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Selection of Surfactants for Micellar-Enhanced Ultrafiltration

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Abstract

The selection of a surfactant is an important issue in designing separations processes based on micellar-enhanced ultrafiltration. The binding of hydrophillic solutes to both ionic and nonionic micelles is considered and shown to be a function of the molecular structure of the surfactants, the concentration of the surfactant, and the electrolyte composition of the water. It is also shown that the passage of micelles is only partly restricted by polycarbonate membranes with 100 Å pores but is effectively restricted by some cellulose acetate membranes. Swelling the micelles by cosolubilizing certain nonpolar compounds was found to only marginally improve the separation efficiency. There appears to be an optimum surfactant molecular structure, but it will not be possible even under the best conditions to completely remove a hydrophilic solute such as phenol in a single stage. Thus, the process will necessarily be multistage.

INTRODUCTION

One of the most pernicious problems confronting separations scientists is the removal of toxic organic material present in small or trace quantities from aqueous solutions. Membrane separation processes, while attractive in principle, are not technically viable. Membranes capable of passing water but rejecting small organic molecules are simply not now available. The process most frequently adopted is fixed-bed adsorption. This procedure is neither selective nor particulary energy efficient. Other alter-

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natives such as distillation or solvent extraction are aparently even more unattractive.

Scamehorn et al. (*1, 2*) recently proposed a process whereby surfactant is added to the water stream. Surfactants self-aggregate to form micelles, and dissolved organic matter will tend to be solubilized into the micelles. Some selectivity is possible because the extent of solubilization will depend on both the structure of the solubilizate and the surfactant. The micellar solution is filtered through a membrane capable of rejecting micelles. The solubilizate is, therefore, also rejected. The retentate contains the rejected organic solubilizate and the surfactant.

Scamehorn et al. (*1, 2*) termed this process micellar enhanced ultrafiltration (MEUF) and demonstrated the technique by recovering 4-*tert*-butylphenol from aqueous solutions. In this case the surfactant used was hexadecylpyrinium chloride and the membranes tested were cellulose acetate with Dalton cutoffs ranging from 1,000 to 50,000. They found that membranes with cutoffs greater than 10,000 were too porous and tend to permit the passage of micelles ("leakage"). At a certain critical surfactant concentration ($\approx$ 225 m*M*) even the 10,000 Dalton cellulose acetate membrane leaked severly. This critical transition was attributed to the formation of surfactant dimers, trimers, etc.

This paper considers the separation of phenol from water using MEUF. Phenol was seleceted because of its relatively strong hydrophilicity and because phenolic materials are highly toxic. Pentachlorophenol is, for example, a highly toxic organic chemical used as a wood preservative which has limited concentrations to provide for the protection of aquatic life (*3*). Several researches have considered removing phenolic compounds by froth flotation techniques (*4, 5*), and MEUF, if successful, would provide a low energy alternative to this or other processes such as adsorption.

Since MEUF processes may provide an attractive economic scheme for selectively removing solutes from water, it is crucial to ascertain the conditions under which the process is optimal. Specifically, one should seek to know the following:

(1) To what extent does a hydrophilic compound such as phenol partition between the aqueous phase and the micellar phase? How is this degree of partitioning related to the molecular structure of the surfactant? What are the limitations on the efficiency of the process?

(2) What are the characteristics of a suitable membrane? What is the maximum pore size that can be permitted and still reject micelles? Does the presence of the solute alter the type of membrane required?

(3) What are the characteristics of a separation process designed to remove phenol from water?

The primary focus of this paper concerns the questions relating to surfactant structure. These are fundamental issues that must be addressed to design successful MEUF systems, but the performance of the membranes cannot really be separated from a discussion of optimal surfactant structures nor can one ignore the characteristics of the overall process.

EXPERIMENTAL

Dodecyltrimethylammonium bromide (DTAB) (Aldrich Chemical Company), sodium dodecylbenzene sulfonate (SDBS) (Alcolac Company), and nonylphenol ethoxylates were used as surfactants. DTAB and SDBS were of 99 and 98% purity, respectively, and were used as received. The nonionic surfactants were of the Igepal CO series manufactured by the GAF Corporation. The particular species used were the CO-880, CO-850, and CO-630 surfactants. These commercial surfactants are polydisperse mixtures with the average number of ethylene oxide units (EON) being 30, 20, and 9, respectively. Reagent-grade phenol (Fisher Scientific) was also used as received. For the tracer diffusion experiments, the radioactive species used was ^{14}C-labeled phenol obtained from ICN Radiochemicals and ^{3}H-labeled sodium *p*(1-propyl nonyl) benzene sulfonate, specially prepared by Ashland Chemical Company. Distilled water was further purified in a Technic Lab Five ion-exchange apparatus.

The YM-5 type and PCTE membranes used in the ultrafiltration study were obtained from Amicon Corporation, Danvers, Massachusetts, and Poretics Corporation, Livermore, California, respectively. The YM-5 membrane had a polymer filter made up of cellulose acetate with a molecular weight cutoff of 5000 and PCTE membranes also had a polymer filter made up of polycarbonate with precise pore sizes (100 Å, 300 Å). The membranes used had a diameter of 76 mm.

Solubility measurements were performed by a titration method in a constant temperature bath. Ten milliliters of surfactant solution was titrated with added phenol and agitated during each titration. Solubility data for this system were determined by visual inspection. Electrical conductivity measurements were made using a Cole-Parmer Model 148100 conductivity meter. The viscosity of the solutions was measured with a Ubbelohde viscometer.

