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Robert O. Dunn Jr[a]; John F. Scamehorn[a]; Sherril D. Christian[b]
[a] SCHOOL OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE, UNIVERSITY OF OKLAHOMA, NORMAN, OKLAHOMA [b] DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OKLAHOMA, NORMAN, OKLAHOMA

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Use of Micellar-Enhanced Ultrafiltration to Remove Dissolved Organics from Aqueous Streams

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ROBERT O. DUNN JR. and JOHN F. SCAMEHORN*

SCHOOL OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

SHERRIL D. CHRISTIAN

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF OKLAHOMA
NORMAN, OKLAHOMA 73019

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Abstract

Traditional ultrafiltration is ineffective at removing dissolved low molecular weight organics from water. In micellar-enhanced ultrafiltration (MEUF), surfactant is added to the water at concentrations well above the critical micelle concentration. Almost all of the organic originally dissolved (the solute) solubilizes in the micelles formed by the surfactant. The solution then passes through an ultrafiltration membrane with pores small enough to block micelle passage. The permeate contains (at most) only the unsolubilized solute and the surfactant monomer, both at very low concentrations. In this work, the criteria for selecting a surfactant are considered and MEUF is tested on an aqueous stream containing 4-tert-butylphenol with hexadecylpyridinium chloride as the surfactant. At high surfactant concentrations (0.25 *M*) in the retentate, rejections decrease, probably owing to the formation of *n*-mers (e.g., dimers, trimers, etc.) which are able to pass through the pores along with some solubilized solute. Also under these conditions, the viscosity increases while fluxes decline sharply. So long as these high surfactant concentrations are avoided, MEUF is an extremely effective separation technique, resulting in an average solute rejection of 99.7%, a permeate/feed ratio of 87%, and good fluxes under the conditions studied.

*To whom correspondence should be addressed.

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INTRODUCTION

The need to separate water-soluble organic compounds from aqueous streams is a frequently encountered industrial problem. Traditional methods of separating soluble compounds from a stream often involve a phase change, as in distillation, or extraction followed by distillation. These techniques are energy intensive and it is desirable to develop low-energy separation processes.

Micellar-enhanced ultrafiltration (MEUF), a recently proposed technique for water clean-up, is illustrated in Fig. 1. In this process, surfactant is added to the aqueous stream containing organic solute. The bulk of the

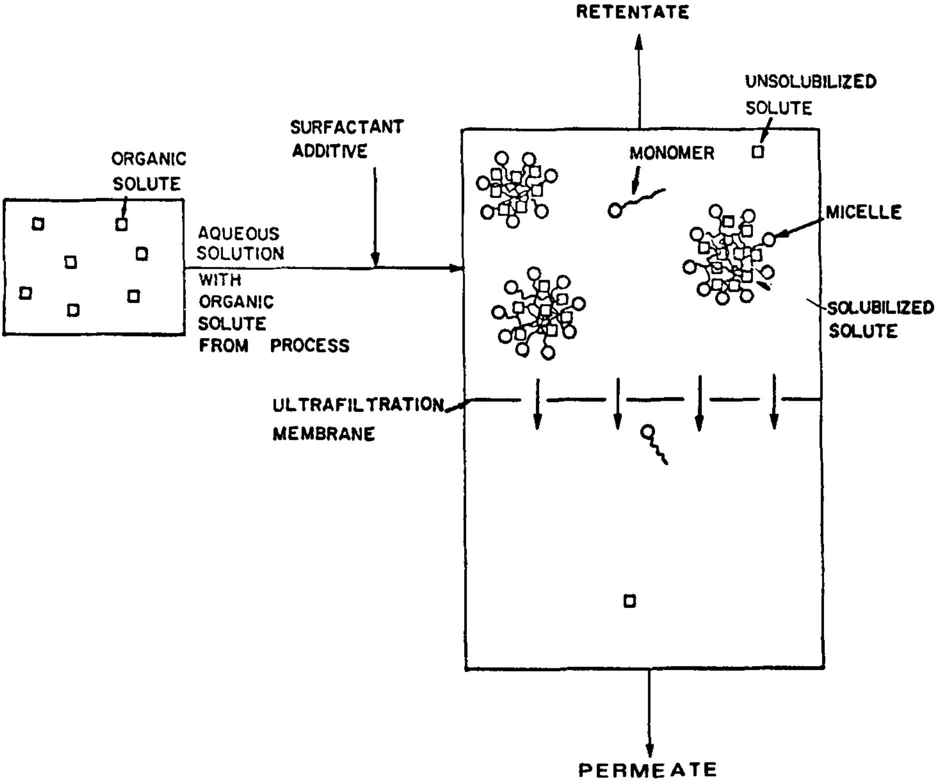

FIG. 1. Schematic of micellar-enhanced ultrafiltration.

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solute dissolves or solubilizes in the micelles (surfactant aggregates of about 20–200 molecules in size) formed in solution. The aqueous stream is then passed through an ultrafiltration membrane with pore sizes just small enough to reject the micelles. The permeate contains very low concentrations of organic solute and surfactant, and it can be discharged or recycled. The retentate contains very high concentrations of both solute and surfactant and has a much lower volume than the original process stream. Therefore, subsequent further purification or disposal of this retentate is less expensive and requires less energy than treating the original stream. The ultrafiltration step requires little energy and relatively low pressures and is generally much less expensive than other separation techniques per unit volume of solution processed.

BACKGROUND

Ultrafiltration

The lowest molecular weight cut-off generally attainable in standard ultrafiltration membranes is about 300 (*1*). Since fluxes generally decrease as pore diameters and molecular weight cut-offs decrease (*2, 3*), direct ultrafiltration of low molecular weight compounds from water is often economically, if not technically, unfeasible. In the present work, the low molecular weight organics are "dissolved" or solubilized into larger aggregates, which can be rejected by a high molecular weight cut-off ultrafiltration membrane.

Micelle Formation and Solubilization

When surfactants are present in aqueous solutions above a certain concentration (the critical micelle concentration, or CMC), micelles form (*4–7*). That surfactant which is not present as micelles exists primarily as unassociated molecules or ions in solution (monomer). For the high molecular weight surfactants useful in MEUF, the CMC is very low. As the total concentration of surfactant is increased beyond the CMC, most of the added surfactant goes to increase the micelle concentration. Therefore, when the total surfactant concentration in solution greatly exceeds the CMC (as in MEUF), the surfactant present as monomer constitutes a very small fraction of the total concentration—the remainder of the surfactant consists of micelles.

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Organic compounds may solubilize or dissolve within micelles at four different locations (*8–10*): a) in the hydrocarbon core, b) in the palisade layer, c) adsorbed on the micelle surface, and d) in the polyoxyethylene shell of nonionic micelles. Organic solute species tend to locate preferentially in regions within the micelle that are similar chemically and in polarity to these molecules.

The distribution of organic solutes between the aqueous solution (as unsolubilized molecules) and the micelles may be described by

$$K = C_s/C_mC_u \tag{1}$$

where K is the distribution or solubilization constant, C_s is the concentration of solubilized organic, C_m is the concentration of surfactant in micellar form, and C_u is the concentration of unsolubilized organic solute. It is frequently assumed that Henry's law applies to the solubilization equilibrium—i.e., that K is independent of concentration (*10, 11*). The larger the value of K, the greater the proportion of the organic solute that will be present in the micelles of a surfactant solution.

