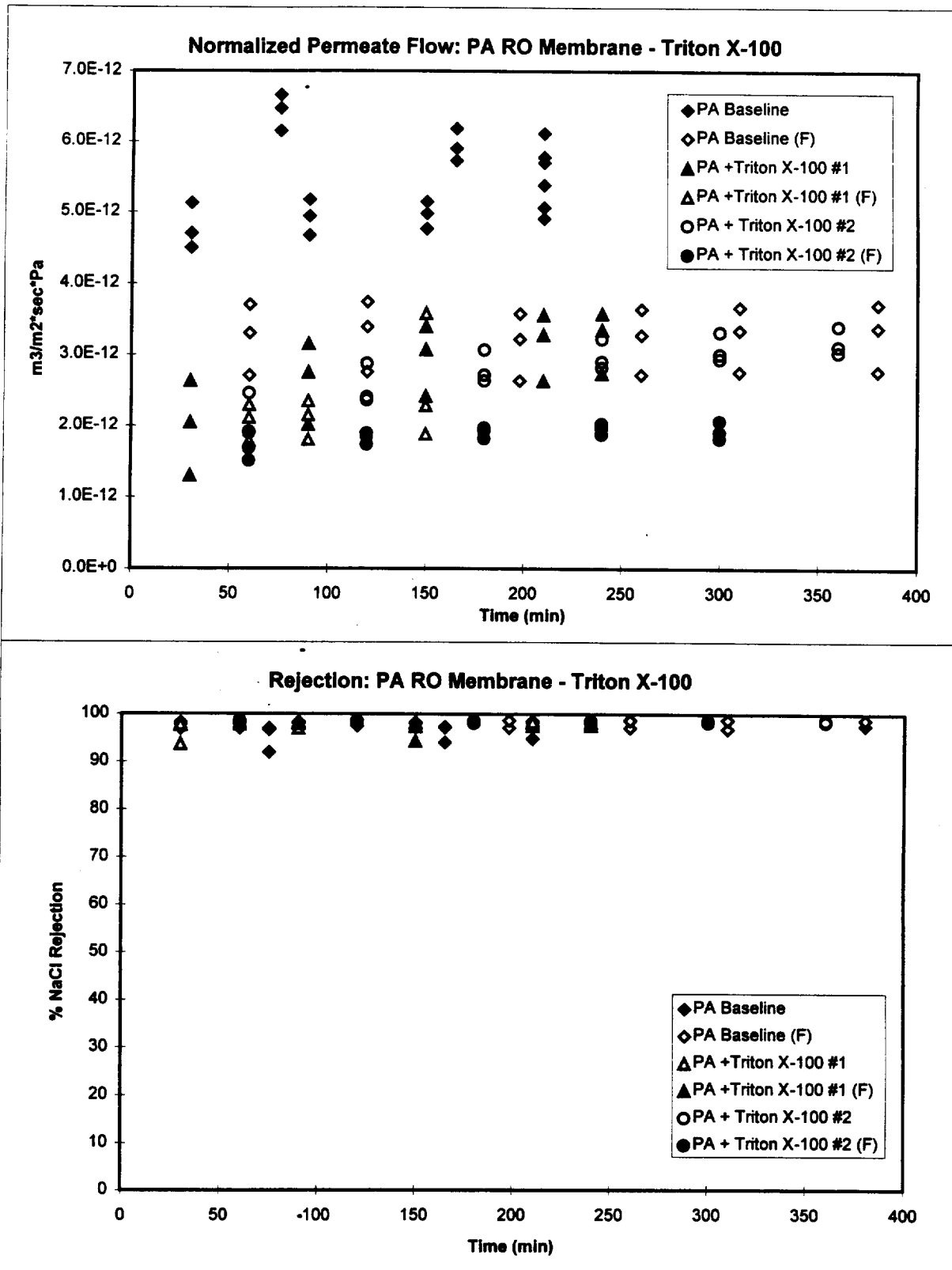
Figure C.7 Comparison of normalized permeate flow and rejection for untreated and Triton X-100 treated PA RO membrane. All observations are shown - solid symbols represent clean membrane performance, open symbols represent performance after fouling.

Figure C.8 Comparison of normalized permeate flow and rejection for untreated and Triton X-705 treated PA RO membrane. All observations are shown - solid symbols represent clean membrane performance, open symbols represent performance after fouling.

Figure C.9 Comparison of normalized permeate flow and rejection for untreated and Pluronics P84 treated PA RO membrane. All observations are shown - solid symbols represent clean membrane performance, open symbols represent performance after fouling.

Figure C.10 Comparison of normalized permeate flow and rejection for untreated and Pluronics F87 treated PA RO membrane. All observations are shown - solid symbols represent clean membrane performance, open symbols represent performance after fouling.

Figure C.11 Comparison of normalized permeate flow and rejection for untreated and Triton X-100 treated CA
NF membrane. All observations are shown - solid symbols represent clean membrane performance, open
symbols represent performance after fouling.

Figure C.12 Comparison of normalized permeate flow and rejection for untreated and Triton X-100 treated PA NF membrane. All observations are shown - solid symbols represent clean membrane performance, open symbols represent performance after fouling.