The ultrafiltration runs were carried out in low pressure cells made of Plexiglas, with a capacity of 400 mL. Each cell was equipped with a magnetic stir bar supported above the membrane along with a magnetic stirrer to provide for adequate mixing in the cells. Pressure exerted on the mother liquor was supplied by a nitrogen cylinder, and the effluent was collected at atmospheric pressure. The experiments required pressures of only 2 to 8 psig. The resultant rates of flux across the membrane were fixed at 8×10^{-4} cm/min by adjusting the pressure and did not vary significantly over the course of each experiment or with repaeated use of the membranes. The stirring rate was such that the depth of the vortex was at least a third of the total liquid depth. The collection of filtrates did not begin until 7 h after the start of the experiment in order to eliminate the effect of adsorption of surfactant and phenol molecules on the membrane.

The concentrations of surfactants and phenol in the filtrates were determined by a Beckman Model DU-40 ultraviolet (UV) spectrometer. The concentration of DTAB was measured by UV at a wavelength of 486 nm using the orange II method (*6*). The concentration of CO series surfactants in the absence of phenol was measured by UV at a wavelength of 220 nm, but it was measured by UV at a wavelength of 318.5 nm using the ammonium cobalt thiocyanate method (*7*) in the presence of phenol.

The rejection of micelles, R_j, was calculated from the following equation:

$$R_j\ (\%) = \frac{[C_{ini}] - [C_f]}{[C_{ini}] - [C_{cmc}]} \times 100 \tag{1}$$

where $[C_{ini}]$ is initial concentration of surfactant, $[C_f]$ is concentration of surfactant in filtrate, and $[C_{cmc}]$ is cmc of surfactant.

Tracer diffusion coefficients of labeled species were determined by the Taylor dispersion technique. This experimental apparatus and procedure have been described in detail in our previous papers (*8–10*). All experiments for this study were done at 25°C.

RESULTS AND DISCUSSIONS

Phenol-Surfactant Interactions

Phenol present in an aqueous solution containing micelles is found in essentially two states. A part of the phenol will be molecularly dispersed whereas the remaining part will be associated with micelles. For hydrophilic molecules like phenol, the portion molecularly dispersed will be significant. Since molecularly dispersed phenol will pass through the ultrafiltration membrane together with the water, it is crucial to evalute the molecularly dispersed fraction and to understand how this fraction will vary with surfactant concentration and with the molecular structure of the surfactant.

A second issue of importance is the influence of the phenol on the form and stability of micelles. In particular, it is interesting to compare ionic with nonionic surfactants and to inquire as to which of the different types is best suited for MEUF. The phase boundary of solutions of DTAB, a cationic surfactant, and phenol is shown in Fig. 1. Note that the hydrophilicity of phenol is manifested by its substantial water solubility in the absence of surfactant. Upon increasing the surfactant concentration, the solubility of phenol is correspondingly increased. It is known that the phenol which is associated with the micelles is initally solubilized in the

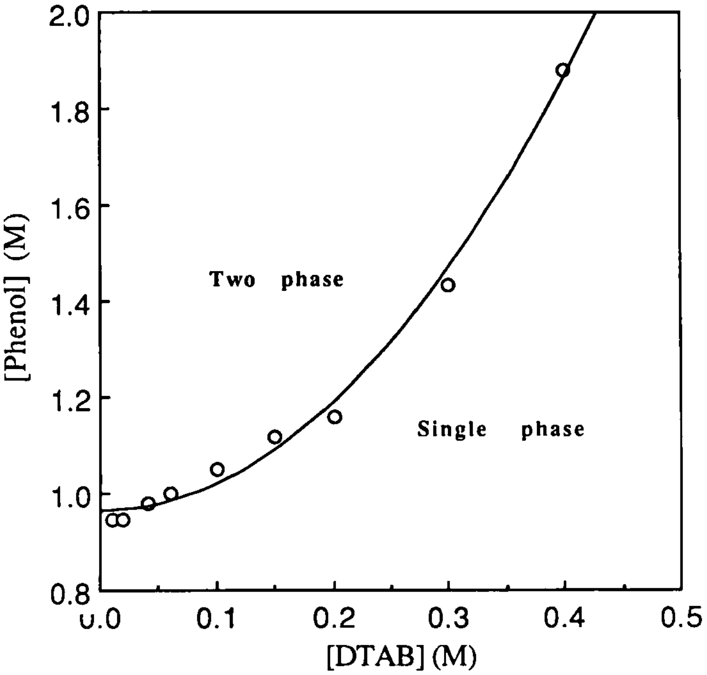


FIG. 1. Solubility diagram of phenol in DTAB micellar solution.

palisade or interfacial region of the micelles as depicted by Fig. 2 (*8*). Phenol will continue to be solubilized into this region until a stoichiometric ratio of one phenol to one surfactant molecule is attained. Once solubilization exceeds this stoichiometric ratio, phenol molecules apparently bind to the outside of the micelle. To accommodate these attached phenol molecules, the micelle tends to become cylindrical in shape (*8*). With any modification of the surfactants, hydrophile which increases the electrostatic free energy contributed when micelles form will likely increase the partitioning of phenol into the micelles (*11*). For example, adding an inorganic salt such as sodium bromide will reduce the electro-