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Micellar-Enhanced Ultrafiltration (MEUF)

Figure 1 is a schematic diagram illustrating micellar-enhanced ultrafiltration. In the process, a surfactant (either pure surfactant or a concentrated surfactant solution) is added to the aqueous stream containing the organic solute. The surfactant concentration in the combined stream is considerably greater than the CMC, so that the surfactant consists mainly of micelles in equilibrium with a small concentration of monomeric surfactant. The solute largely solubilizes in the micelles, with only a small fraction of the solute remaining unsolubilized at equilibrium. When this solution is forced through an ultrafiltration membrane having pore diameters smaller than the micelle diameters, the micelles (and the solubilized solute within them) are rejected by the membrane. If micelle rejection were 100%, the permeate would be very pure, containing the surfactant at a concentration near or below the CMC and the organic solute at a concentration equal to or less than that of the unsolubilized molecules.

The permeate may be recycled to the process or disposed of without expensive treatment techniques. If the solute concentration is still too great, staged MEUF could be used to reduce it further. Because the surfactants used in MEUF can be biodegradable, their presence in small concentrations in the permeate will not create a problem in disposal. The retentate, which does not pass through the membrane, becomes concentrated with respect to both the organic solute and the surfactant. This stream might be treated to recover the organic solute and the surfactant, or it could be properly discarded. The surfactant and solute will normally differ greatly in boiling point and solubility in solvents; therefore, separation of solute from surfactant (by techniques such as distillation, crystallization, or extraction) should not be difficult in most cases. The retentate stream will be much smaller in volume or flow rate than the original process stream being treated. Therefore, treatment of it for recovery or disposal will be much less expensive and energy intensive than the treatment of the original process stream. The resulting reduction in downstream treatment costs could make the concentration or separation achieved by MEUF economical.

In previous studies, MEUF has been used as an analytical tool. It has been shown that the organic concentration in the permeate approximately equals the concentration of unsolubilized solute determined by other methods (*12, 13*). Studies have also been performed using ultrafiltration to determine monomer concentrations in equilibrium with micelles (*14–20*). Under the proper conditions, the permeate surfactant concentration may nearly equal that of the monomer, whereas at high flow rates (*14*) or with small UF pore diameters (*21*), the monomer may be partially rejected. There has been one report (*22*) of the use of MEUF as an industrial separation technique. Solute rejections up to 95% were reported in that study.

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GENERAL CONSIDERATIONS

We discuss here the major factors that need to be considered systematically in applying MEUF. Some of these factors are:

(a) Solubilization capacity for solute
(b) Maximum acceptable UF pore size to reject micelles
(c) Surfactant monomer concentration under conditions of interest
(d) Maximum surfactant concentration attainable under expected conditions before phase separation problems become prohibitive
(e) Concentration polarization of the surfactant–solute mixture

These factors will be discussed sequentially.

Solubilization Capacity

The solubilization capacity of the micelles for a given solute will depend upon the solubilization location in the micelle, and therefore on the specific nature of the solute and surfactant. One effect that is commonly observed is that the solubilization capacity on a molar basis increases as the surfactant hydrocarbon chain length increases (*8*).

UF Pore Size

It is desired to form large micelles so that large membrane pore diameters can be used (to permit high flow rates) while still rejecting micelles. The aggregation number and micelle effective diameter can vary greatly among surfactants having different structures. For example, a Nuclepore 5000 dalton molecular weight cut-off ultrafiltration membrane will reject micelles of nonylphenol polyethoxylate with ten ethylene oxide units, but it will not completely reject micelles of sodium dodecylbenzene sulfonate. A 1000-dalton cut-off membrane rejects both types of micelles. It is important to note that the solubilization of solute in micelles can swell the micelle (*9, 10, 23–25*). Therefore, a micelle that might leak through a given membrane in the absence of solute may be retained in a MEUF process. Other variables can also influence micelle size; for example, added salts may increase the micelle aggregation number (*26*). This effect probably accounts for the observation that the addition of electrolytes in MEUF increases rejection of the surfactant (*22*).

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Surfactant Monomer Concentration

It is desirable for the concentration of monomeric surfactant to be quite small (relative to the micelle concentration) so that the total concentration of surfactant in the permeate will be a minimum. Nonionic surfactants generally have smaller CMC values than ionic surfactants (*5, 9, 26*), because the micelles of the nonionic compounds lack electrostatic repulsion forces. The addition of methylene groups to surfactants in general reduces the CMC of both nonionic and ionic surfactants (*9*).

Phase Changes

If the surfactant micelles are completely rejected, an obvious way to increase the rejection of solute in MEUF is to decrease the concentration of the unsolubilized organic molecules. This may be accomplished by increasing the surfactant concentration; however, a physical limitation is that at high concentrations, surfactant solutions may undergo a phase change, so that the system will no longer be isotropic. For example, ionic (*8*) or nonionic (*23*) surfactants may form liquid crystals, and nonionic surfactants (*23*) may undergo phase separation as the surfactant concentration increases. The temperature range at which the process takes place is also crucial. The process must operate above the Krafft temperature (*5, 24*) (where the surfactant forms solid hydrates) for ionic surfactants and below the cloud point (*24, 27*) (where phase separation can occur) for nonionic surfactants. It may be difficult to meet these requirements in the MEUF process, because the solute can affect the surfactant concentration and the temperatures at which these transformations occur. For example, organic solutes may lower the cloud point of nonionic surfactants (*23*).

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Concentration Polarization

In traditional ultrafiltration, the flux rate is often limited by the formation of a gel layer next to the membrane (concentration polarization) (*1*). In the gel layer, the rejected species (solute and surfactant) exist at higher concentrations than in the bulk retentate. Obviously, gel layer formation is deleterious to the process and conditions (such as high shear at the membrane interface) need to be sought to avoid gel layer formation and to minimize its impact. One difficulty encountered in the ultrafiltration of biological materials is degradation at high shear rates (*3, 28*). No such limitation will exist in the present application, so high shear rates using thin channel ultrafiltration, high cross flows, or high stirrer speeds (agitation) can eliminate gel formation as a problem.

SELECTION OF MODEL SYSTEM

Considering the factors just discussed, we may describe a procedure for choosing an optimum surfactant for the model solute. The discussion should also provide insight into the development of general guidelines for surfactant selection.

The model solute selected for the present study is 4-tert-butylphenol (TBP), a representative of the class of phenolics. The phenolics are major pollutants in chemical, synfuel, and petroleum process wastewater streams.

Three major categories of surfactants are considered: nonionic, anionic, and cationic.

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Nonionic Surfactants

The nonionic surfactants considered here are polyethoxylated alkylphenols or alcohols. The possible advantages of using nonionic rather than ionic surfactants are that the nonionics have very low CMC values and their micelles are quite large, thus permitting the use of very high molecular weight cut-off ultrafiltration membranes (and consequently higher flux rates).

We have observed that very stable macroemulsions form upon mixing nonionic surfactants with a variety of compounds, including TBP, so that their use in the present MEUF application was precluded. Another problem was that the nonionic surfactants have much larger molecular weights than the ionic compounds. For example, a nonylphenol polyethoxylate with ten ethylene oxide units has a molecular weight about double that of a typical ionic surfactant. One may expect that solubilization of many solutes will increase in nonionic micelles owing to the presence of the ethylene oxide chains. However, in the absence of strong specific interactions between the solute and the ethylene oxide, the ratio of the extent of solubilization achieved with the nonionic surfactant to that obtained with the ionic surfactant will not be as great as the ratio of the surfactant molecular weights. Therefore, because surfactants are sold on a weight basis, the use of ionic surfactants in MEUF should be economically favorable in comparison with nonionics.