APPENDIX D

Acoustic Time-Domain Reflectometry Data
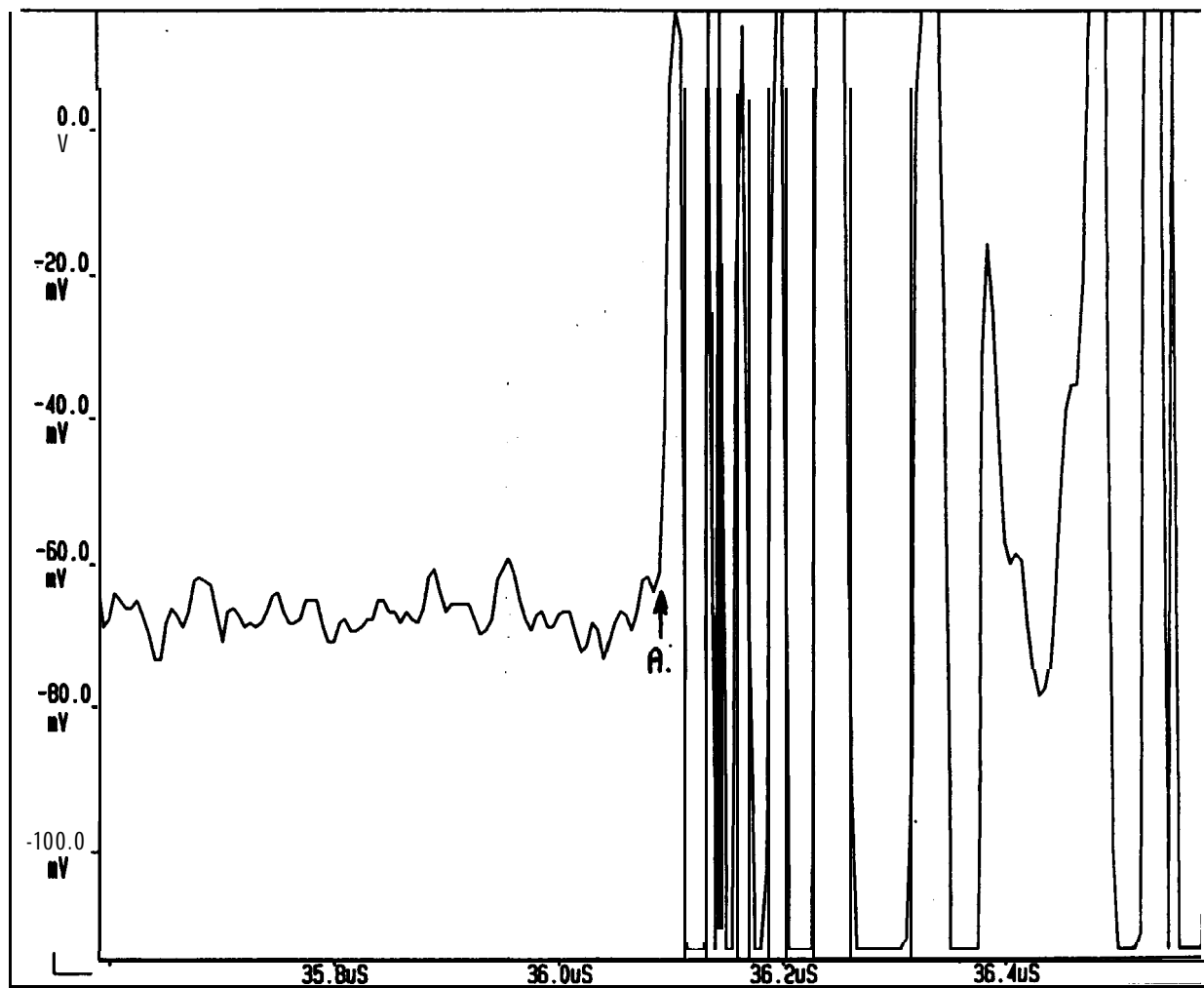
Figure D.1 ATDR Signature for CA RO Clean Untreated Membrane. There is a clear and abrupt start to the main surface echo (marked A). This is the type of response seen for all the control samples; the abrupt start of the main echo is indicative of a clean surface.
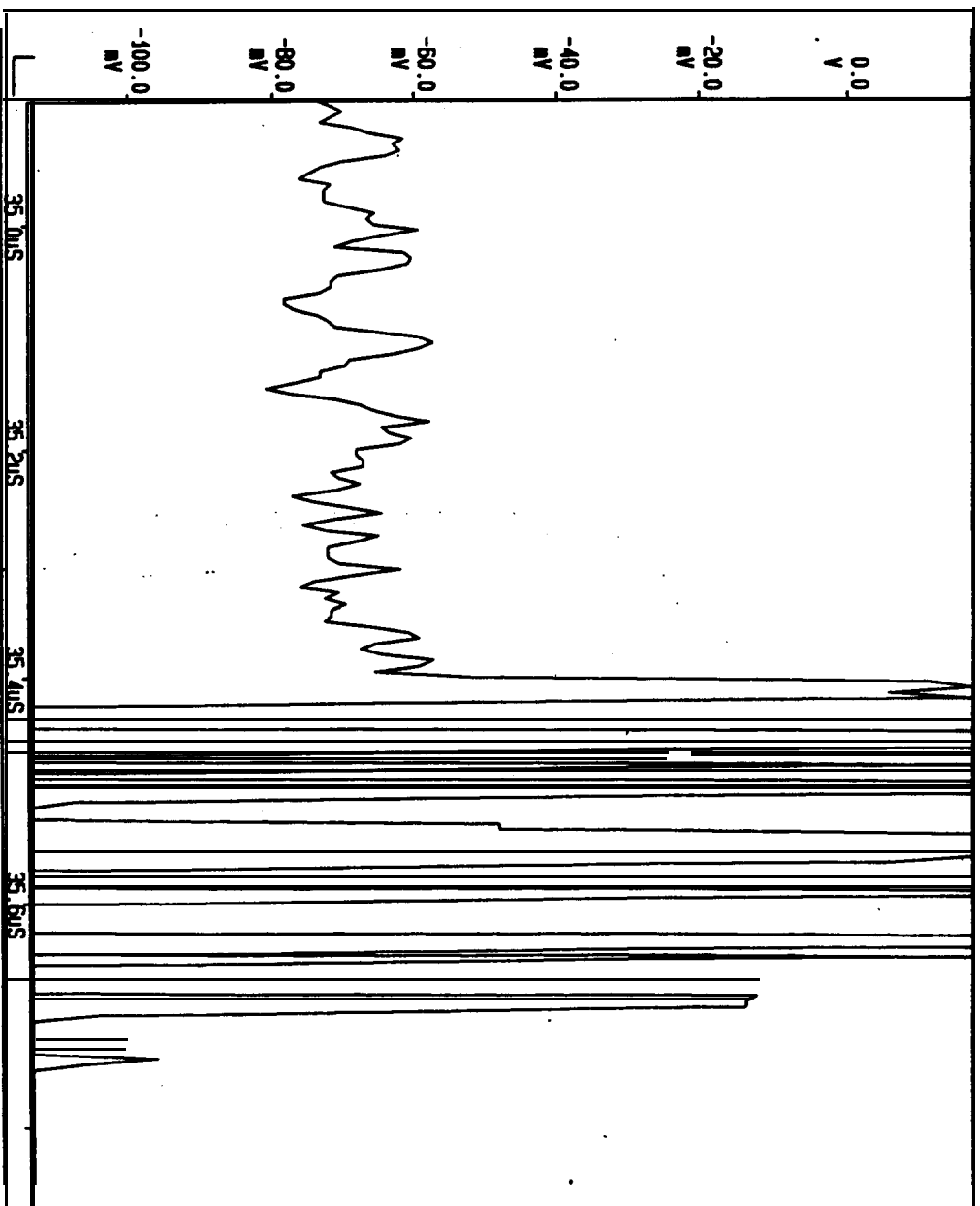
Figure D.2 ATDR signature for a lightly fouled CA RO untreated membrane.
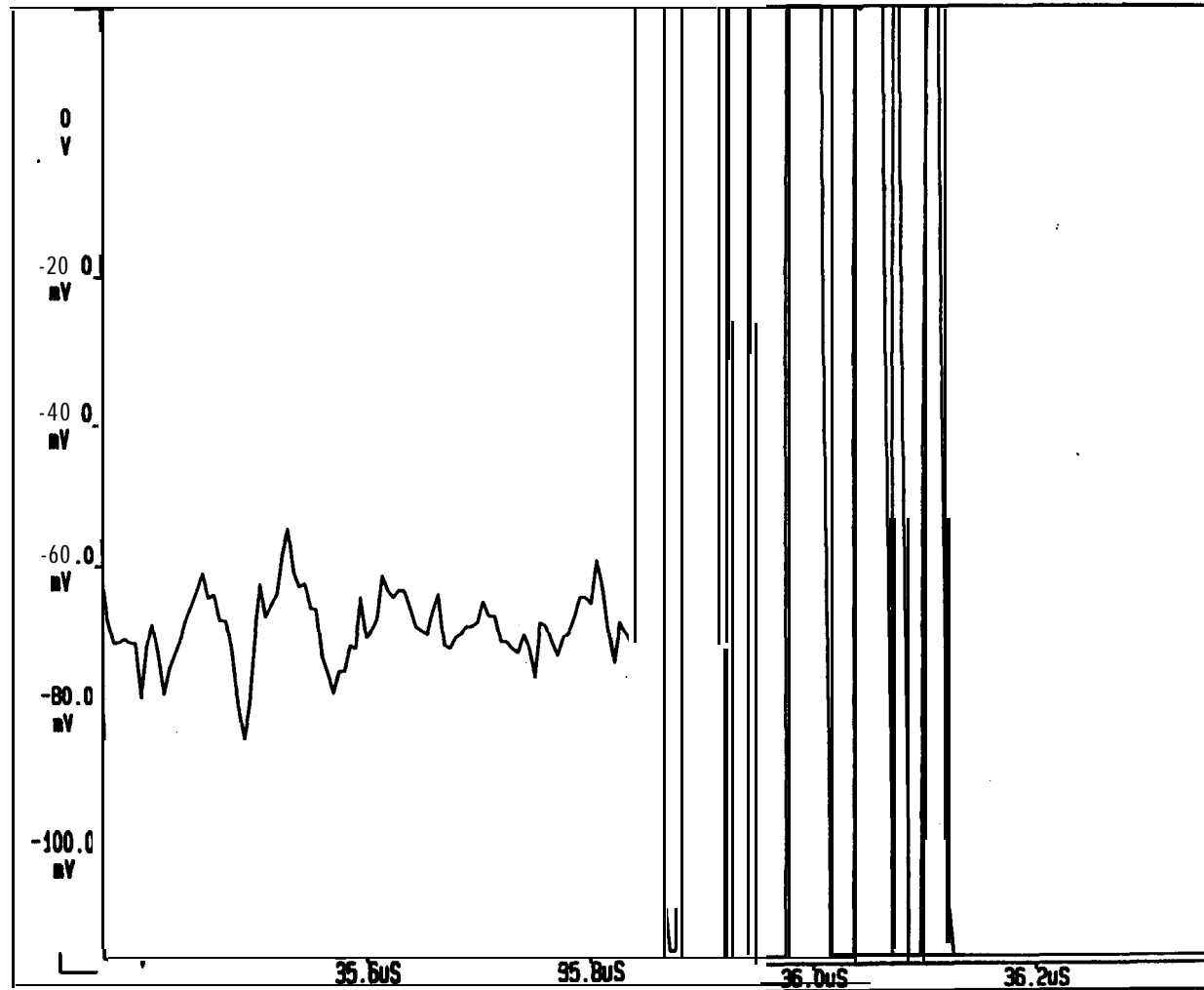
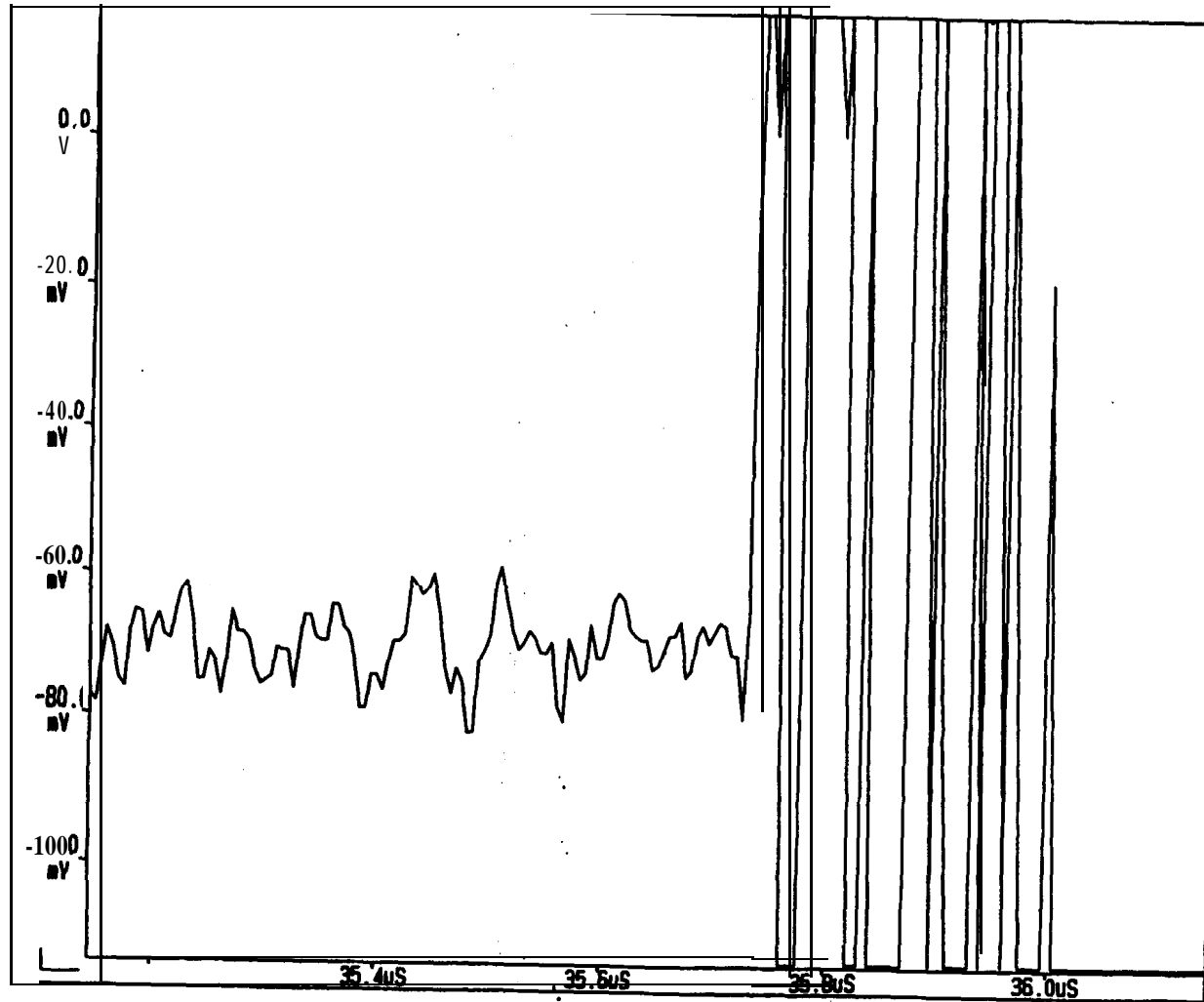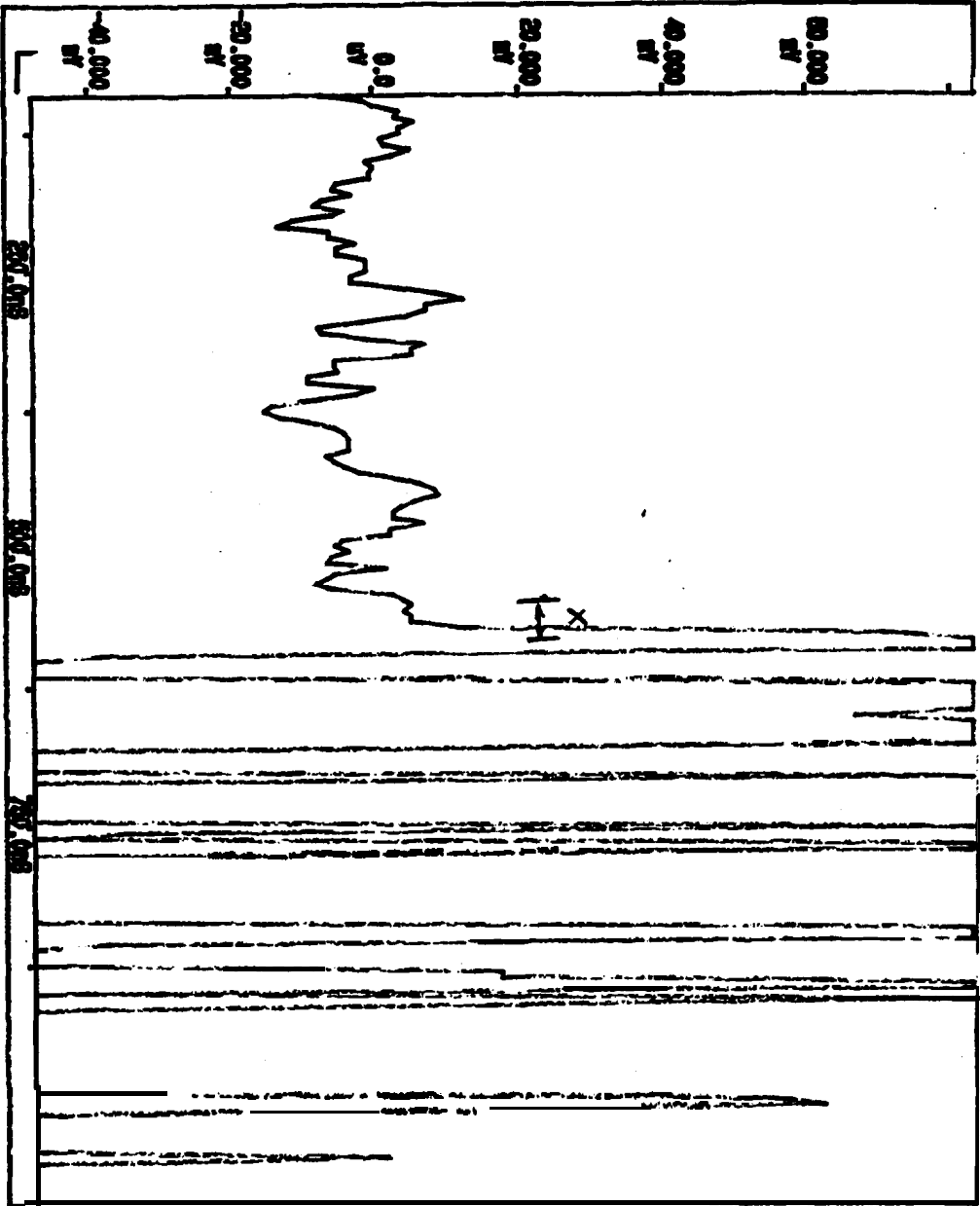**Figure D.3** ATDR signature for fouled CA RO membrane treated with Triton X-35: clean area.
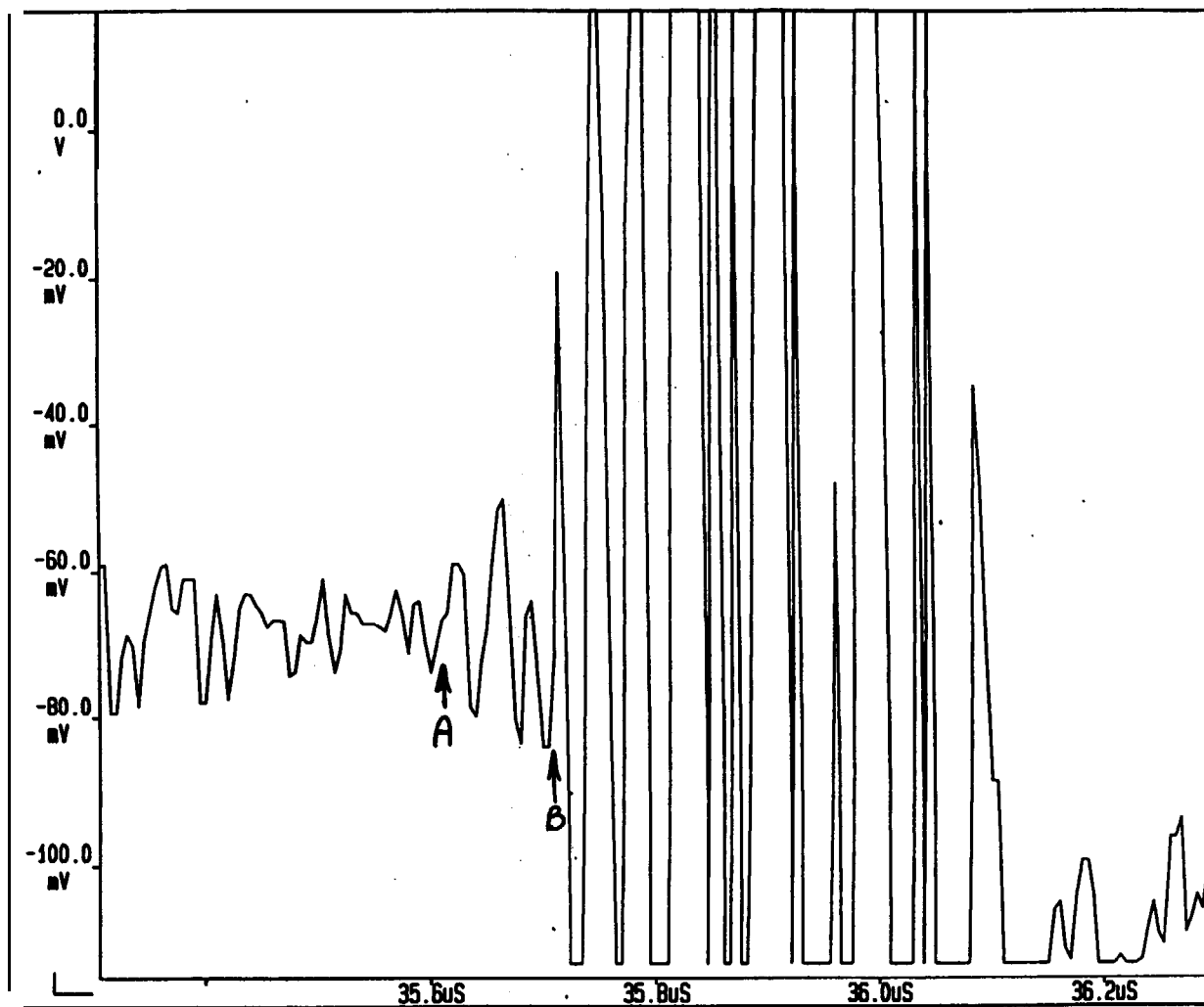