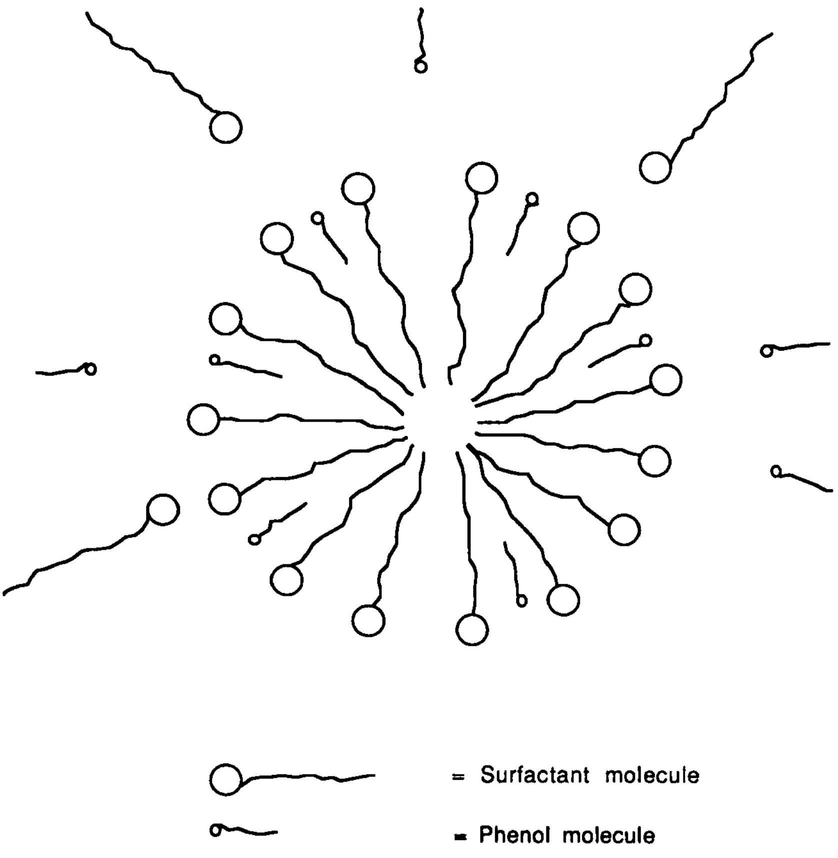


FIG. 2. Micelle in equilibrium with surfactant and phenol monomer. The phenol is bound within the palisade layer.

static free energy and should reduce phenol solubilization. Figure 3 shows that the solubility of phenol is markedly decreased by adding sodium bromide.

The behavior of nonionic surfactants can be contrasted with ionic surfactants. Figure 4 shows the phase diagram for both CO-880 and CO-850. Comparing this phase diagram with Fig. 1, it is seen that nonionic surfactants apparently tend to reduce the solubility of phenol in water. In fact, however, the contray case is true; namely, phenol reduces the solubility of nonionic surfactants. Because phenol binds to the ethylene oxide chain (*9*), it reduces the interaction between water and the ethylene oxide, thereby reducing surfactant solubility. Increasing temperature also decreases hydrogen bonding and tends to depress the solubility. This trend is also shown in Fig. 4.

Phenol binds to nonionic micelles by associating with the ethylene oxide units. One phenol molecule occupies about 5.3 ethylene oxide units at saturation (*9*). Thus, increasing the number of units will increase the number of binding sites that are available at constant surfactant concentration.

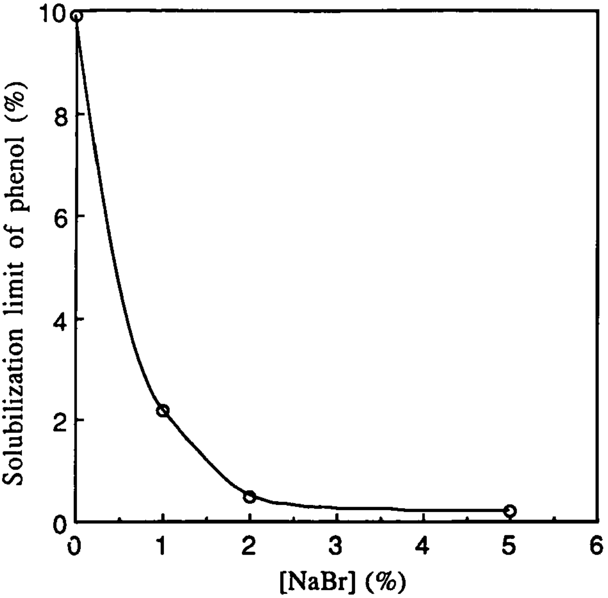


FIG. 3. Effect of NaBr on solubilization limit of phenol: [DTAB] = 0.1 *M*.

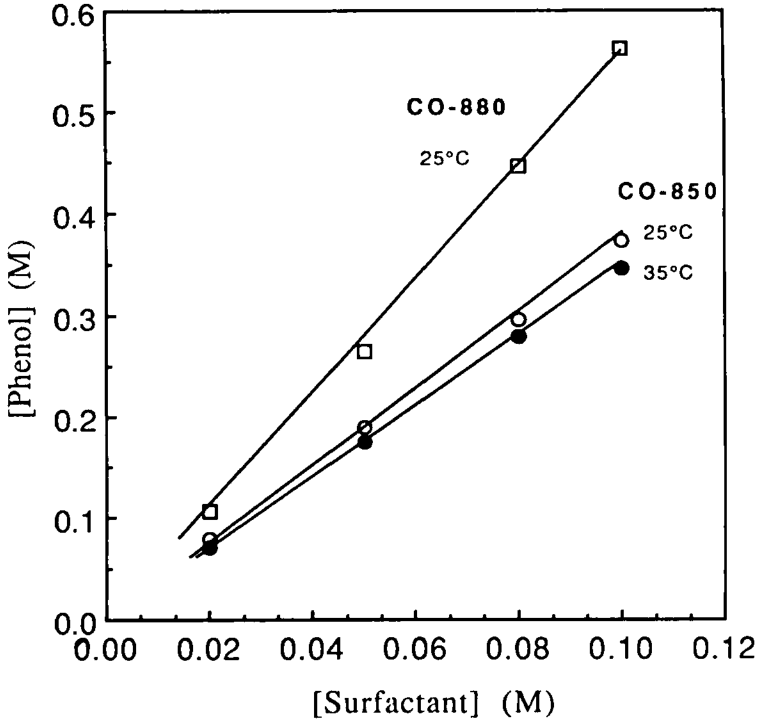


FIG. 4. Solubility diagram of phenol in CO-850 and CO-880 micellar solutions.