In general, the apparent advantages of a low CMC and larger micelles are outweighed by the disadvantages. Ethoxylated nonionic surfactants should only be considered for use in MEUF if the presence of the ethylene oxide groups will greatly increase solubilization of the organic solute. Other nonionics (e.g., alkanolamides) may find more general use in MEUF, but the only major potential advantage of these surfactants would appear to be their low CMC values.

Anionic Surfactants

Sodium dodecylbenzene sulfonate was studied as a model anionic surfactant. The micelles formed were found to be rejected by a 1000-dalton cut-off membrane, but not by a 5000-dalton cut-off membrane. A simple way to increase micelle size, to lower the CMC, and to increase solubilization capacities is to increase the length of the alkyl chain of the surfactant (*4*). However, anionic surfactants having longer hydrocarbon chains tend to undergo phase transitions more readily. The Krafft temperature of ionic surfactants increases with increasing alkyl chain length (*29–32*), signaling an increasing tendency to precipitate. As a result, if sodium alkylbenzene sulfonates or sodium alkyl sulfonates were to be used in MEUF at room temperature, it would probably be necessary to limit alkyl chain lengths to no more than 12 carbons in order to avoid these problems. Therefore, considering only molecules with acceptable Krafft temperatures, the disadvantages of using anionic surfactants in MEUF are their small micelle size, high CMC, and relatively low solubilization capacity.

Cationic Surfactants

Cationic surfactants have much lower Krafft temperatures than anionic surfactants of the corresponding alkyl chain length. For example, we have determined that the Krafft temperature for hexadecylpyridinium chloride (CPC) is 10.8°C. A typical anionic surfactant having a hydrophobic group of the same size would have a Krafft temperature greater than 50°C. As a result, high molecular weight cationic surfactants, having large micelles, can be used at room temperature. These surfactants will also have low CMC values and large solubilization ratios with typical organic solutes.

Another advantage in using cationic surfactants to remove arenes (such as TBP) from water is the increased solubilization in the cationic micelles arising from attractive forces between the aromatic ring and the positively charged head groups (*33, 34*). Therefore, after considering the most important criteria involved in surfactant selection, we conclude that the cationic surfactants will be the best candidates for general use in MEUF. The cationic chosen for study here is CPC. The phase boundaries occurring in the system used and the concentration polarization characteristics will be shown to be quite acceptable, further strengthening arguments that these compounds will be the best class of surfactants for use in MEUF.

EXPERIMENTAL

Materials

The 4-tert-butylphenol (TBP) was obtained from Aldrich Chemical Company and purified by recrystallization from hexane, redissolved in about 15–20 mL ethanol per 50 g of solute, and recrystallized by addition of water. The purity of the final product was verified by high performance liquid chromatography (HPLC). The hexadecylpyridinium chloride mono-

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hydrate (CPC) was obtained from Hexcel Corpation. Its purity was also confirmed by HPLC and by the lack of a minimum in the surface tension vs concentration curve; hence it was used as received. Water used in all of the experiments was distilled and deionized.

Ultrafiltration Runs

The ultrafiltration experiments were carried out in Nuclepore 400 mL batch-stirred cells, wrapped with tubing containing circulating water for temperature control. Pressure was maintained by nitrogen gas and stirrer speed was measured with a strobe light. The temperature and pressure were 30°C and 414 kPa gauge, respectively, for all runs. The membranes were Nuclepore anisotropic cellulose acetate, 76 mm diameter, 1000 dalton molecular weight cut-off UF membranes having an effective area of 3848 mm^3. They were soaked overnight in the feed solution to saturate the pores before the ultrafiltration runs were started. The cell was initially filled with 300 mL of feed solution. The permeate flux was measured and samples were taken periodically throughout the run. Data from the first few samples were disregarded because the sample contained residual fluid from the membrane pre-soak. A run was terminated before the stirrer-induced vortex reached the membrane (or after about 200 mL of permeate had been collected). TBP concentrations were determined using HPLC with ultraviolet detection (at 225 nm). CPC concentrations were determined by HPLC, using a conductivity detector. The retentate composition corresponding to the permeate concentration at any time was calculated by a material balance and double-checked by analysis of the retentate at the end of a run. The flux rate is reported here as a relative flux (i.e., the ratio of the observed flux to the flux of water alone under the same conditions). Under the conditions of the experiment, the flux of water only was measured to be $34.5\ L/h \cdot m^2$.

Semiequilibrium Dialysis

In order to determine the concentrations of CPC and TBP that would be expected to transfer through filtration membranes under near-equilibrium conditions, we have used a new experimental technique (*35*), given the name "Semi-Equilibrium Dialysis" (SED). Ordinary commercial 5-mL equilibrium dialysis cells (Fisher Scientific) were used to determine the concentrations of CPC passing through a cellulose acetate dialysis membrane (~6000 dalton molecular weight cut-off) at times varying from

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a few minutes to more than 24 h. Initial concentrations of CPC varying from 0.01 to 0.68 *M* were placed on one side of the membrane, and pure water was added to the other side; the apparatus was thermostatted at 25°C. Concentrations of CPC were determined conductimetrically or by measuring the ultraviolet absorbance at approximately 258 nm. In several experiments, TBP was initially present along with the CPC. A nearly constant concentration of either CPC or TBP appears to be reached within 16 to 24 h in the SED experiments. The CPC concentration is a quasi-equilibrium quantity, corresponding approximately to the mean ionic molality of the unassociated CPC, as inferred from vapor pressure osmometry measurements (*36*). The TBP concentration after 16–24 h may be considered to be very nearly an equilibrium value. The difference between the concentrations of TBP on the two sides of the SED cell (determined by ultraviolet spectral analysis) may be equated to the concentration of TBP in the micellar species in the concentrated TBP/CPC solution.

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Viscosity

Viscosities of simulated retentate solutions were measured with Cannon-Fenske Routine Viscometers (Induction Lab Glass Co.) at 30°C.

Phase Boundaries

The phase boundary concentration values were determined by visual observation of phase separation occurring when incremental amounts of CPC or TBP were added to isotropic solutions of known composition at 30°C.

RESULTS

Phase Boundary

The retentate solution in MEUF runs should be isotropic to prevent membrane fouling. Therefore, the minimum rejected species concentrations at which anisotropic phase behavior (phase boundary) occurs correspond to the theoretical maximum retentate concentrations in MEUF. The phase boundary curve determined for the CPC/TBP system is shown in Fig. 2.