Figure D.4 ATDR signature for fouled CA RO membrane treated with **Triton** X-35. The response shown **is** from a **"clump"** on the membrane surface. The initial echo (A) is followed by a second echo much closer to the surface **(B).** The second echo has a larger amplitude than **"A"** and may correspond to the response for a layer of a higher density fouling material close to the surface.
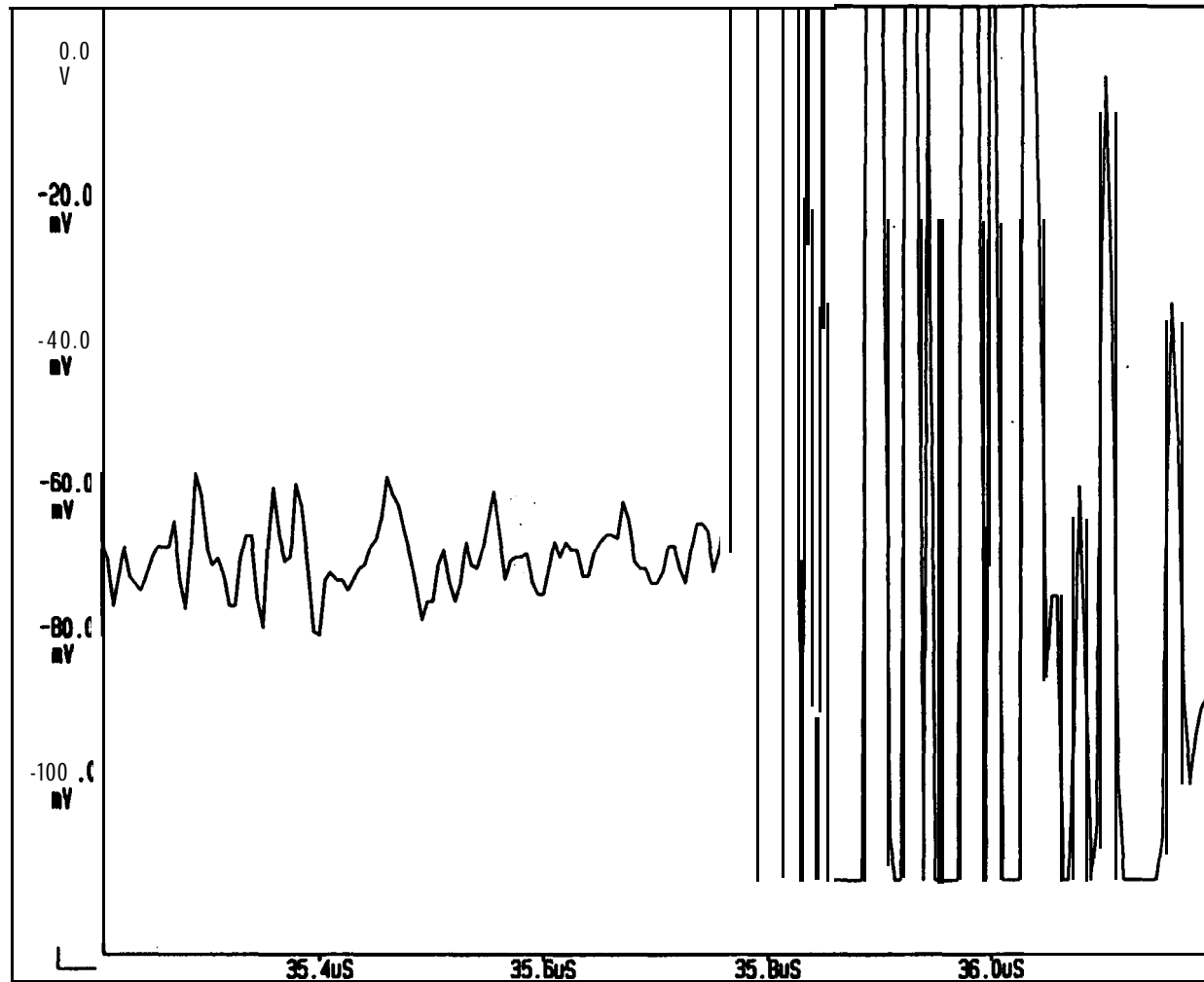
Figure D.5 ATDR signature for fouled CA RO membrane treated with Triton X-100: clean area,
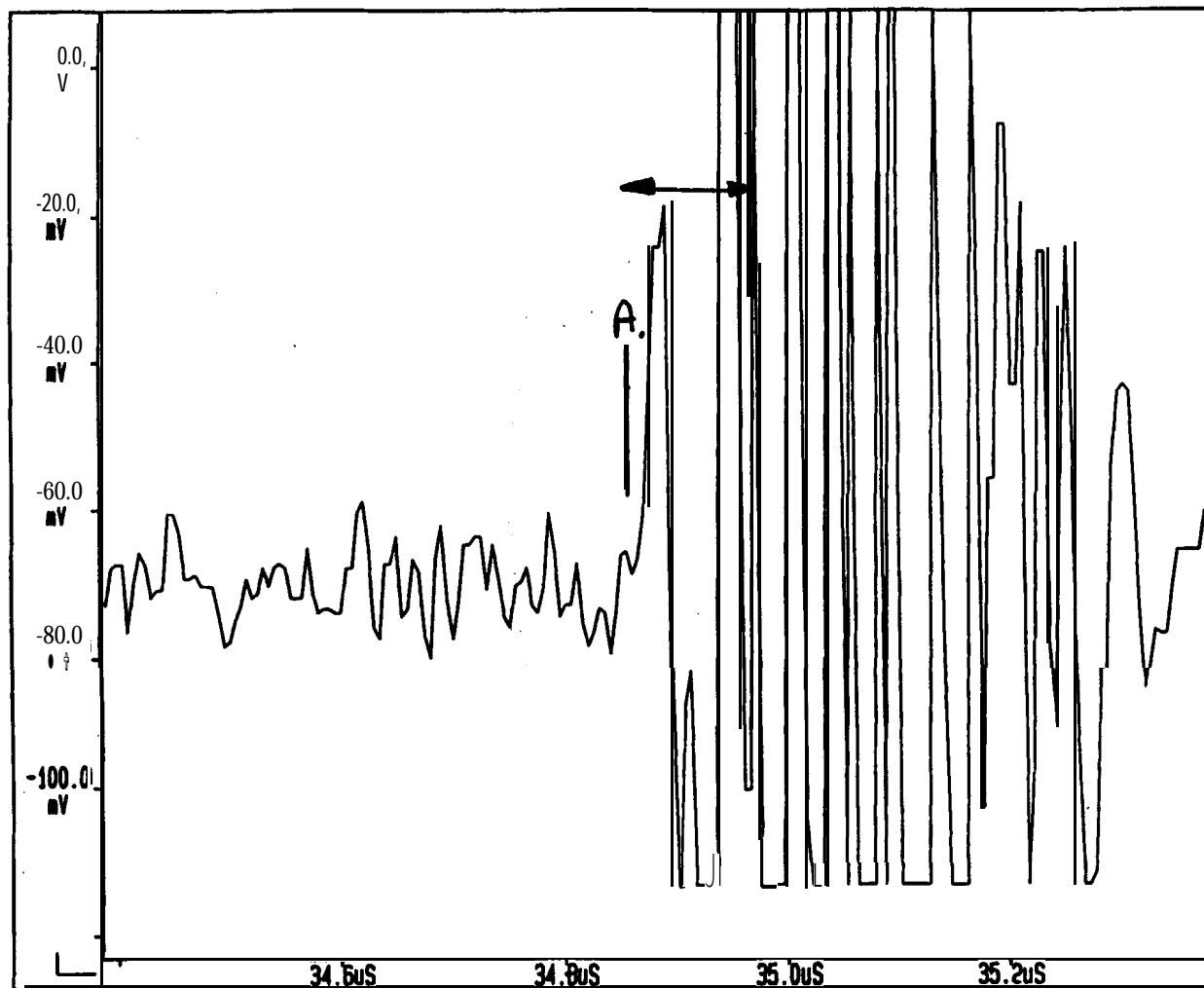
Figure D.6   ATDR signature for fouled CA RO membrane treated with Triton X-100. Response shows a well formed fouling layer starting at the time indicated as "A".
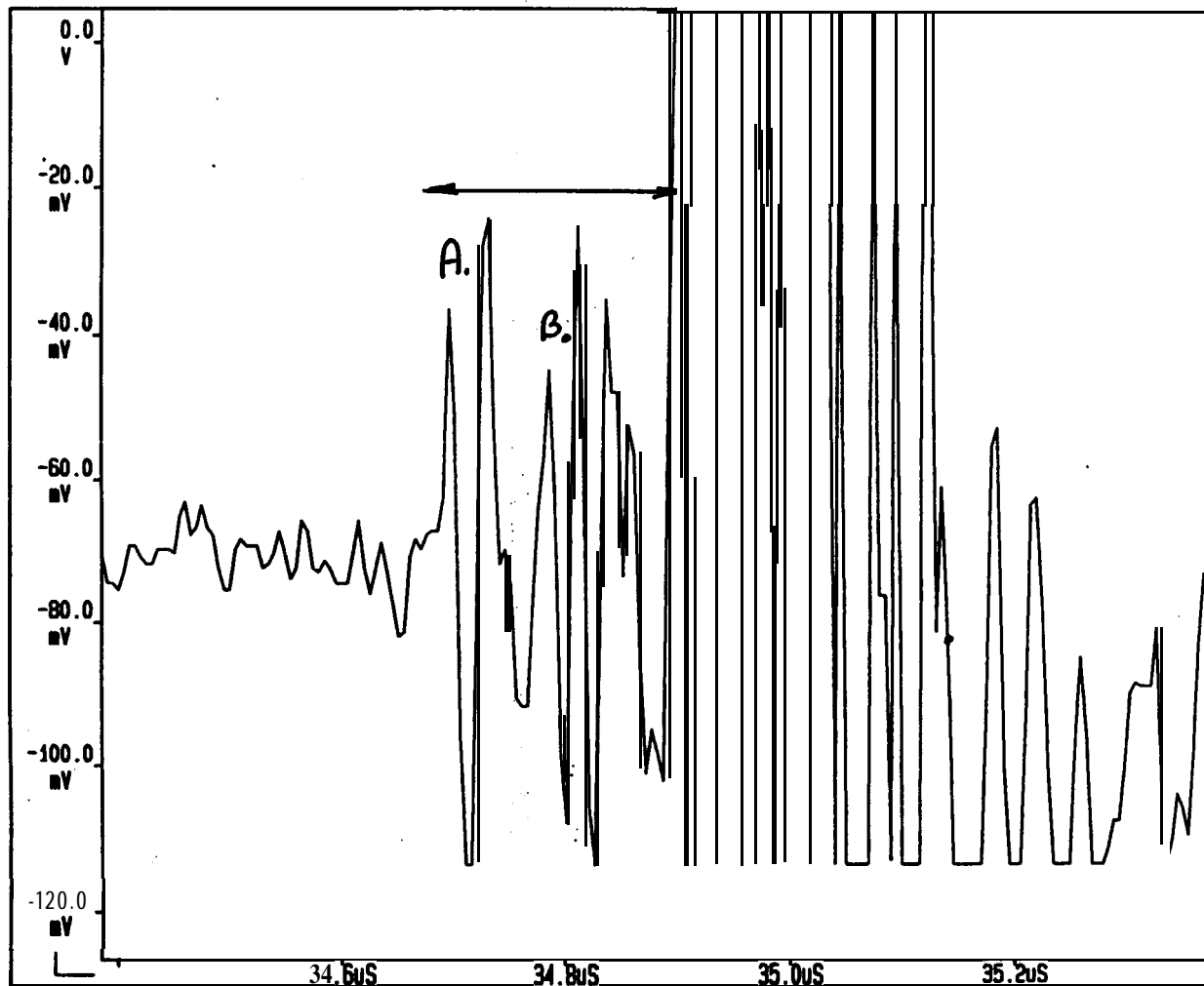