The extent to which phenol partitions into micellar phase is defined by Figs. 5 and 6. These are plots of the fraction of the total phenol present in the system that resides in the micelle $(1 - \alpha_p)$ shown as a function of the phenol in the micelle to the moles of surfactant (R). Thus, if N_p is the concentration of phenol, the a_pN_p is the molecularly dispersed phenol concentration and $(1 - \alpha_p)N_p$ is the concentration of bound phenol molecules. As shown by Fig. 6, α_p depends on the total surfactant concentration.

Optimization requires that the surfactant molecular structure be selected so that α_p be reduced to as small a fraction as is possible. Figure 5 shows that as the phenol to surfactant ratio, R, increases, the proportion of phenol bound to the micelle decreases. Thus, high phenol to surfactant ratios are unfavorable. For ionic surfactants, high surfactant concentrations also appear to be favored. There is, however, a limitation on the

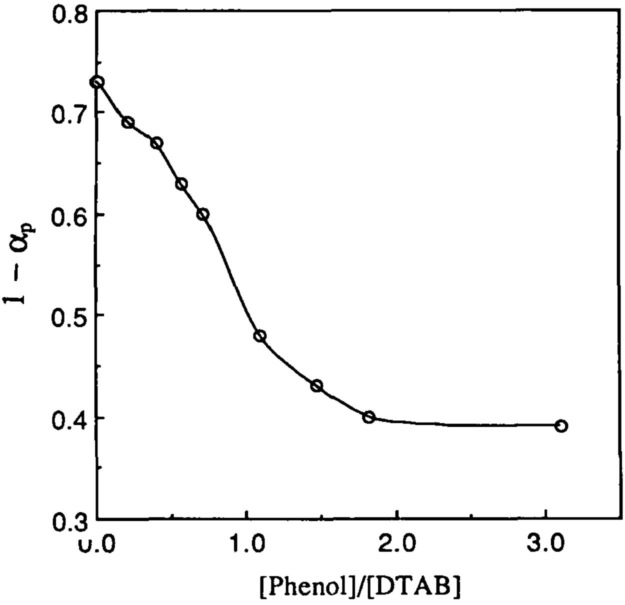


FIG. 5. Change in micellar partitioning of phenol: [DTAB] = 0.1 *M*.

benefits derived from increasing the surfactant concentration. This limitation will become apparent.

To decrease α_p for ionic surfactants, the hydrophile and the lipophile can be changed to increase the contribution of the electrostatic free energy associated with the formation of micelles (*12, 13*). There is, however, a limited benefit of doing this since any variation of the surfactant structure which increases the electrostatic free energy will generally increase the surfactant monomer concentration (the critical micelle concentration). This reduces the proportion of the total surfactant present which exists as micelles and is clearly counterproductive since monomeric surfactant will also tend to leak through the membrane. As will be seen, the changes in surfactant structure that are potentially useful are quite limited. It seems unlikely that values of α_p much different than those shown in Fig. 5 can be obtained with any ionic surfactant.

The potential for decreasing α_p by changing the structure of the nonionic surfactant is also quite limited. Figure 6 shows that two different

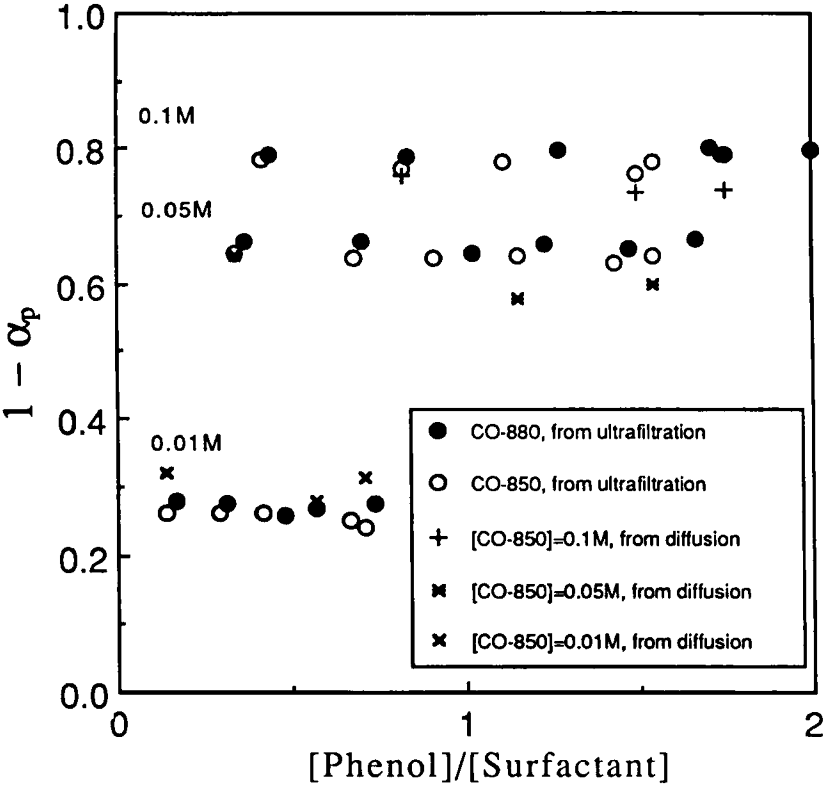


FIG. 6. Change of micellar partitioning of phenol for CO-850 and CO-880 systems.