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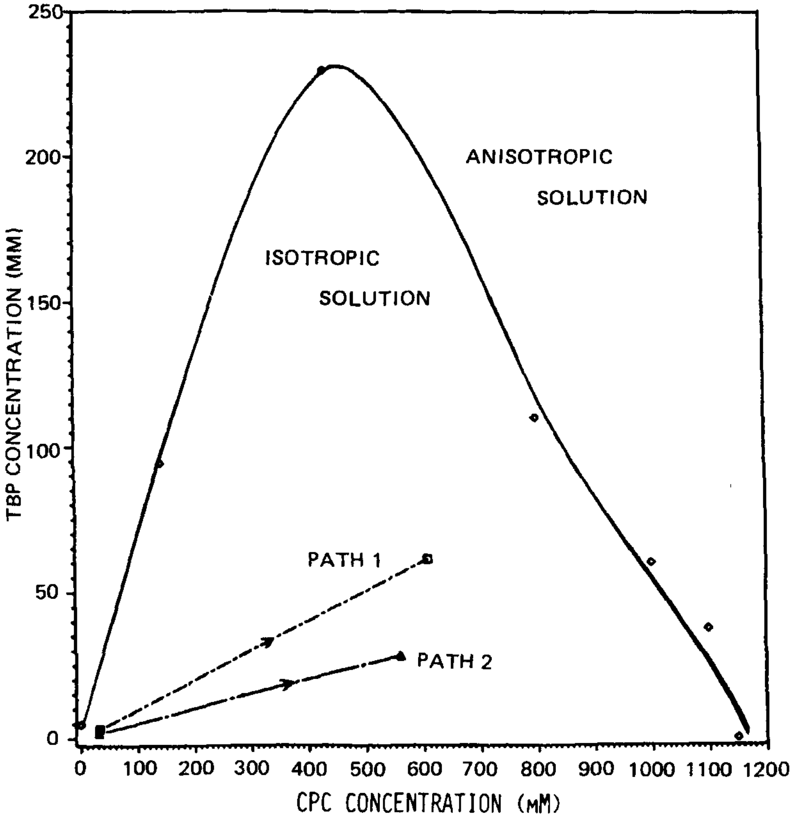

FIG. 2. CPC-TBP system phase boundary.

The boundary corresponds to separation of two liquid phases, except for the solutions containing nearly pure CPC or nearly pure TBP, for which precipitation occurs when the solution becomes anisotropic.

Concentration Polarization

Because the solute is being rejected at the membrane, its concentration will be greater near the membrane surface than in bulk solutions (concentration polarization) (*1*, *3*). This "gel layer" of high solute concentration reduces flux rates (*2*, *3*) and diminishes solute rejection (*1*). In

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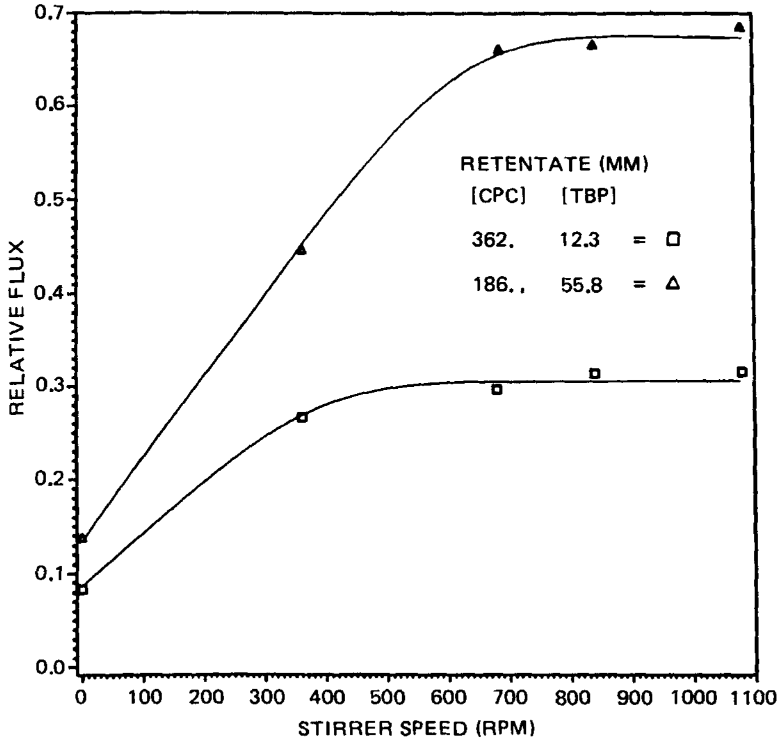

FIG. 3. Relative fluxes demonstrating concentration polarization effects.

a stirred cell, concentration polarization is controlled by using a stirring bar spinning at high speed next to the membrane surface. In Fig. 3, the relative flux is shown as a function of stirrer speed for two retentate compositions; as the speed decreases, a point is ultimately reached where the flux declines sharply, indicating the formation of a gel layer. After examining data like these, we decided to use a stirrer speed of 840 rpm in the MEUF experiments to be described here; this rate of stirring is great enough to prevent concentration polarization from becoming a significant factor under the stated conditions.

Semiequilibrium Dialysis

The concentrations of CPC in the permeate solutions in SED cells are given in Table 1, corresponding to 18-h dialysis experiments. The molarity

TABLE 1
CPC Concentrations from Semiequilibrium Dialysis

Retentate CPC concentration (M)	Permeate CPC concentration (mM)
0.00905	0.95
0.0440	1.05
0.0919	1.15
0.269	1.40
0.458	1.55
0.678	1.70

of CPC in the permeate increases gradually as the concentration of CPC on the high-concentration (retentate) side of the cell increases.

In the MEUF experiments described here, the unsolubilized TBP remains at quite low concentrations (both in the retentate and in the permeate). The CMC of the CPC solutions is not greatly affected by the presence of the TBP under these conditions (*37*). For this reason, the results in Table 1 should be relevant in interpreting all of the ultrafiltration data.

SED was also used to determine the concentration of unsolubilized TBP in the permeate, in equilibrium with several solutions of CPC and TBP having compositions falling within the isotropic solution region (see Fig. 2). From a number of SED experiments, the value of K, the distribution or solubilization constant defined by Eq. (1), was found to be 1350 ± 100 M^{-1}; K was nearly constant throughout the range of concentrations of CPC used in the MEUF experiments.

The SED experiments were performed at 25°C, but these results will be compared to ultrafiltration runs made at 30°C. The monomer–micelle equilibrium [as indicated by the CMC (*38*)], and therefore the CPC mean ionic molality, varies little with temperature for ionic surfactants in this temperature range, and the distribution constant has also been shown to be nearly constant for similar organic solute–ionic surfactant systems (*39*). Therefore, the permeate CPC and TBP concentrations at 25°C are expected to be nearly the same as at 30°C.

Ultrafiltration

In practical applications of MEUF, the surfactant would be added to the feed stream containing the dissolved solute. This feed stream would then be treated in a batch UF unit or treated by continuous membrane devices

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(such as hollow fiber or spiral-wound UF). As the permeate is removed, the retentate solution becomes more concentrated in the rejected compounds, varying between the feed stream composition and that of the product retentate emitted from the unit. As the retentate changes composition as a function of time in a batch unit, or as a function of position in a continuous unit, it follows a "path." This path, or concentration curve for the dissolved species in the retentate during MEUF, will depend (for a given membrane and operating conditions) on the surfactant and solute concentrations in the feed.

In this study, a batch (stirred cell) experimental unit was used. However, the resulting differential flux and permeate concentration data, measured as a function of retentate composition, can be integrated to calculate the total membrane area required and the average permeate concentrations that would be obtained in a continuous unit, for treatment of a feed stream having a known recycle ratio (permeate/feed) and a specified flow rate. Because only a limited permeate/feed ratio could be attained in a single batch run, several runs were made to follow a given path throughout a wide range of conditions.