Figure D.7   ATDR signature for fouled CA RO membrane treated with Tritoo X-100. The response **"A"** is from the top of the fouling layer. The **"B"** response indicates ao inner layer with a similar acoustic impedance contrast to the water foaling interface.
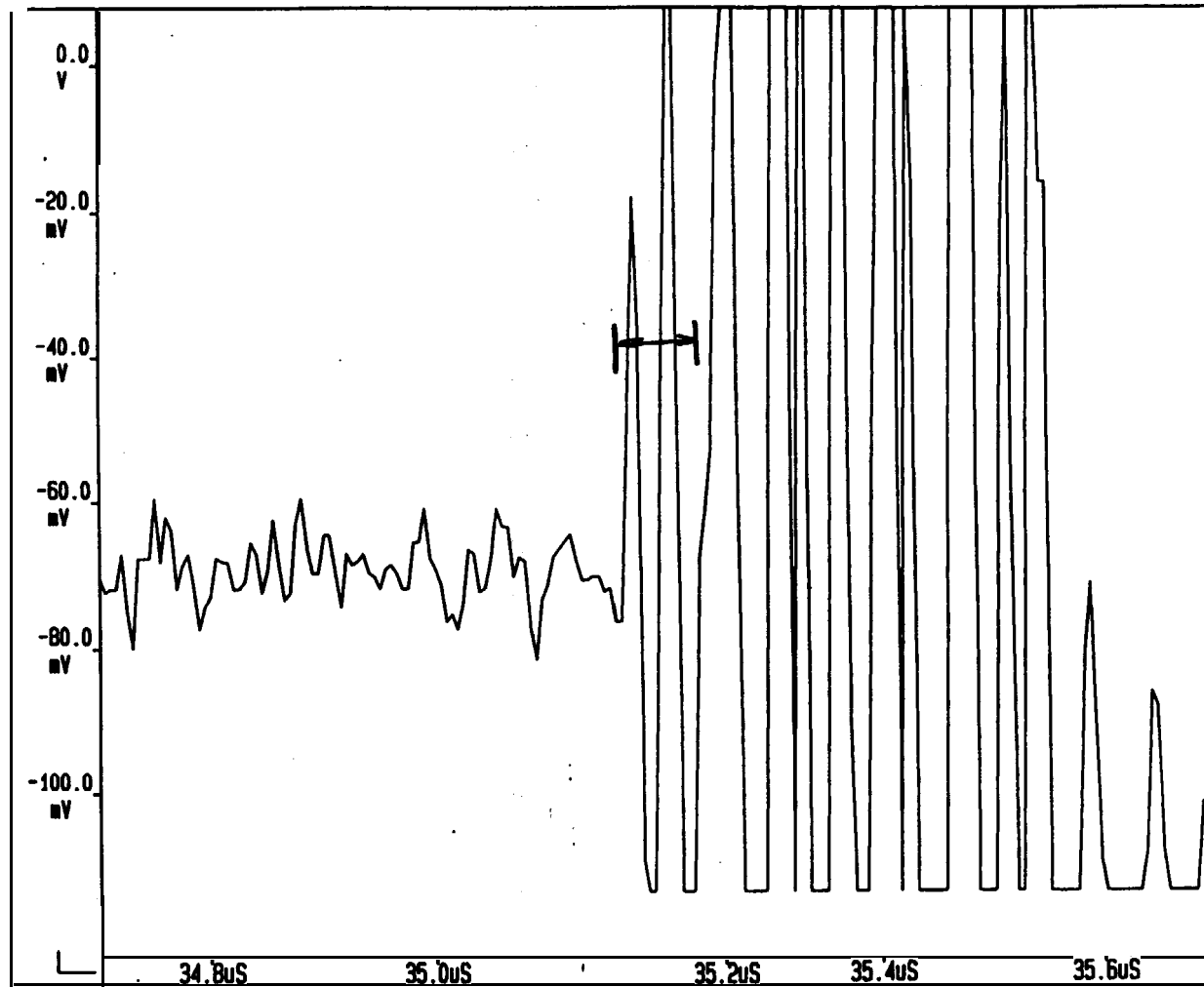
Figure D.8   ATDR signature for fouled CA RO membrane treated wlth Trlton X-705. The response indicates a hard well formed fouling layer about 48 micron thick. This material exhibited the largest acoustic impedance contrast between fouling and membrane seen on any of the samples.
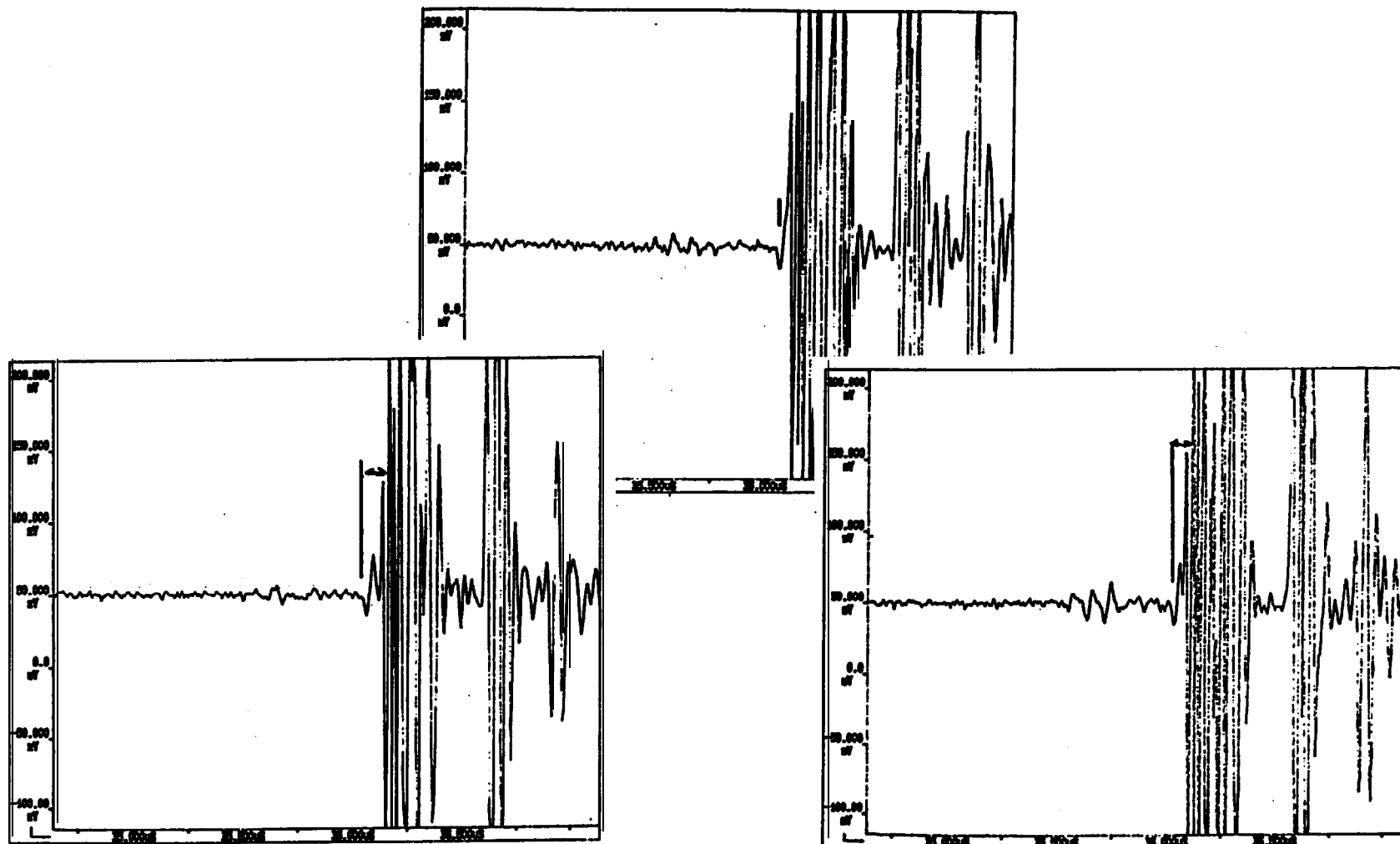
FIgureD.9   ATDR signature for fouled CA RO membrane treated with Triton X-705: Line sequence of a clean area.