nonionic surfactants, one having 30 EO units (CO-880) and another with 20 EO units (CO-850), yield about the same α_p and are practically independent of R. Since at complete saturation, one phenol occupies 5.3 EO units, the values shown in Fig. 6 are far from saturation, which accounts for the relative independence of α_p over the limited range of R as shown. It is, however, not possible to obtain higher values of R because increasing the phenol concentration results ultimately in the formation of a second phase as shown by Fig. 4. Thus, increasing the hydrophile beyond 20 EO units is not helpful in decreasing α_p. If the EO is decreased, then the cloud-point of the surfactant becomes the limiting factor (*14*).

Increasing the surfactant lipophile will also decrease the cloudpoint and give a smaller single-phase region than either of the surfactants considered there. Decreasing the lipophile might initially be beneficial by decreasing α_p, but it also increases the tendency for micelles to penetrate the membrane (*15*).

Rejection of Micelles

Scamehorn et al. (*1, 2*) examined the rejection of micelles by cellulose acetate membranes and found that those with a rating of 10,000 Daltons or less effectively rejected hexadecylpyridinium micelles, at least for modest surfactant concentrations. The pores in cellulose acetate membranes are not really well defined nor does one derive much information when rejection levels are near 100%. Polycarbonate membranes do have sharply defined pore size distributions (*16, 17*), and two different membranes have been used in this study. Micelles were found to pass freely through the membrane with 300 Å diameter pores, and the results are not reported here.

Figure 7 shows the rejection of DTAB micelles as a function of the solubilized phenol to surfactant ratio, *R*. In the absence of phenol, the rejection of micelles is quite small—about 8%. Since these micelles are thought to be spherical—about 50 Å in diameter—it was anticipated, based on calculations presented by Davidson and Deen (*18*), that the rejection efficiency should be about 60%. Davidson and Deen considered the movement of a spherical particle through a cylindrical pore. They considered both diffusional and hydrodynamic effects.

It is believed that the rapid movement of the micelles compared to the expected rate is a result of electrostatic forces produced by a diffusion potential. The counterions pass freely through the pores of the membrane and thereby create a diffusion potential which then acts on the micelles.

As the amount of phenol solubilized increases, so does the rejection. This is interpreted to imply that the size of the micelles increases and the shape becomes ellipsoidal. The rejection apparently reaches a plateau or declines slightly at higher values of *R*.

Figure 8 shows the rejection of DTAB micelles by a cellulose acetate membrane rated at 5,000 Daltons. The results are strikingly similar to those obtained using a polycarbonate membrane. Although the levels of rejection are somewhat higher, they are probably not sufficient for com-

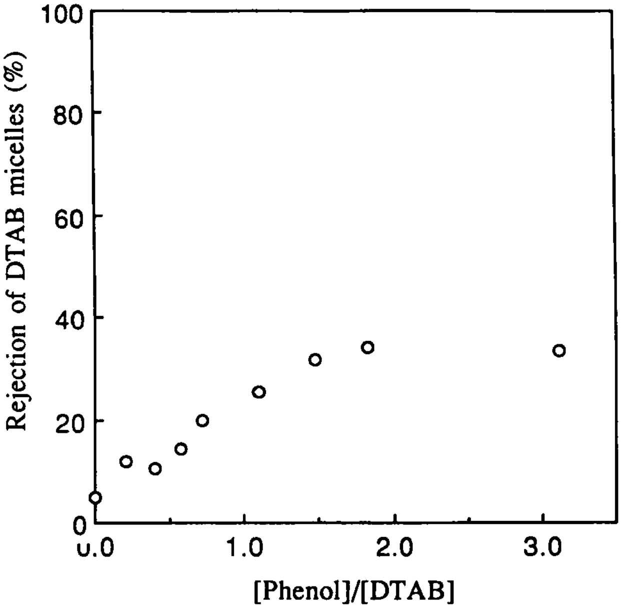


FIG. 7. Rejection of DTAB micelles by PCTE 100 Å polycarbonate membrane: [DTAB] = 0.1 *M*; [NaBr] = 0%.

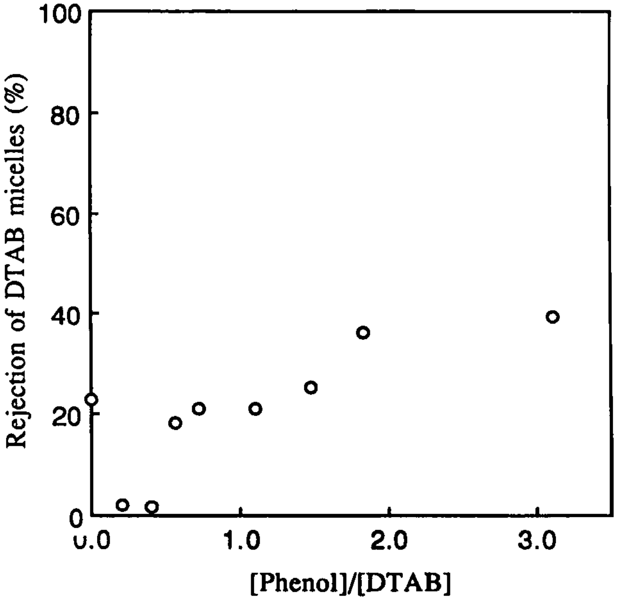


FIG. 8. Rejection of DTAB micelles by YM-5 membrane: [DTAB] = 0.1 *M*; [NaBr] = 0%.

mercial application. It will, therefore, be necessary to increase the surfactant's lipophile (see Table 1), add inorganic salt, or find a suitable membrane.