Two paths were studied in detail in the present research. The initial retentate or feed composition for each path were:

Path	[CPC]	[TBP]
1	31.9 m*M*	3.19 m*M*
2	31.6 m*M*	1.58 m*M*

The feeds correspond to streams containing different CPC/TBP ratios. The paths were followed until the retentate became so viscous that fluxes were quite low.

The CPC and TBP concentrations in the permeate and retentate, and relative fluxes are shown for Path 1 in Table 2 and for Path 2 in Table 3. The variation in TBP concentration with CPC concentration in the retentate along both paths is shown in Fig. 2. It can be seen that the retentate remained well within the phase boundaries for both paths.

Viscosity

Viscosities of the retentate solutions for Path 1 are given in Table 2.

DISCUSSION

Before giving a detailed discussion of the results, we may offer some general comments regarding them. From Tables 2 and 3, it appears that the

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TABLE 2
Ultrafiltration Results for Path 1

Retentate concentration (m*M*)		Permeate concentration (m*M*)		Rejection (%)		Relative flux	Viscosity (cP)
TBP	CPC	TBP	CPC	TBP	CPC		
3.19	31.9	0.0751	0.568	97.6	98.2	0.903	
3.33	33.3	0.0779	0.568	97.7	98.3	0.925	
3.52	35.2	0.0808	0.528	97.7	98.5	0.936	
3.73	37.3	0.0808	0.528	97.8	98.6	0.949	1.3
3.96	39.7	0.0791	0.548	98.0	98.6	0.928	
4.22	42.3	0.0762	0.598	98.2	98.6	0.915	
4.52	45.3	0.0794	0.608	98.2	98.6	0.914	
4.86	48.6	0.0832	0.608	98.3	98.7	0.883	
5.24	52.5	0.0802	0.608	98.5	98.8	0.877	1.1
5.68	56.9	0.0842	0.628	98.5	98.9	0.868	
6.21	62.2	0.0793	0.648	98.7	99.0	0.858	
6.83	68.5	0.0788	0.628	98.8	99.1	0.842	
7.57	75.9	0.0845	0.658	98.9	99.1	0.826	
8.47	85.0	0.0791	0.708	99.1	99.2	0.812	1.4
10.2	102	0.0645	0.768	99.4	99.2	0.781	
10.8	108	0.0698	0.768	99.4	99.3	0.769	
11.4	114	0.0684	0.848	99.4	99.2	0.759	1.5
12.1	120	0.0745	0.778	99.4	99.4	0.733	
12.8	128	0.0701	0.828	99.4	99.4	0.714	
13.6	136	0.0728	0.828	99.5	99.4	0.696	
14.5	145	0.0770	0.828	99.5	99.4	0.681	
15.5	155	0.0747	0.848	99.5	99.4	0.664	1.5
16.9	168	0.0735	0.828	99.6	99.5	0.637	
18.4	184	0.0781	0.828	99.6	99.6	0.607	1.7
20.2	202	0.0744	0.818	99.6	99.6	0.573	
22.3	222	0.0755	0.868	99.7	99.6	0.537	
25.0	249	0.0750	0.888	99.7	99.6	0.489	1.8
26.9	269						2.2
30.1	301	0.0866	2.37	99.7	99.2	0.409	2.4
31.8	317	0.0973	2.31	99.7	99.3	0.385	2.6
33.4	333	0.101	2.28	99.7	99.3	0.338	2.5
35.2	351	0.104	2.44	99.7	99.3	0.304	2.6
37.2	371	0.118	2.63	99.7	99.3	0.273	
39.5	394	0.155	2.65	99.6	99.3	0.239	2.9
42.1	420	0.163	3.19	99.6	99.2	0.202	
44.9	448	0.182	3.22	99.6	99.3	0.165	3.7
48.0	478	0.245	4.01	99.5	99.2	0.127	
51.6	514	0.355	4.90	99.3	99.0	0.0868	5.4
55.4	552	0.642	8.55	98.8	98.4	0.0483	
58.8	585	1.48	19.2	97.5	96.7	0.0213	5.9
61.1	608	3.50	40.7	94.3	93.3	0.00948	

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TABLE 3
Ultrafiltration Results for Path 2

Retentate concentration (m*M*)		Permeate concentration (m*M*)		Rejection (%)		
TBP	CPC	TBP	CPC	TBP	CPC	Relative flux
1.58	31.6	0.0344	0.568	97.8	98.2	0.887
1.67	33.4	0.0346	0.558	97.9	98.3	0.892
1.78	35.5	0.0369	0.568	97.9	98.4	0.894
1.91	38.2	0.0387	0.568	98.0	98.5	0.856
2.06	41.2	0.0386	0.568	98.1	98.6	0.847
2.24	44.8	0.0369	0.578	98.4	98.7	0.845
2.44	49.0	0.0404	0.568	98.3	98.8	0.840
2.69	54.0	0.0379	0.588	98.6	98.9	0.823
3.00	60.0	0.0368	0.588	98.8	99.0	0.818
3.36	67.5	0.0404	0.608	98.8	99.1	0.793
3.83	76.8	0.0318	0.618	99.2	99.2	0.782
4.58	91.4	0.0291	0.768	99.4	99.2	0.802
4.85	96.9	0.0313	0.748	99.4	99.2	0.798
5.16	103	0.0333	0.738	99.4	99.3	0.784
5.49	110	0.0321	0.758	99.4	99.3	0.758
5.85	117	0.0331	0.758	99.4	99.4	0.726
6.32	126	0.0344	0.748	99.4	99.4	0.723
6.84	136	0.0358	0.768	99.5	99.4	0.689
7.42	148	0.0338	0.808	99.5	99.4	0.662
8.11	162	0.0342	0.808	99.6	99.5	0.650
8.89	178	0.0331	0.828	99.6	99.5	0.624
9.89	197	0.0341	0.848	99.6	99.6	0.578
11.3	226	0.0360	0.858	99.7	99.6	0.548
14.1	282	0.0414	1.42	99.7	99.5	0.446
14.9	297	0.0533	1.45	99.6	99.5	0.399
15.7	313	0.0453	1.46	99.7	99.5	0.372
16.6	332	0.0514	1.80	99.7	99.4	0.341
17.6	350	0.0515	2.18	99.7	99.4	0.310
18.8	374	0.0642	2.02	99.6	99.4	0.277
20.2	402	0.0700	2.21	99.6	99.4	0.237
21.7	433	0.0895	3.21	99.6	99.2	0.193
23.5	468	0.109	3.38	99.5	99.3	0.147
25.6	510	0.153	4.46	99.4	99.1	0.0968
28.1	559	0.364	9.29	98.7	98.3	0.0442