Figure D. 10   ATDR signature for fouled CA RO membrane treated with Pluronics F87: clean area.

Figure D.11   ATDR signature for fouled CA RO membrane treated with Pluronics P84: "x" marks a light fouling interval.
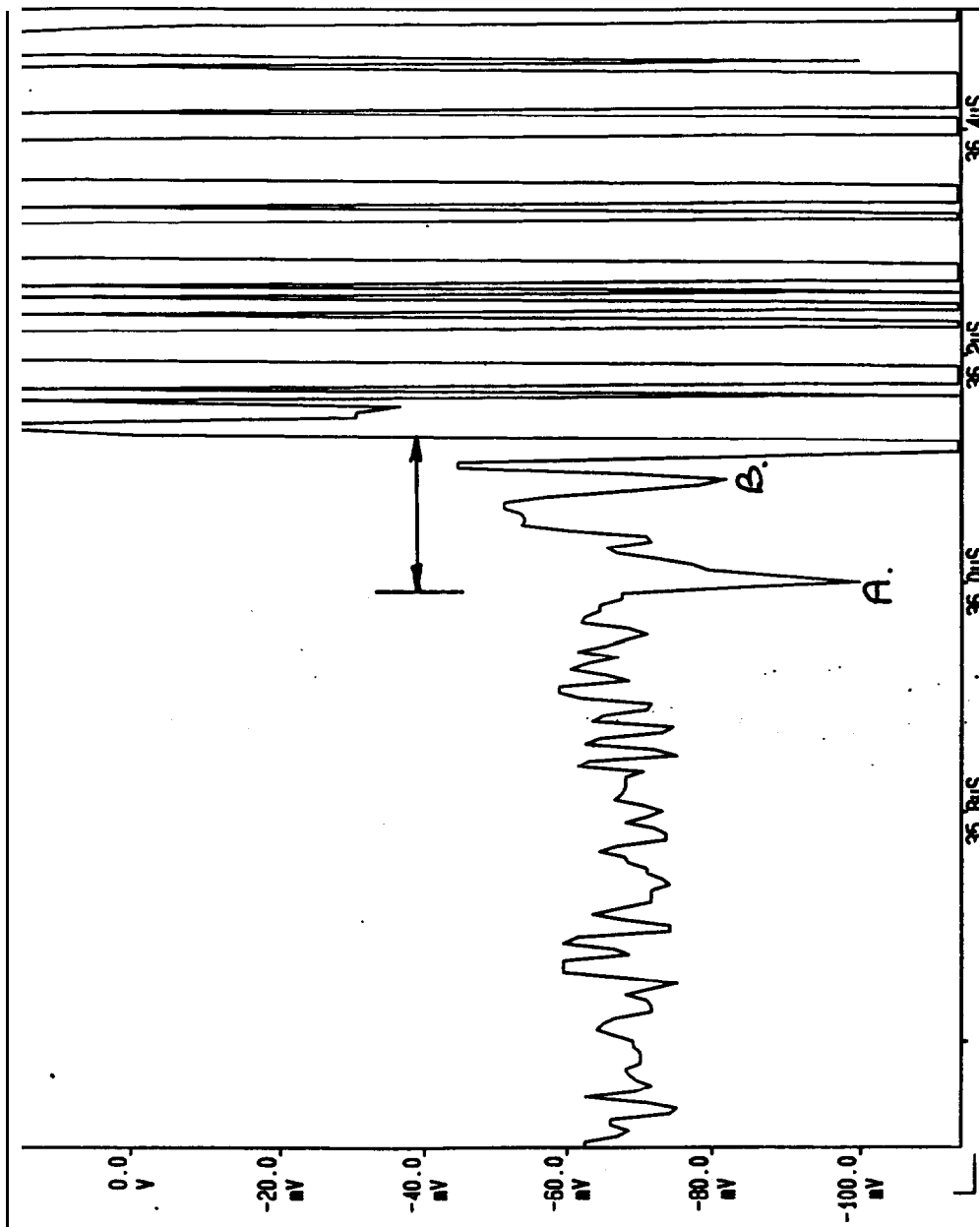
Figure D.12 ATDR signature for fouled CA RO membrane treated with Pluronics P84: Clumping.
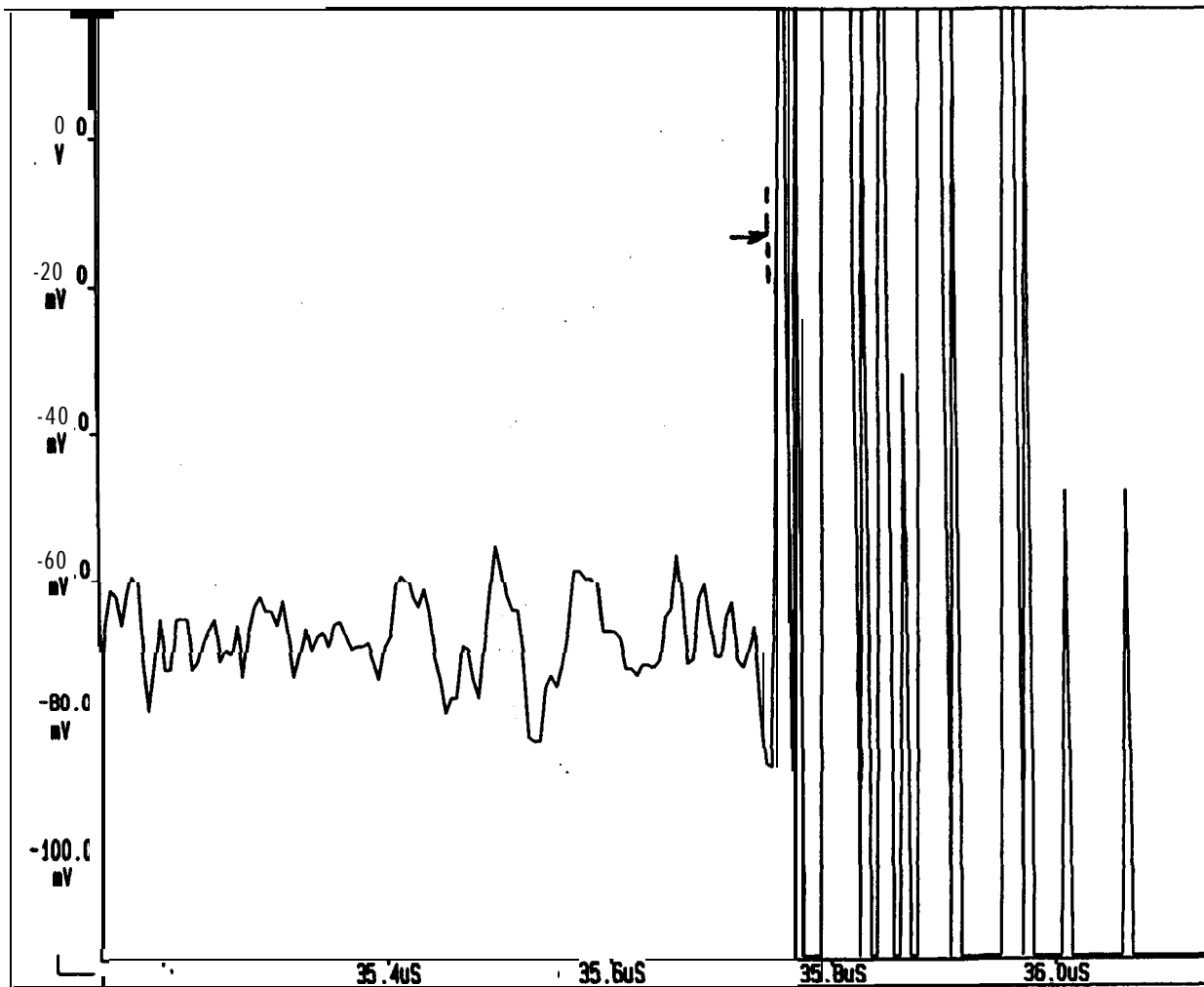
Fin D. 13   ATDR signature for fouled CA RO membrane treated with Pluronics P84: thin layer.
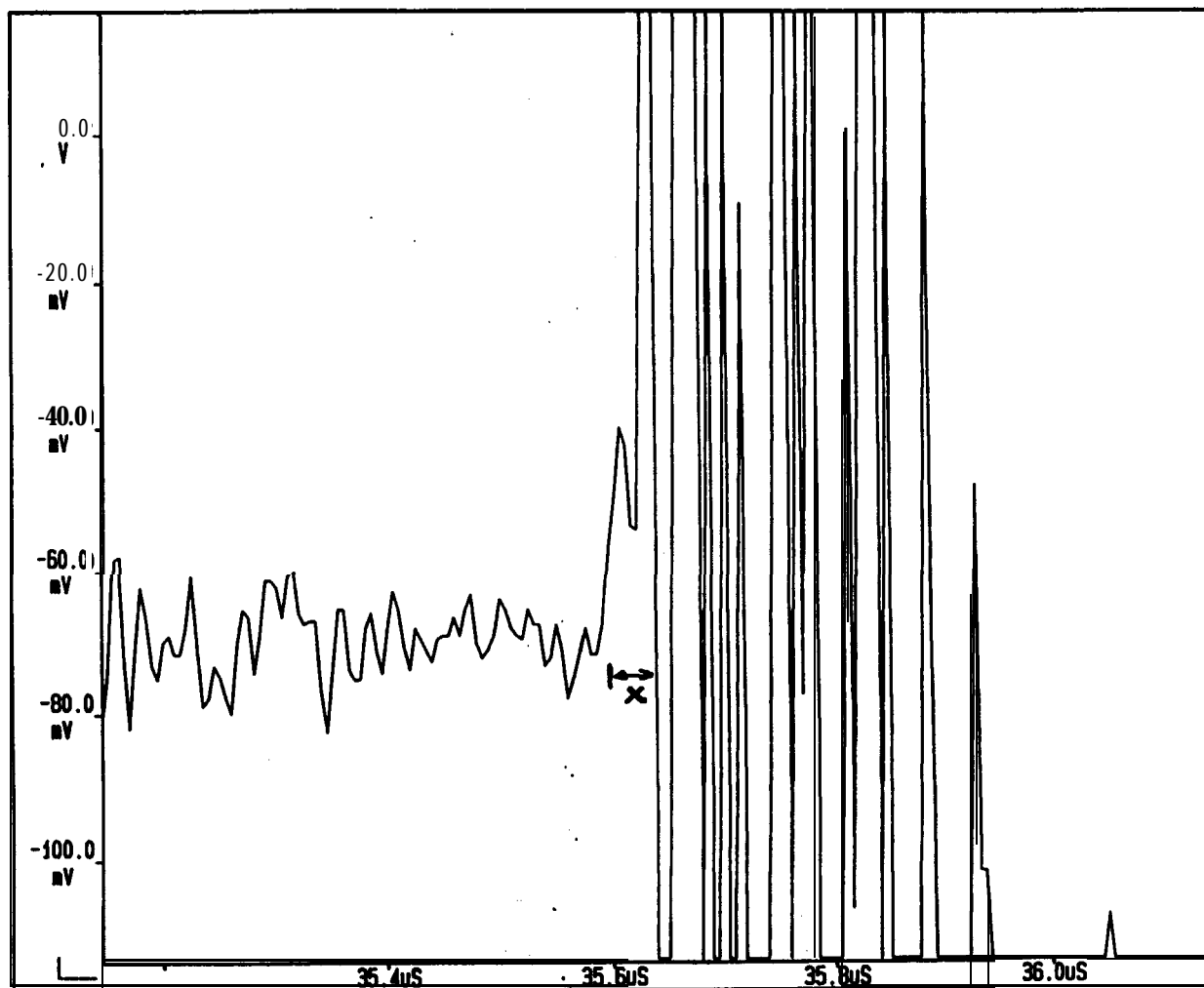
Figure D. 14 ATDR signature for fouled CA RO membrane treated with Phonies P84: "X" marks the interval of a soft, thick layer.
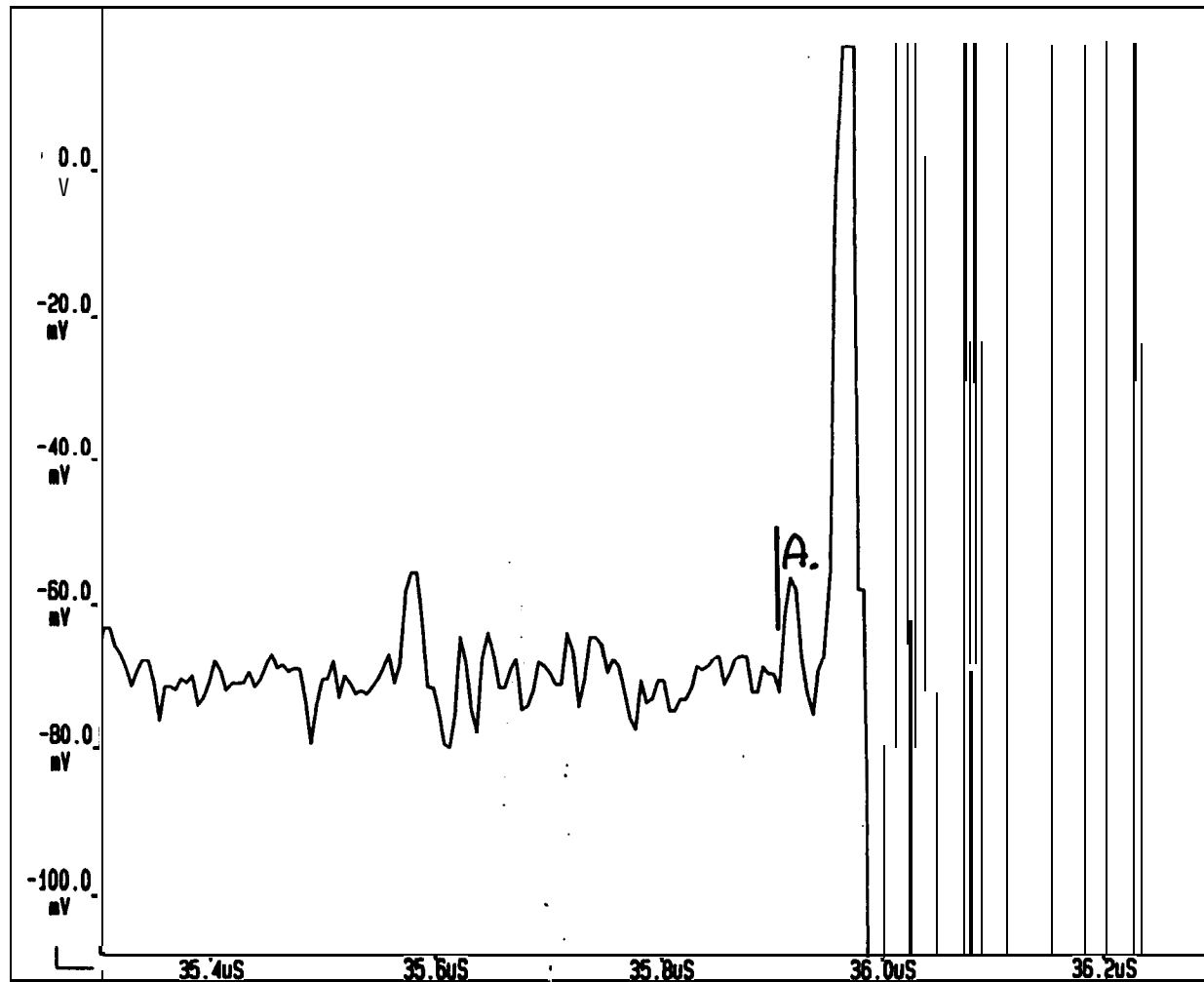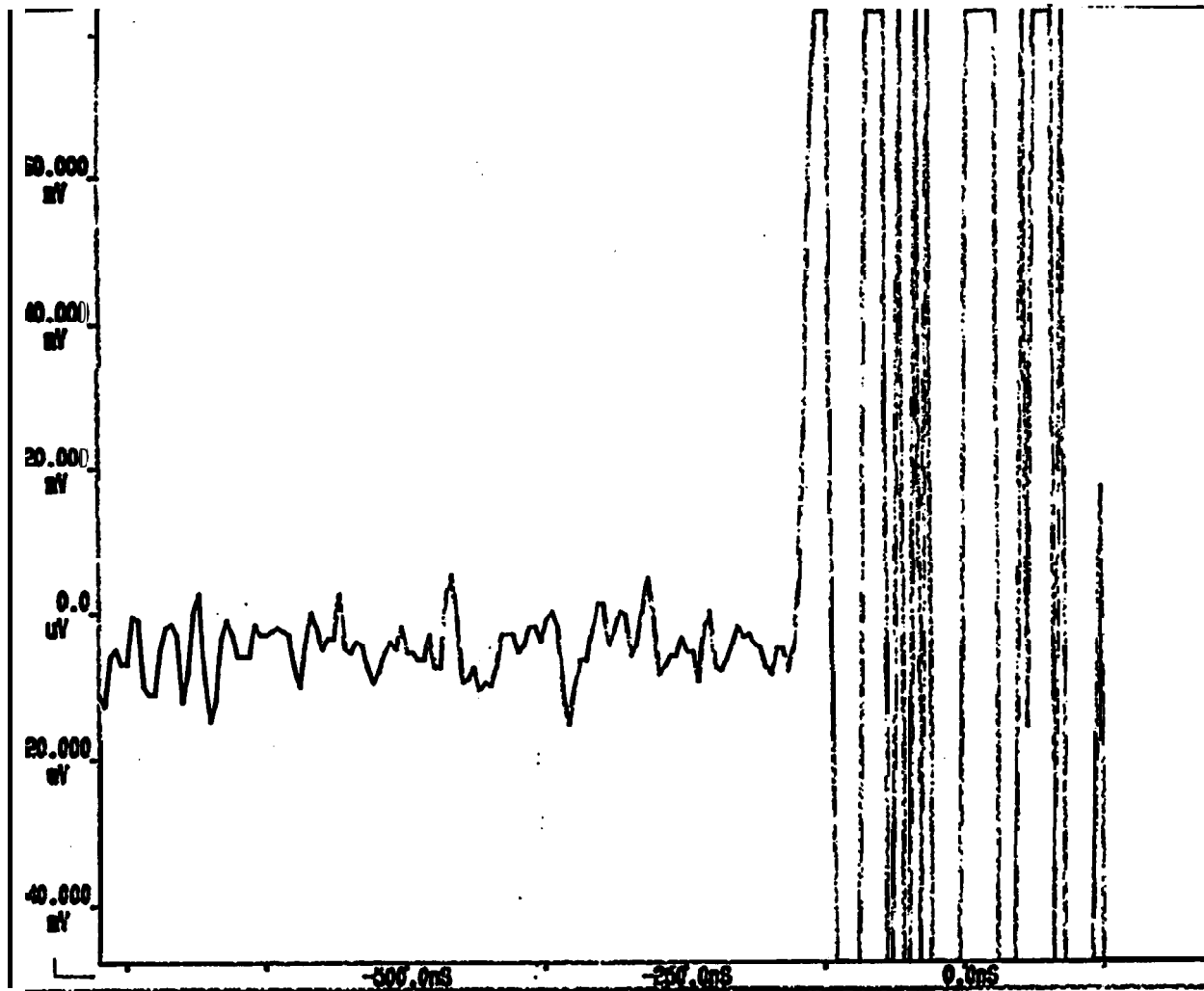
Figure D. 15   **ATDR** signature for fouled **CANF** membrane treated with **Triton X-100: "A"** marks the response from a very thin layer.
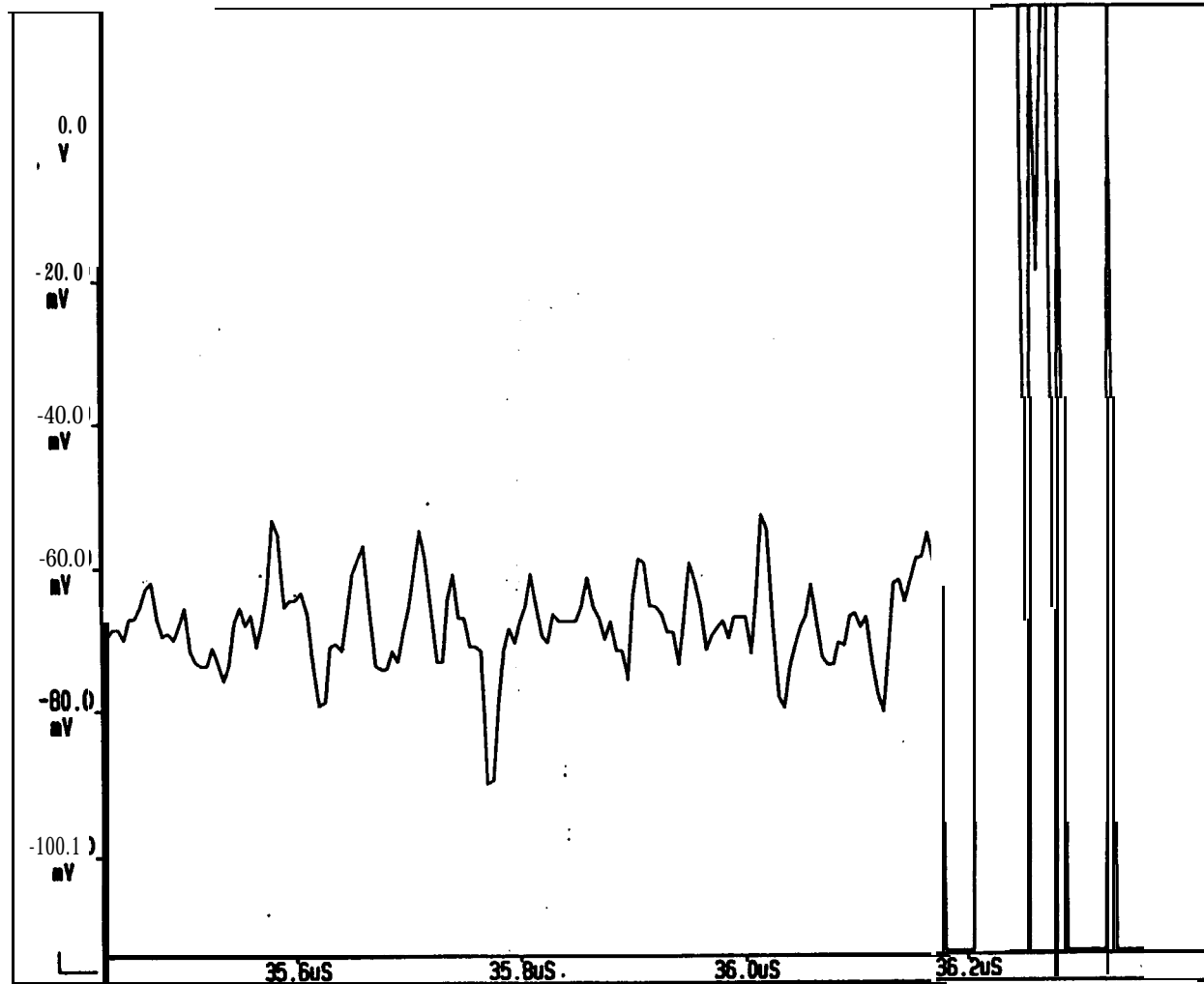
Figure D. 16   ATDR signature for clean untreated PA RO membrane.