Figure 9 shows both the rejection and the filtrate surfactant concentration for a nonionic surfactant as a function of concentration. The rejection appears relatively constant for retentate concentrations less than about 100 times the critical micelle concentration (cmc). At concentrations exceeding the cmc by two orders of magnitude, the rejection decreases rapidly. At surfactant concentrations which are 1000 times the cmc, micelles apparently flow freely through the 100 Å pores in the polycarbonate. This remarkable transition would seem to indicate that the micelles have suddenly decreased in size. Indeed, Scamehorn et al. observed a similar phenomenon and attributed it to the formation of surfactant dimers, trimers, etc. (*2*). This explanation is not likely to be correct

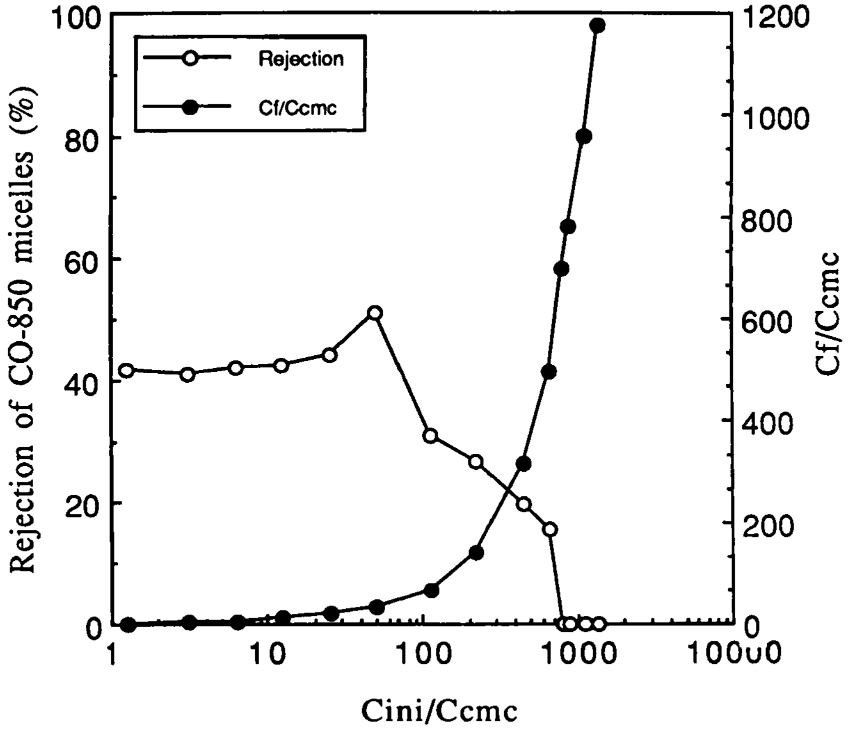


FIG. 9. Effect of CO-850 concentration on rejection of micelles by PCTE 100 Å membrane.

although the tendency for an increase in micelle penetration cannot be attributed to a specific interaction between the micelles and the membrane. It must have to do with the structure of micelles and the stability of these structures. The lack of a membrane-specific interaction can be demonstrated experimentally. Consider Fig. 10: the rejection efficiency of a cellulose acetate membrane, while still high, does decrease dramatically in the same concentration range as seen for the polycarbonate membrane.

The viscosity of the micellar solution is shown as a function of surfactant concentration by Fig. 11. The rapid increase of viscosity at higher surfactant concentrations indicates that the micelles are becoming longer and rodlike, not smaller as suggested by Scamehorn et al. This is, in fact, the genereal trend expected (*19*) with increasing surfactant concentrations. The fact that the micelles are increasing in length and that there

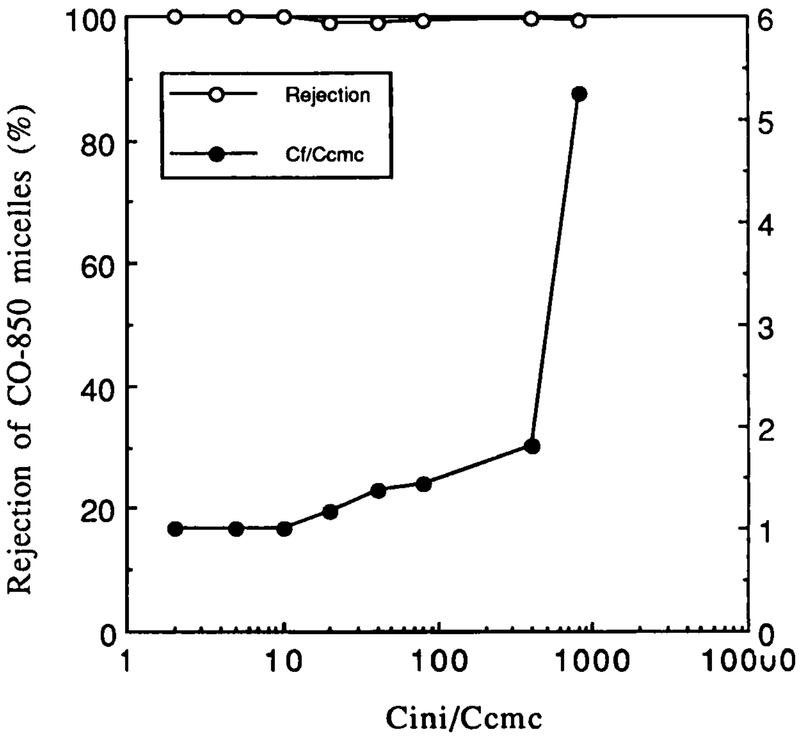


FIG. 10. Effect of CO-850 concentration on rejection of micelles by YM-5 membrane.