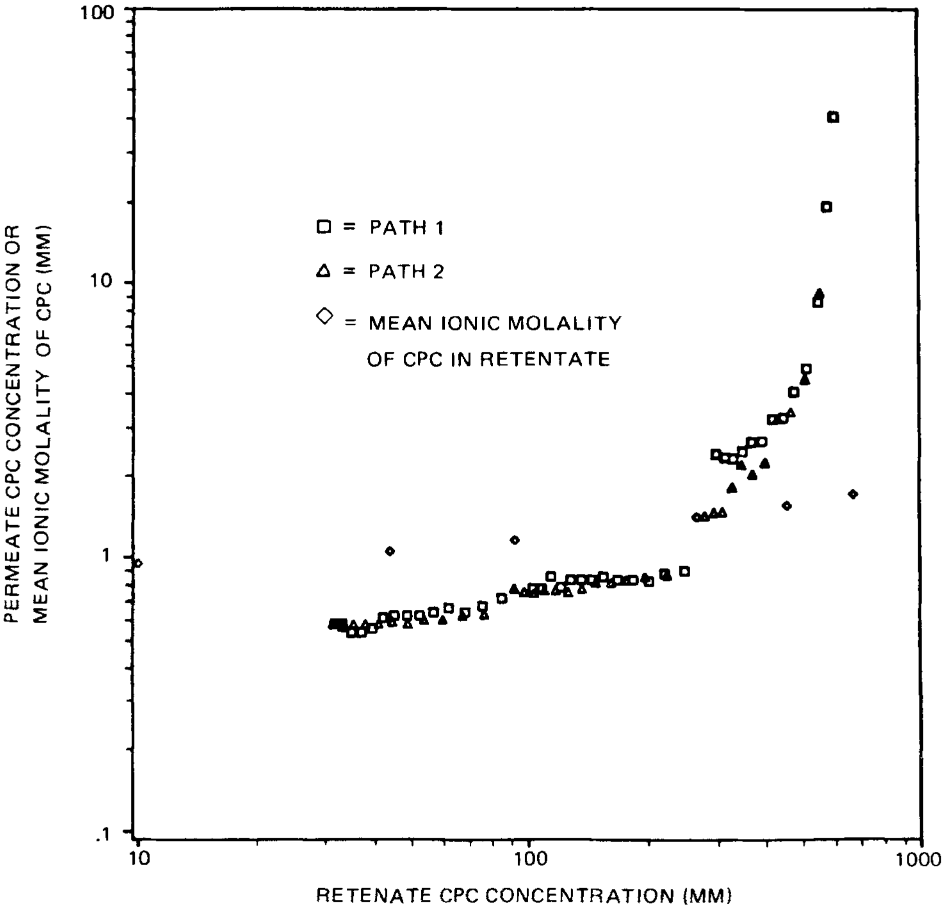

FIG. 4. Permeate CPC concentrations and mean ionic molality of CPC.

rejection of both TBP and CPC remains high under all conditions for both paths, reaching a value as great as 99.7% for TBP and 99.6% for CPC. These results alone clearly indicate the technical feasibility of MEUF in systems such as the present one.

Rejection of Solute and Surfactant

The concentration of CPC in the permeate is plotted vs the CPC concentration in the retentate for both paths in Fig. 4. The monomer

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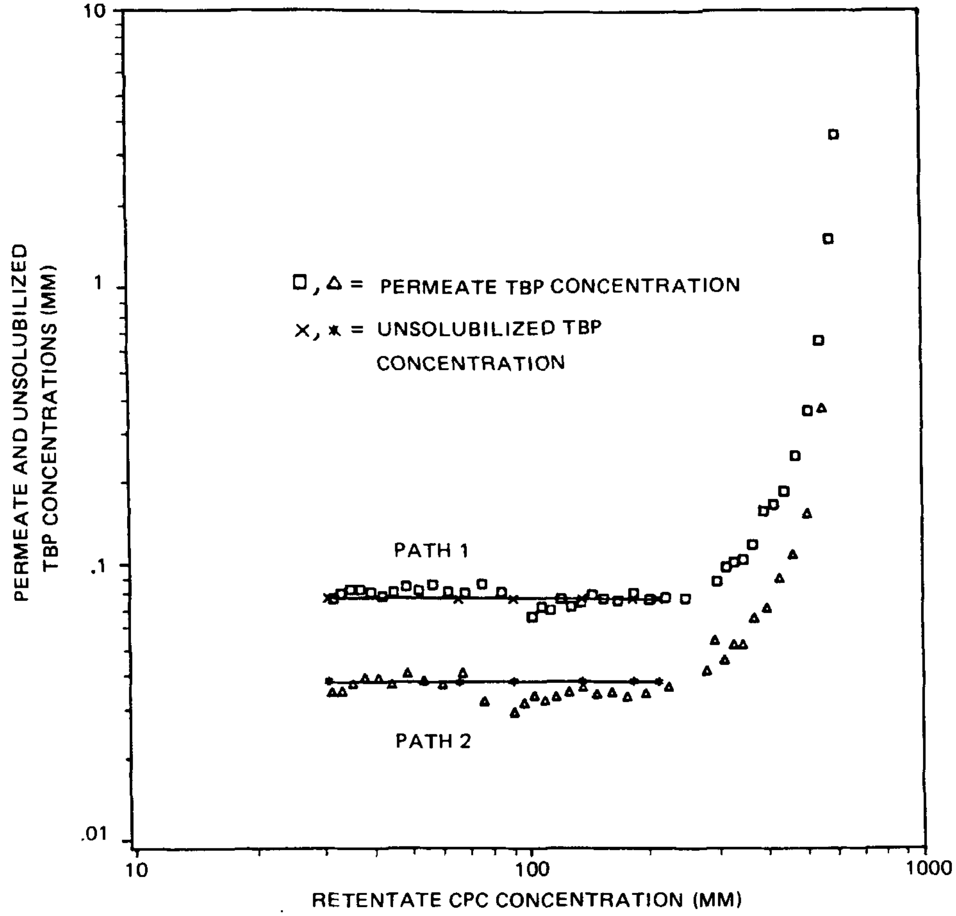

FIG. 5. Permeate and unsolubilized TBP concentrations.

concentration in the permeate in the SED experiments (in the absence of TBP) is shown for comparison. In the MEUF experiments, at retentate concentrations below about 0.25 *M*, the CPC concentrations vary from about half to two-thirds of the value of the permeate concentrations determined from SED experiments. If there were complete rejection of micelles and no hindrance of the monomer, the permeate CPC concentration would approximately equal that measured in the SED experiments. These results taken together provide clear indication that ***micelles are essentially completely rejected and that monomer hindrance is a significant*** *factor in the MEUF experiments under the conditions used.* At the retentate CPC concentrations used here, only a very small fraction of the surfactant exists as monomer; most of the surfactant is in micelles having aggregation numbers on the order of 100 (*36*). This explains the high rejections of CPC in the MEUF experiments (Tables 2 and 3). The situation that results when there are very high concentrations of CPC in the retentate are discussed later.

The permeate TBP concentration is plotted as a function of retentate CPC concentration for the two paths in Fig. 5, along with results from the SED experiments. As was the case with CPC, if the highly concentrated CPC retentate regions are avoided, the TBP permeate concentration remains quite low, nearly independent of retentate composition. Under these conditions, the permeate concentration of TBP is equal to that of unsolubilized TBP in the retentate as inferred from the SED experiments (within experimental error); therefore, there is no significant hindrance of the unassociated TBP molecules during passage through the membrane. Because TBP is a much smaller molecule than CPC (molecular weight 150 vs 340 daltons), and because it possesses no electric charge, it is reasonable that TBP should be less hindered in UF experiments than the surfactant. Previous workers have also observed that the solute concentration in the permeate (in MEUF experiments) equals the concentration of the unsolubilized solute in the retentate (*12, 13*).