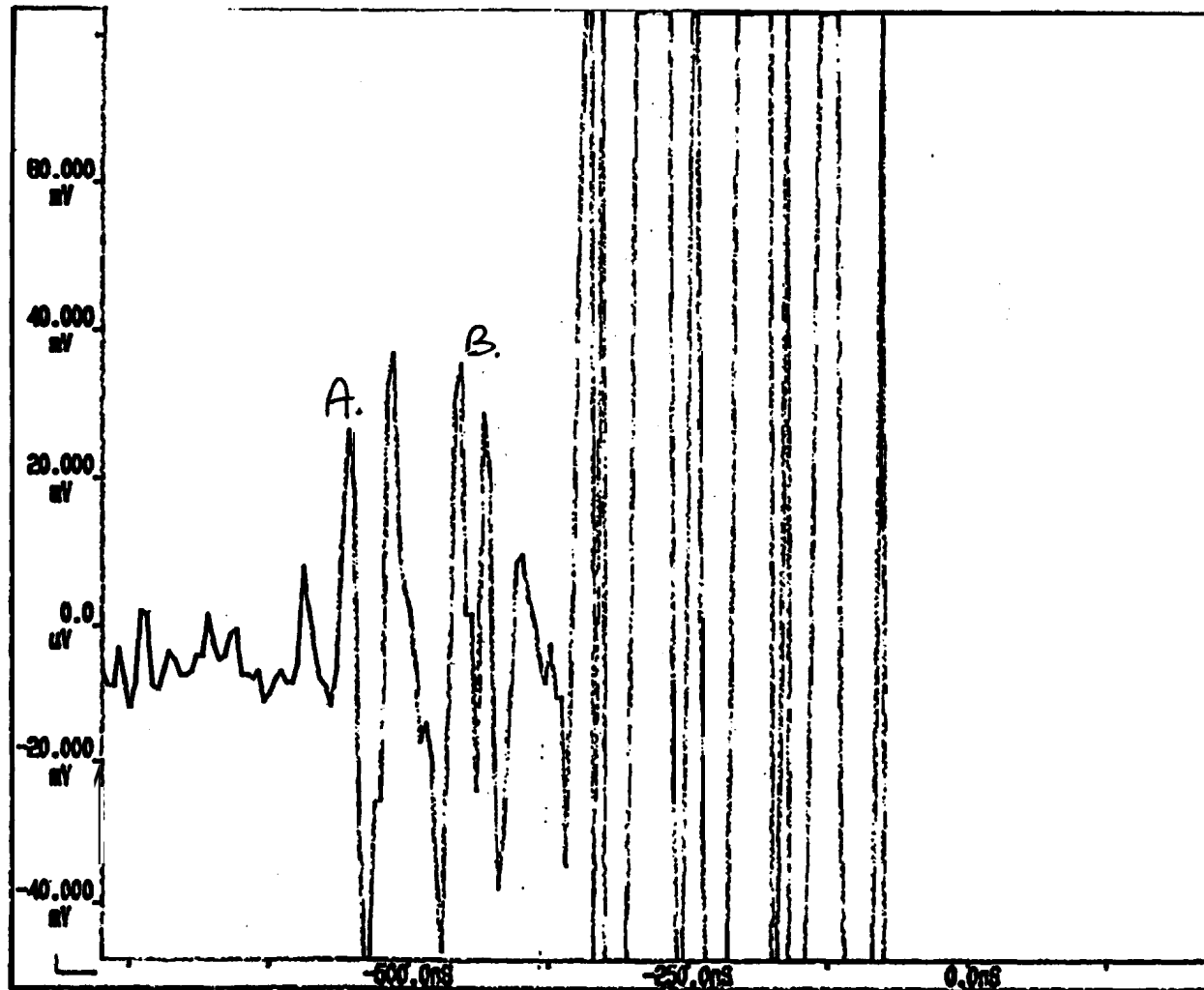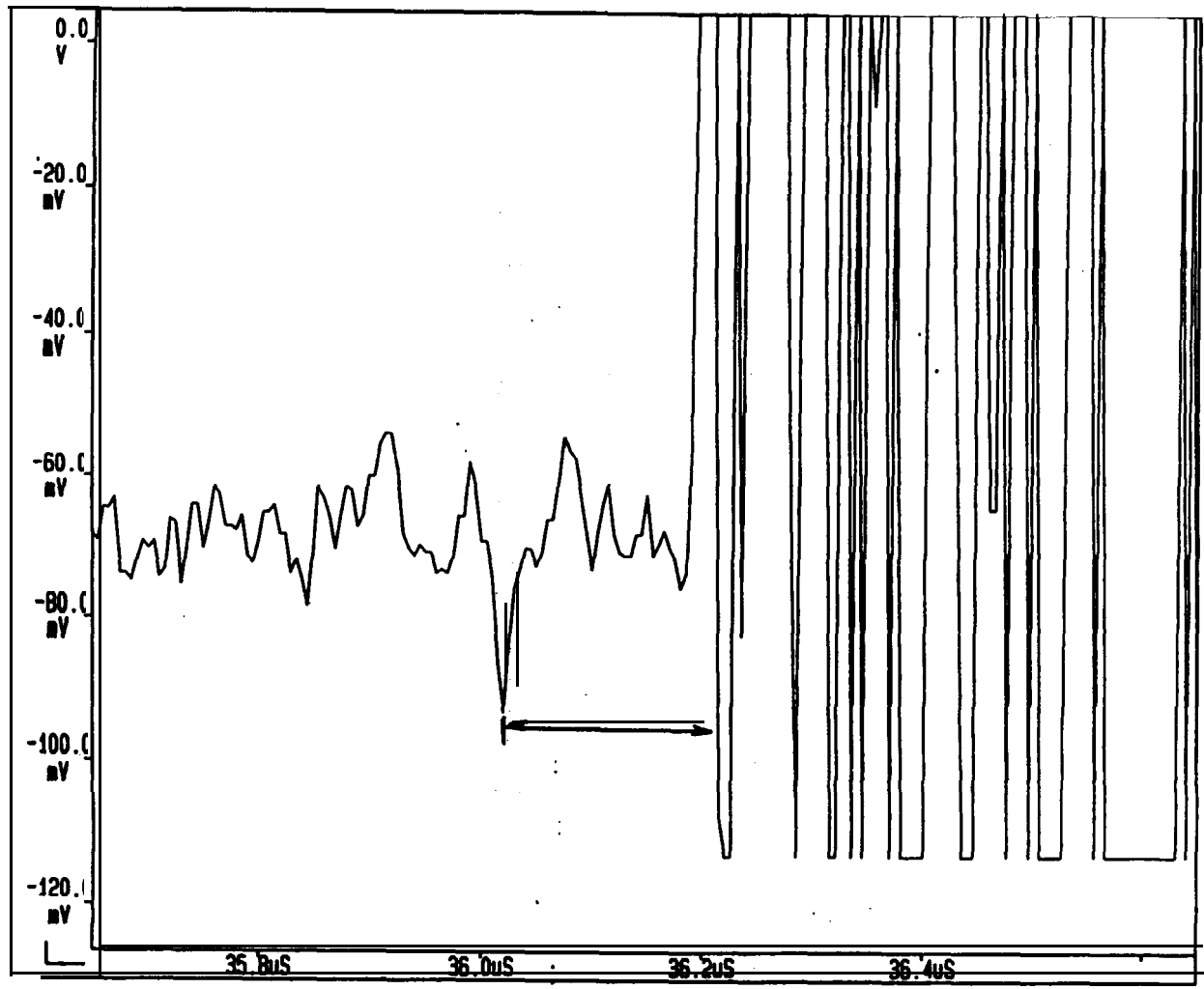FiireD.17   **ATDR signature for a fouled untreated PA RO membrane: clean** area.