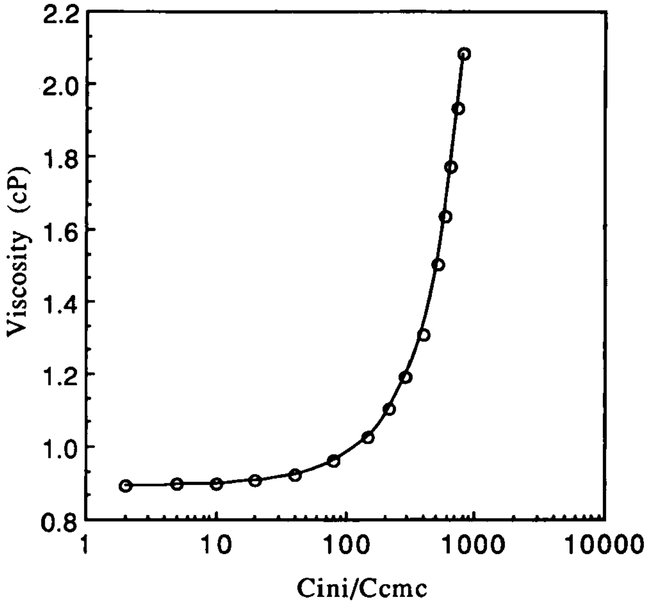


FIG. 11. Change of viscosity with concentration of CO-850.

is not a significant increase in the concentration of smaller aggregates can be confirmed by measuring the diffusion of surfactant molecules as a function of concentration. The diffusion coefficient of the surfactant is a weighted average of the various modes of surfactant diffusion. Surfactant monomer diffuses as individual molecules whereas surfactant present as aggregates diffuses at a rate dictated by the Brownian movement of the aggregate. The weighting factor is the average fraction of the surfactant molecules in the particular aggregated state. Figure 12 shows that the diffusion coefficient decreases markedly in the same concentration range as the increased viscosity and the increased micelle permeation. This again indictes that the micelles are becoming longer and rodlike. Thus, there exists a paradox. Longer, rodlike micelles exhibit a greater tendency to permeate through a cylindrical hole than smaller ellipsoidal or spherical micelles.

One possible explanation for this result might be thought to be related to the alignment of rodlike molecules by fluid shear so that they can readily flow through the cylindrical holes. Long and Anderson (*20*) found that polystyrene polymer molecules, which were longer than the diameter

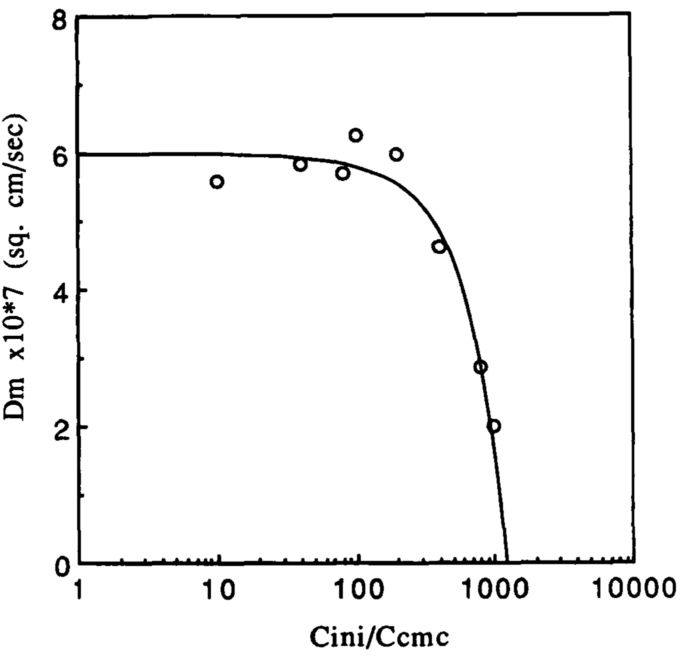


FIG. 12. Change of CO-850 micellar diffusion coefficients with CO-850 concentration.

of the holes in a membrane, readily permeated through the membrane when the solvent velocity was high enough, even though they were essentially entirely rejected at low solvent velocities. The correlating parameter is apparently $S = \mu Q/kT$, where Q is the volumetric flow rate through a single pore and μ is the fluid viscosity. The transition from complete rejection to substantial penetration occurs for values of $S \approx 1$. For the studies reported here, $S \approx 10^{-4}$. An alignment of rodlike micelles by shear seems unlikely to be the explanation for the decrease in membrane rejection efficiency at high surfactant concentrations.

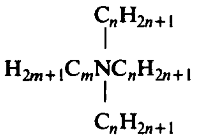
At the present time there does not appear to be a satisfactory explanation for the increase in micelle permeation at high surfactant concentrations. However, since the same phenomenon has been observed by Scamehorn et al. (*2*), we suggest that it might be a distinct feature of all MEUF processes and therfore limits the surfactant concentration which can be used. This phenomenon is being investigated further.