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We have already remarked that only a very small fraction of the TBP molecules in the retentate are unsolubilized; most of the solute exists in micellar aggregates, and this explains why such high TBP rejections are observed (Tables 2 and 3). As the ultrafiltration proceeds and the retentate becomes more concentrated in both TBP and CPC, the molar concentration of micelles increases. However, if the solubilization constant (K in Eq. 1) does not vary along the given path, the concentration of unsolubilized TBP should remain nearly constant. Experimental values of the TBP concentration obtained from the MEUF runs are in quite good agreement with the values predicted from the equilibrium results, except at the large CPC concentrations. Therefore, as the retentate becomes more and more concentrated in the rejected species, *the percentage of rejection actually increases* (see Tables 2 and 3), in marked contrast with normal ultrafiltration results.

Flux Rates

The relative flux rates are shown in Fig. 6 for the two paths, along with retentate viscosities for Path 1. As the retentate becomes more con-

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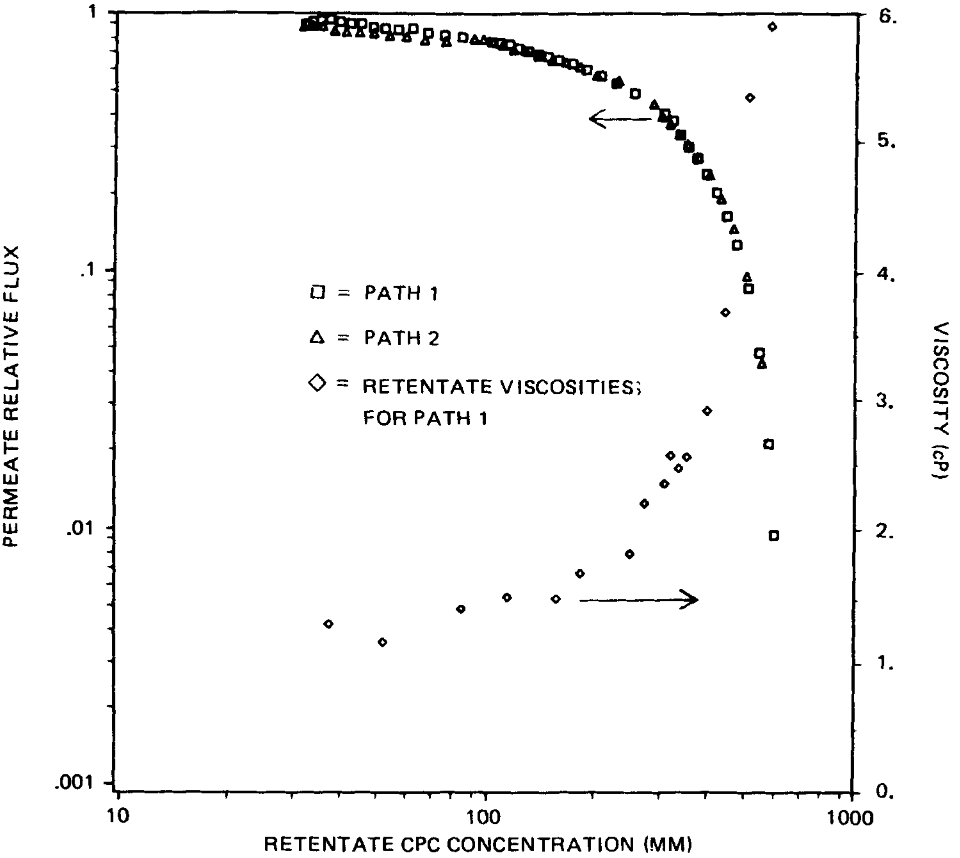

FIG. 6. Relative flux rates and retentate viscosities.

centrated in the rejected species, the flux declines slowly until the CPC concentration reaches about 0.25 *M*, at which point the flux starts to decrease very rapidly. Figure 6 shows that the decline in flux occurs concomitantly with an increase in retentate viscosity. Therefore, in order to avoid low flux rates, the highly viscous solutions obtained at high CPC concentrations should be avoided. The coincidence of flux data for Paths 1 and 2, for differing TBP concentrations at the same CPC concentrations, indicate that the surfactant concentration, not the solute concentration, controls the solution viscosity and the flux rates.

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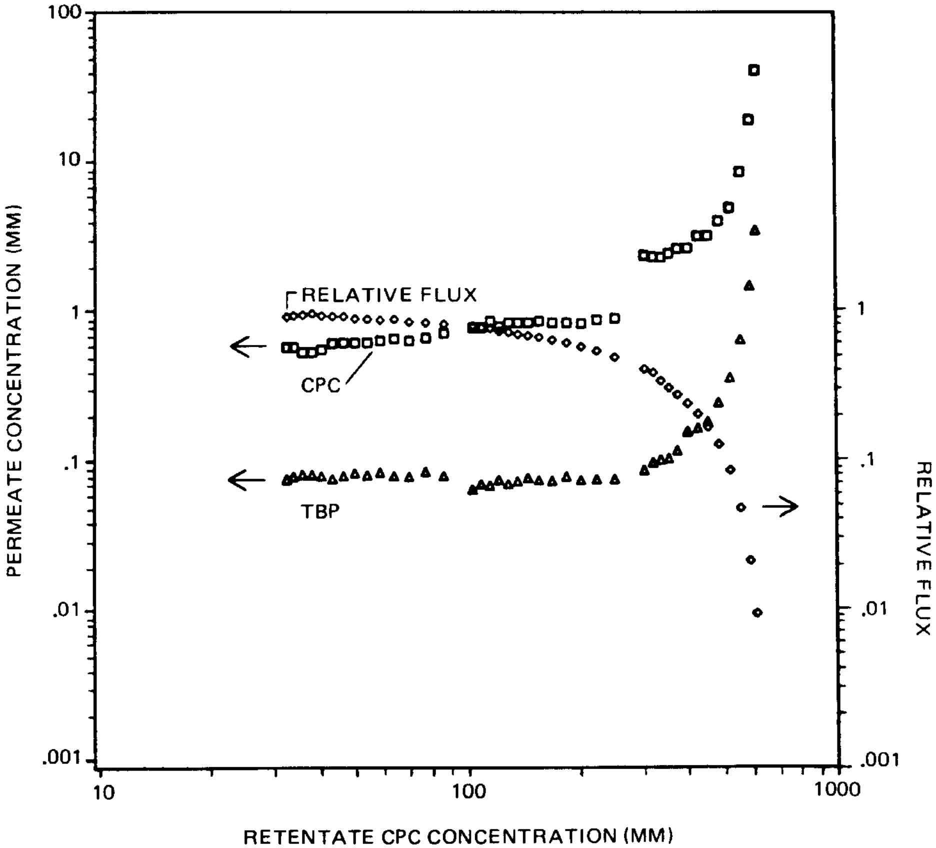

FIG. 7. Permeate composition and relative flux for Path 1.