Figure D. 18   ATDR signature for untreated fouled PA RO membrane: thick fouling layer witb at least a double layer response.

Figure D. 19   ATDR **signature** for foaled PA RO membrane treated with **Triton** X-35.
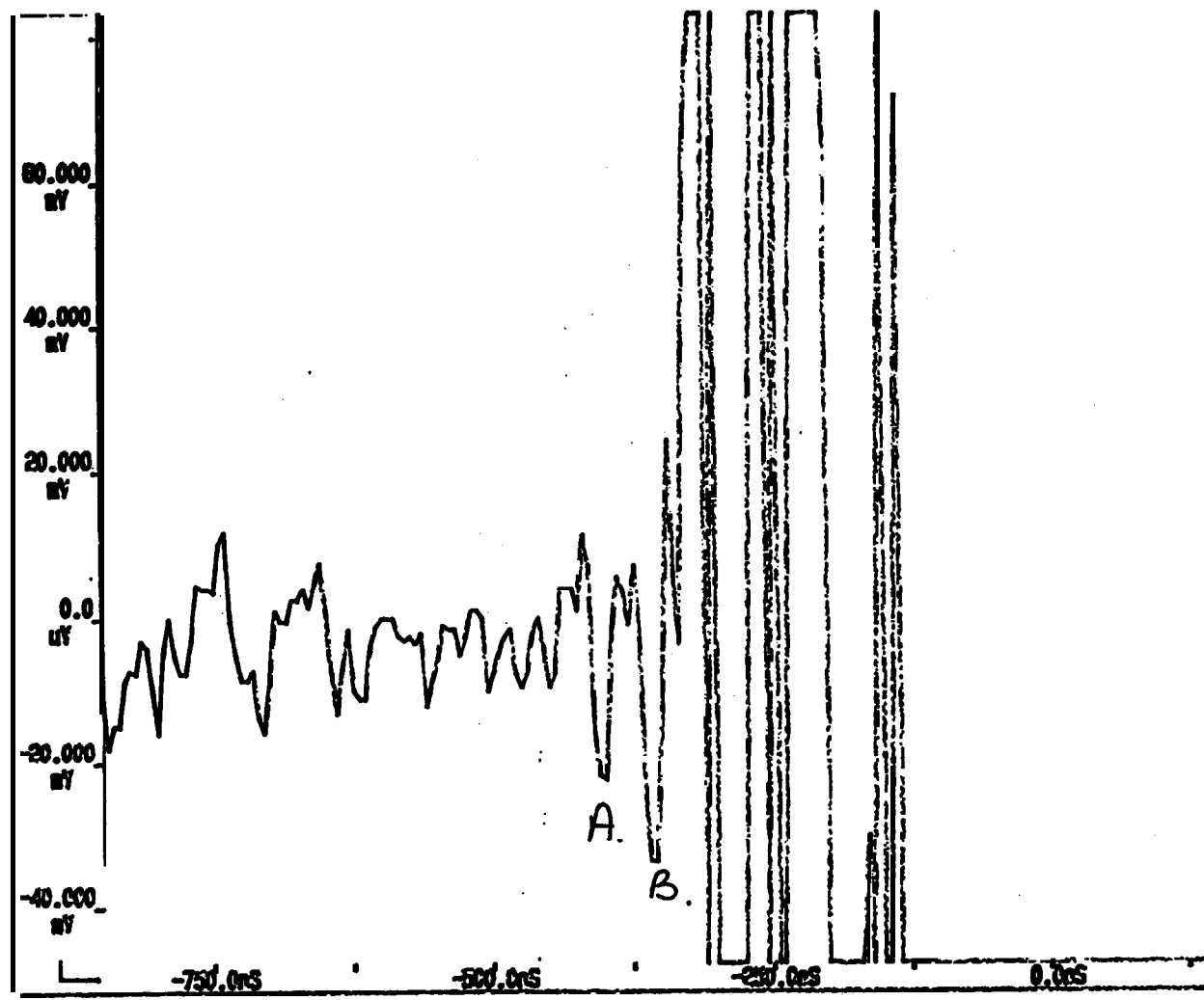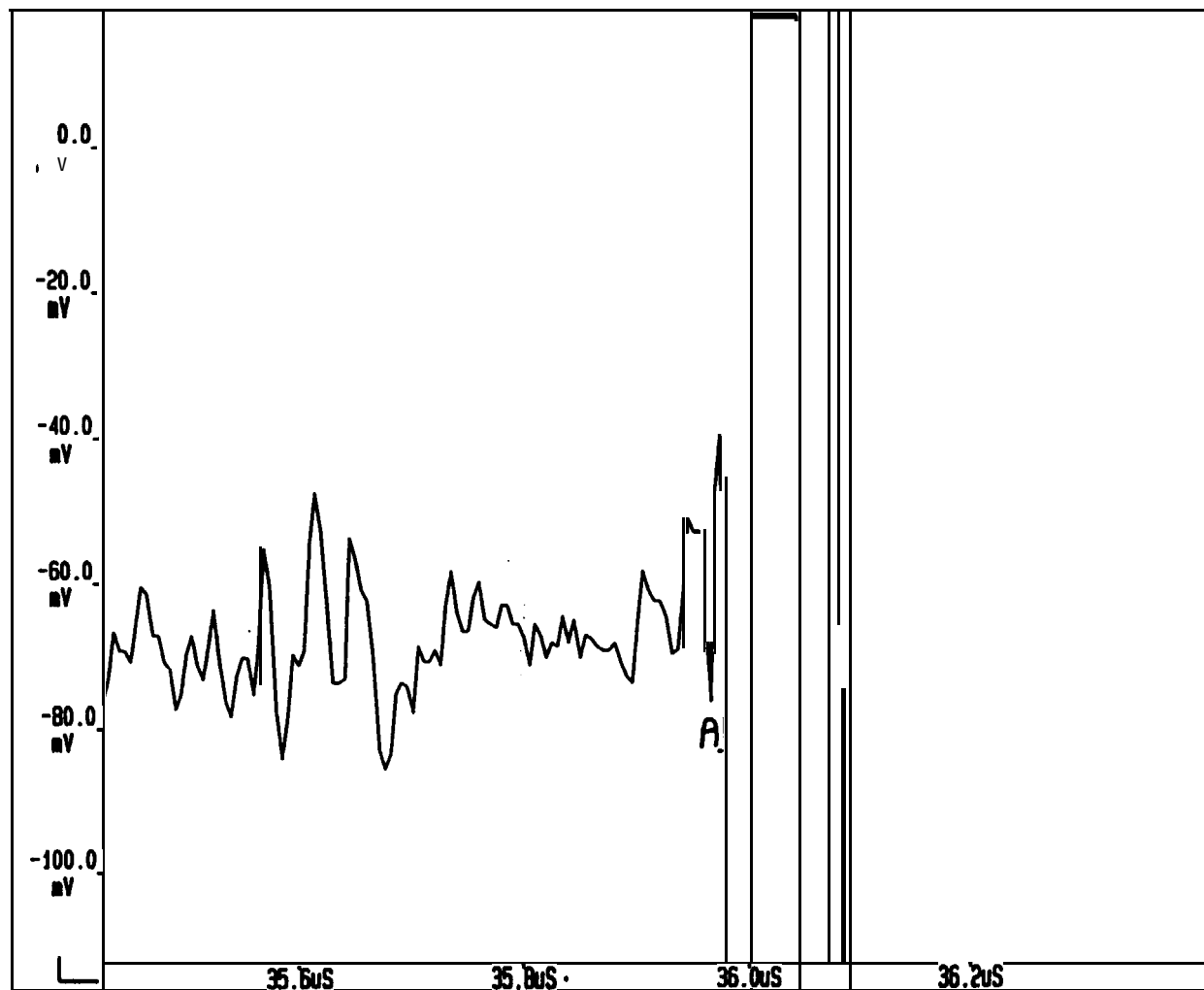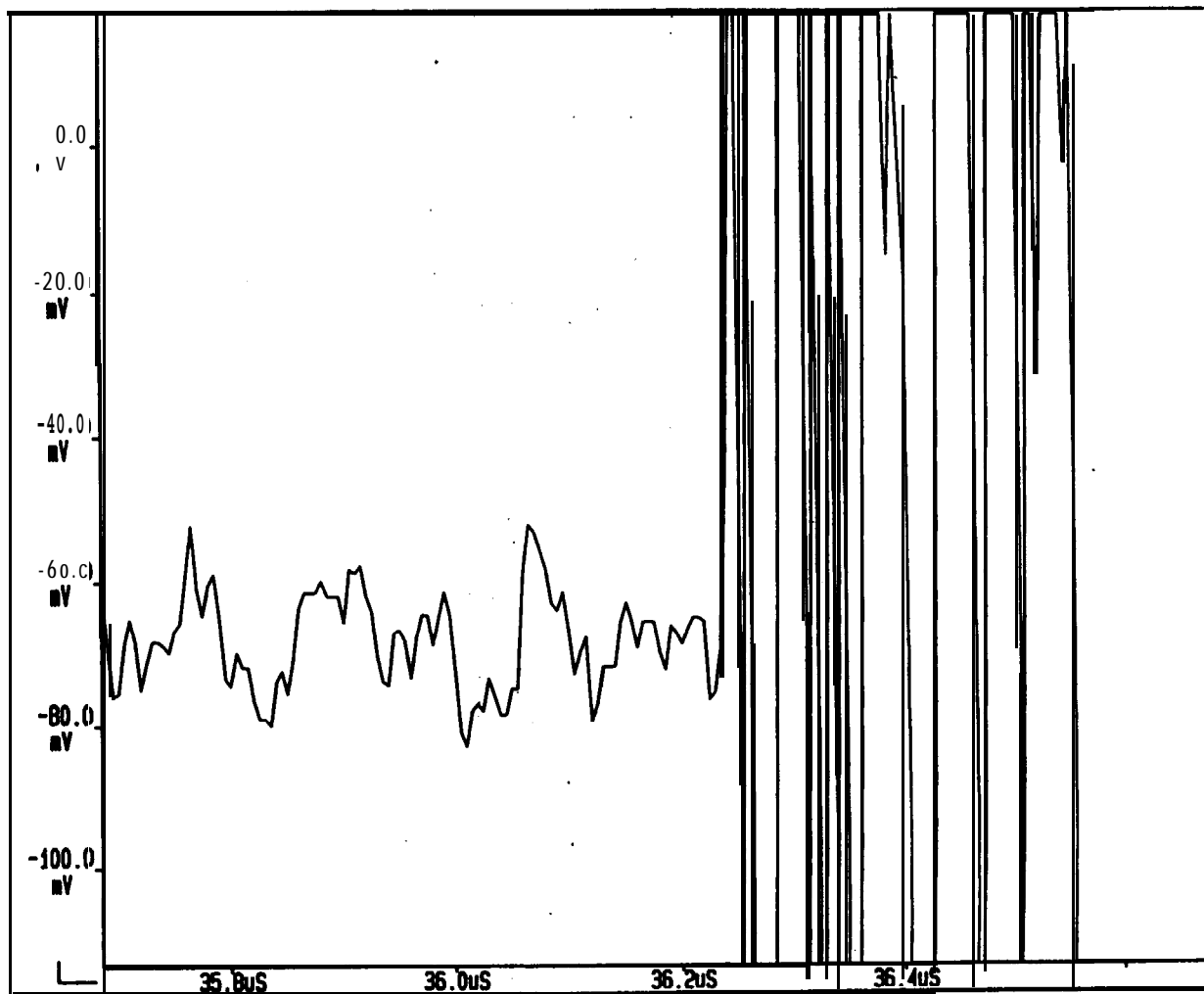
Figure D. 20   ATDR signature for fouled PA RO membrane treated with Triton X-100: patchy fouling.

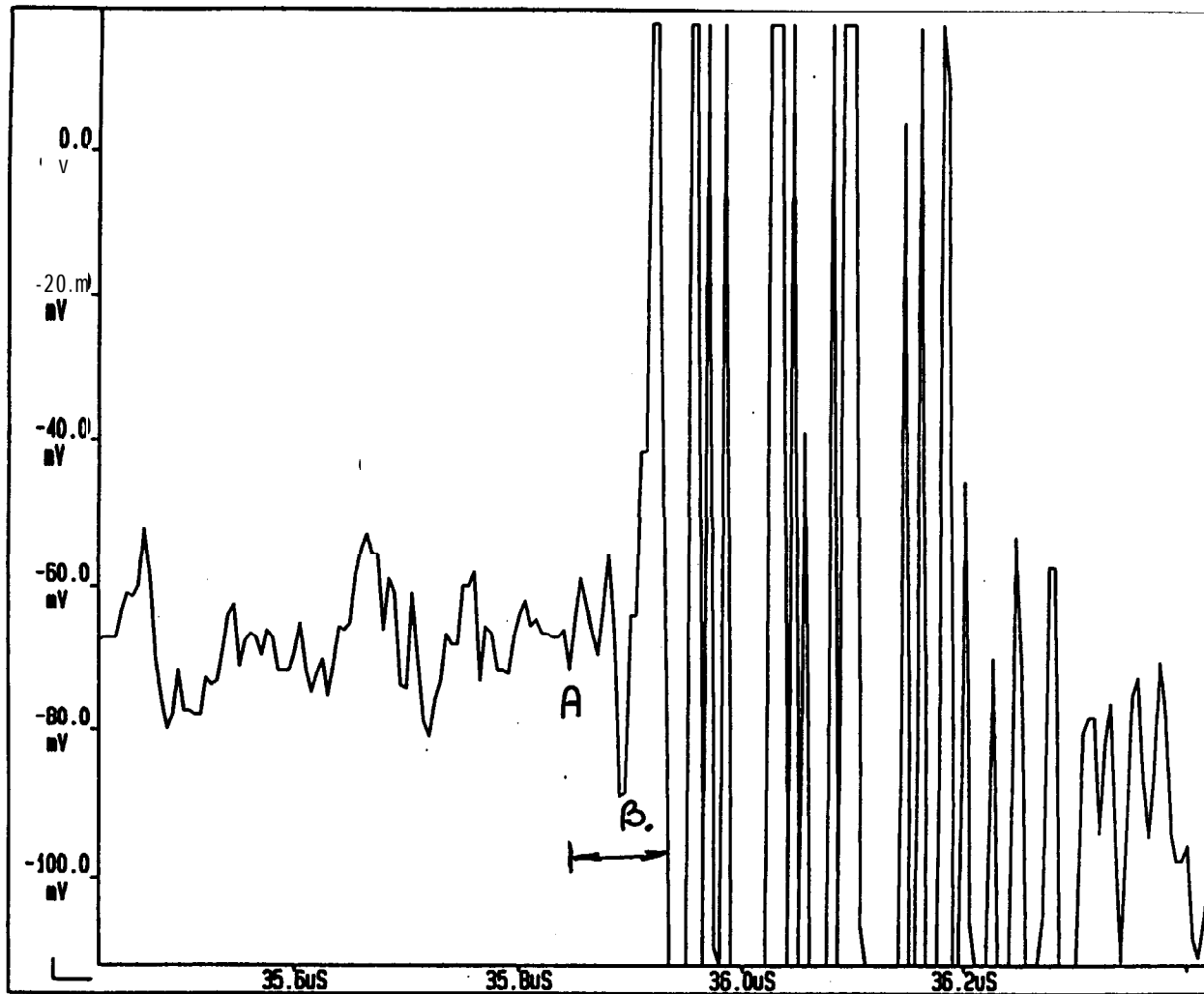**Figure** D. 21   ATDR signature for foaled PA RO membrane treated with Triton X-705: mostly clean.

FigureD.22   ATDR signature for fouled PA RO membrane treated with Phonics **F87:** thin patches of fouling.

Figure D.23   ATDR signature for fouled PA RO membrane treated with Phonies P84: soft and hard layers.
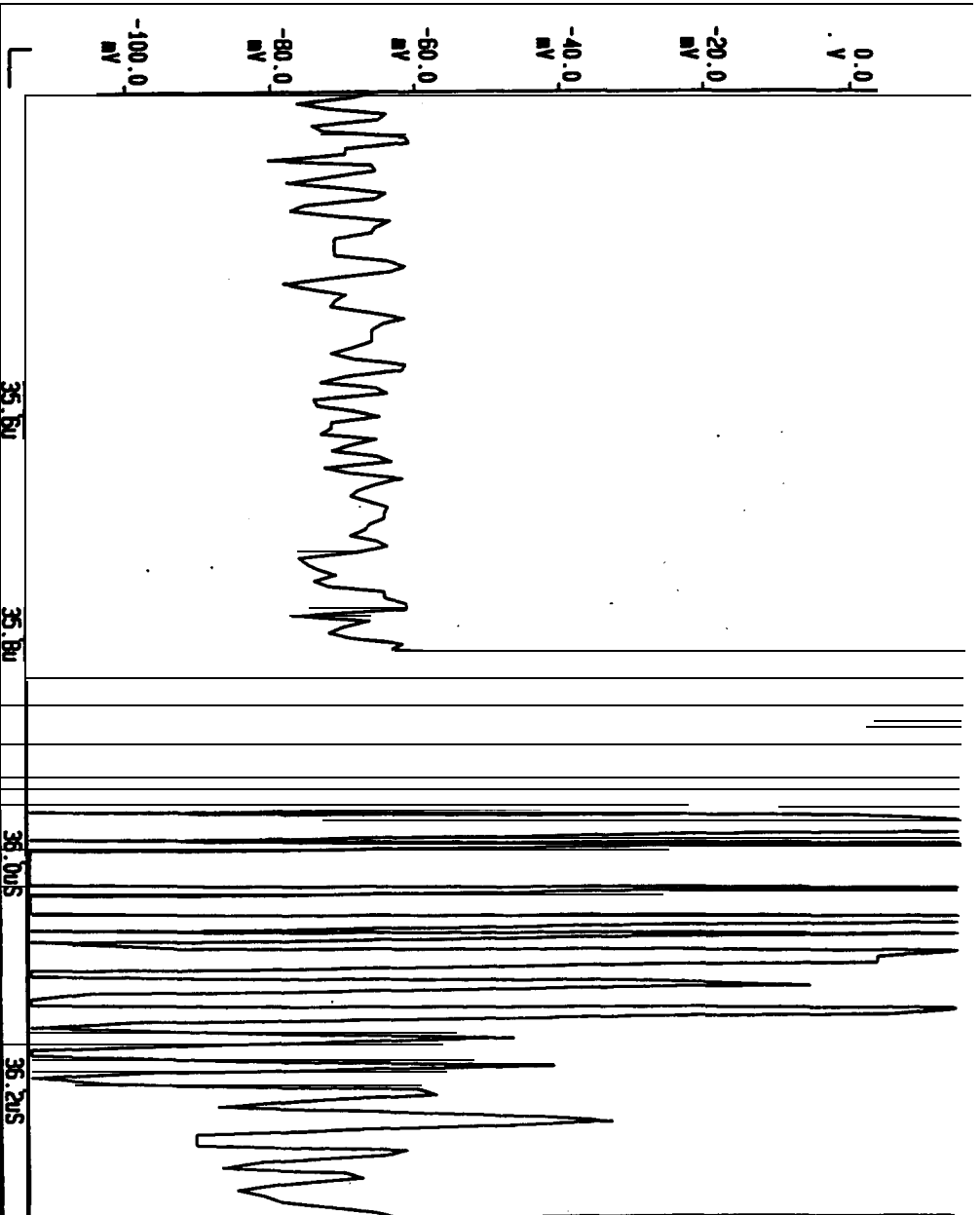
Figure D.24   ATDR signature for fouled PA RO membrane treated with 0.001% wt. solution of Triton X-100: clean.
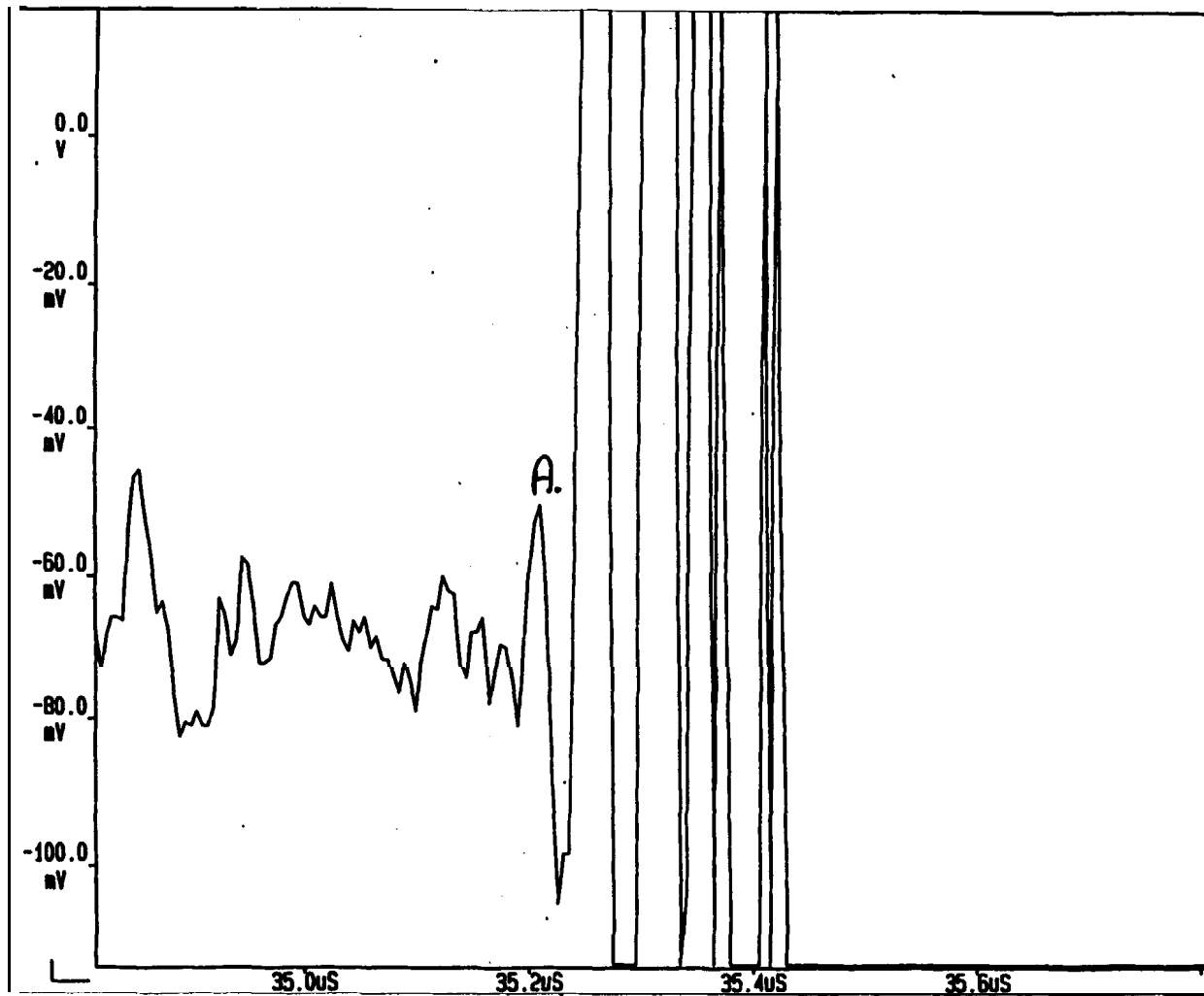
Figure D. 25 **ATDR** signature for fouled **PANF** membrane treated **with** Triton X-100: thin patches.

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13. ABSTRACT *(Maximum 200 words)*

Commercial samples of cellulose acetate and polyamide RO and NF membranes were treated with an homologous series o polyethylene-oxide based surfactants to improve fouling resistance. Various characterization methods were used to quantif membrane surface changes with treatment and fouling with a vegetable broth solution. Streaming potential was used t characterize changes in zeta potential. Atomic force microscopy was used to evaluate changes in surface topography. Water flu and salt rejection were evaluated using a bench scale "swatch-testing" apparatus. Fouling layer thickness was evaluated usin acoustic time domain reflectometry. Results from these methods were compared with performance changes.

The fouling solution degraded the untreated CA-blend membrane. Therefore any surface protection provided by the surfactan was dramatically illustrated. Triton Xl00 and Pluronic P84 provided significant protection. PA membranes treated witl surfactant experienced a severe flux decline. A similar decline was caused by fouling of the untreated PA membrane. The treatec PA membrane did not have *further* flux decline with fouling. These results suggest a need for further studies on whether or no a surfactant pre-treatment will result in improved membrane flux and rejection over many operating and cleaning cycles whei exposed to fouling waters.

14. SUBJECT TERMS--
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