MEUF of Concentrated Solutions of CPC and TBP

The permeate concentrations and fluxes for Path 1 are given in Fig. 7 and analogous results for Path 2 are shown in Fig. 8. The CPC and TBP permeate concentrations start to increase rapidly at about the same CPC concentration (~0.25 *M*) on each path. As the surfactant concentration in solution increases, the micelles may change their size and shape, and in many surfactant systems this change may be from nearly spherical micelles to rodlike aggregates. In some cases, lamellar or cylindrical structures are

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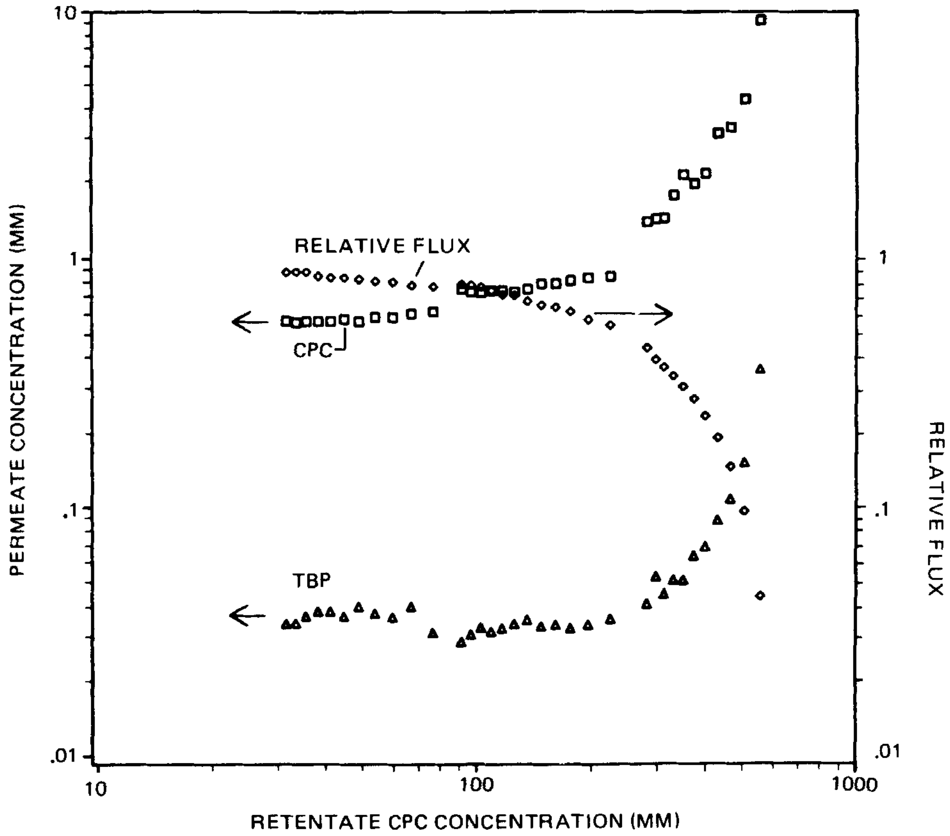

FIG. 8. Permeate composition and relative flux for Path 2.

thought to form. However, these micelles should in general have cross-sectional areas at least as large as those of the spherical micelles that presumably exist at low surfactant concentrations.

We suggest that the increased concentrations of both TBP and CPC in the permeate at the higher CPC concentrations reflect the presence of aggregates ("*n*-mers") having much smaller molecular weights than the predominant CPC micellar species. These oligomers (e.g., dimers, trimers, etc.) may be expected to form in greater concentrations as the total molar concentration of CPC in the retentate (and hence its mean ionic activity) increases. Some TBP may be expected to solubilize in the *n*-mers, and a fraction of these mixed aggregates may be expected to leak through the membrane, contributing to the observed increased concentrations of CPC and TBP in the permeate.

If the increased concentrations of CPC and TBP in the permeate at high retentate concentrations are due to *n*-mer formation, the data shown in Figs. 7 and 8 may be used to calculate the average ratio of TBP to CPC in the leaking *n*-mers.

	TBP/CPC mole ratio	
	n-Mers	Micelles
Path 1	0.089	0.10
Path 2	0.041	0.050

The *n*-mers are not expected to provide as favorable an environment for the solubilization of TBP as do the larger micelles; therefore, the lower molar ratio (TBP/CPC) in the *n*-mers is quite reasonable. The results support the claim that micellar leakage does not account for the decrease in rejection of CPC and TBP, because the transfer of micelles through the membrane would cause the molar ratio of TBP to CPC in the permeate to approach that in the micelles in the retentate.

Figure 4 indicates that the CPC concentration in the permeate starts to increase rapidly at about the same retentate CPC concentration for both paths, even though the TBP concentration is quite different. This indicates that the TBP molecules have little effect on the formation of the *n*-mers. Therefore, the retentate CPC concentration limits the extent to which a solution of the organic solute can be concentrated (in MEUF) before *n*-mer formation causes poor rejection and the viscosity increase induces poor flux. Practically, the use of MEUF at CPC concentrations greater than about 0.25 *M* would not be effective for the present system.

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Summary of Performance of MEUF

Let us now consider the use of MEUF to treat the feed streams used in Path 1 and Path 2, continuing until the CPC concentration in the retentate reaches 0.25 *M*. Integration of the data from Tables 2 and 3 allows calculation of the composition of the overall permeate stream emitted from such a process, as well as the membrane area required per unit volume of feed processed. The applicable results are listed in Table 4.

Path 1 corresponds to using a smaller surfactant to solute ratio than Path

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TABLE 4

Application of MEUF for Treatment of a Process Stream

	Initial feed (m*M*)		Overall permeate (m*M*)		Final retentate (m*M*)		Overall rejection (%)		Membrane area[a] (m^2/(L feed)/h)	Permeate/feed ratio (L/L)
	[TBP]	[CPC]	[TBP]	[CPC]	[TBP]	[CPC]	TBP	CPC		
Path 1	3.19	31.9	0.077	0.860	25.0	250	99.69	99.66	0.0328	0.872
Path 2	1.58	31.6	0.035	0.782	12.5	250	99.72	99.69	0.0343	0.874

[a] For comparison, if water only were being treated under these conditions with this recycle ratio, an area of 0.0253 (m^2/(L feed)/h) would be required.

2. The resultant percent rejections are almost identical for the two paths, but Path 2 has lower solute concentrations in the permeate. Therefore, the amount of surfactant added per unit volume of solution treated represents a trade-off between surfactant cost and permeate purity.

The rejections of both TBP and CPC are extremely high (99.7%). The recycle ratio (permeate to feed) is greater than 87%; this means that the concentrate stream product has less than 13% of the volume of the original stream and the TBP concentration in this concentrate is increased by a factor of 7.8 over that in the feed. The recycle ratio could be made much greater if the feed stream contained smaller concentrations of TBP for the same CPC/TBP concentration ratio. If, for example, the feed concentration of TBP and of added CPC in the feed were both reduced by a factor of 10 on Path 1 and the product retentate composition were still the same as indicated in Table 4 for Path 1, the recycle ratio would be 98.7%. The product permeate would still have about the same composition as shown in Table 4 for Path 1.

The membrane area required to process the stream along Path 1 or 2 is only about 30% greater than that required to ultrafilter water alone. Therefore, fluxes are not greatly reduced by the dissolved species under these conditions. If membranes with larger pore sizes could effectively reject micelles, the fluxes would be even greater, reducing membrane requirements. The study of this variable was not within the scope of the present research.

In conclusion, MEUF has been shown to be technically successful, producing very high rejections, high fluxes, and good recycle rates. MEUF may find wide application in a number of industries where dilute dissolved organics in water streams need to be concentrated. Data such as those reported here will facilitate economic comparisons of MEUF with competitive techniques.

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