The results presented here and those reported by others in the literature can be used to assess qualitative trends associated with changing the surfactant structure to obtain an optimum molecule. The ideal surfactant is one which has a very small cmc to minimize the surfactant in the filtrate, is structured so that the micelles are totally rejected, has a great affinity for the solute ($\alpha_p \cong 0$), and does not solubilize unwanted solute. Table 1 shows the limitations. Within certain rather narrow limits it is possible to find an optimum surfactant structure. Based on these considerations, it appears that ionic surfactants other than DTAB will be more advantageous; however, it seems unlikely that the performance of CO-850 can be much improved by the selection of any other nonionic surfactant. Not considered here, and certainly worthy of further study, is the use of mixtures of nonionic and anionic surfactants.

TABLE 1

Surfactant Structural Considerations

Ionic:



$H_{2m+1}C_m\overset{C_nH_{2n+1}}{\underset{C_nH_{2n+1}}{N}}C_nH_{2n+1}$

Change	Benefit	Limitation
Increase *m*	Increase rejection and decrease cmc	Raises Kraft temperature
Increase *n*	Increase rejection	Increase α_p and cmc
Add inorganic salt	Increase rejection and decrease cmc	Increase α_p
Increase surfactant concentration	Decrease α_p	Critical "leakage" concentration

Nonionic: $H_{2m+1}C_m{-}O(C_2H_4O)_nH$

Change	Benefit	Limitation
Increase *m*	Increase rejection and decrease cmc	Decrease cloudpoint temperature
Increase *n*	None for $n > 15$ to 20	None for $n > 15$ to 20
Increase surfactant concentration	Decrease α_p	Critical "leakage" concentration

Influence of Cosolubilizate

In the previous sections the role of surfactant structure has been related to ultrafiltration performance. It is seen that there are distinct limitations imposed on the effectiveness of phenol removal even when the optimum surfactant is used. Given this limitation, it is natural to consider the addition of a cosolubilizate and to ask whether its presence will improve the removal of hydrophilic compunds by MEUF.

It seems self-evident that if the cosolubilizate competes for binding sites with the solute to be removed, then the process will be less efficient. Thus, attention here is focused on the role of hydrophobic cosolubilizates such as cyclohexane and carbon tetrachloride. The concept that prompted this part of the study is depicted by Fig. 13. A nonionic surfactant micelle is

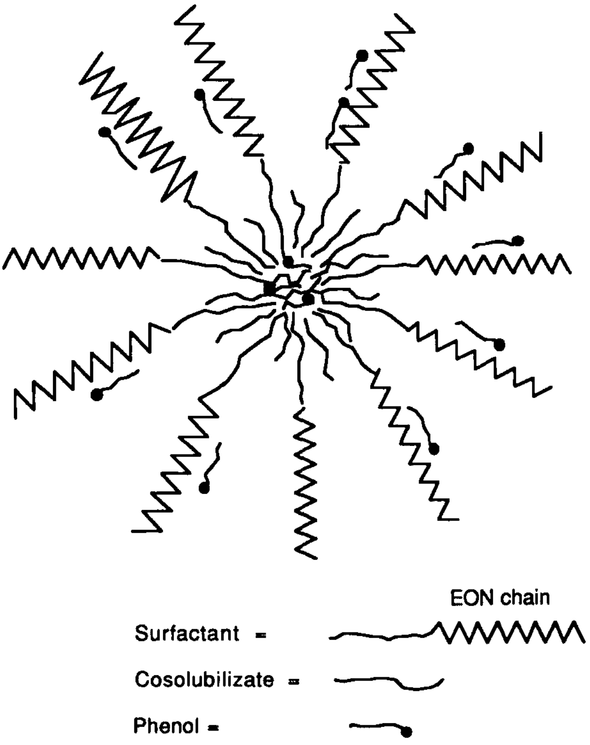


FIG. 13. Micelle with a central core containing mostly the hydrophobic cosolubilizate with some phenol. Most of the phenol is associated with the EO chains.

shown. Phenol is bound to the ethylene oxide units while the hydrophobic cosolubilizate is mingled with the surfactant's lipophile and is also perhaps present in the form of a central core. This microstructure is typical of microemulsions (*19*). A restriction is, therefore, imposed on the amount of cosolubilizate which can be permitted. The micellar phase must retain its water-continuous character rather than becoming bicontinuous (*21*); otherwise, the membrane will not be effective. Systems with limited amounts of cosolubilizate are said to be "suboptimum" (*19*). Table 2 shows that the solubilization of carbon tetrachloride (CCl_4), for the systems studied, is small. These systems are suboptimum and satisfy the condition of water continuity. Since the solubilization into the nonionic micelles is larger than for DTAB, CO-850 was selected for further study.

As shown by Fig. 14, the phase boundary of the phenol/CO-850 system is essentially unaffected by the addition of CCl_4; however, in the single-phase region near the phase boundary, highly viscous solutions form where, in the absence of CCl_4, the systems are quite fluid. Apparently the presence of CCl_4 tends to promote the formation of rodlike micelles.

The invariance of the phase boundary shown in Fig. 14 is disappointing. A substantial increase in phenol solubilization is desired. Evidently a distinct core of CCl_4 in the center of the micelle shown by Fig. 13 has not formed and phenol is still bound to the micelle along the ethylene oxide chain. If this is the case, then only a very small change in α_p is expected. Figure 15 shows this to be the case.

Based on these results, it is apparent that CCl_4 cosolubilized with phenol will not result in a significant improvement in the MEUF process although the presence of the CCl_4 does increase the rejection efficiency as shown by Fig. 16. It is not known whether this increase is due to a change in the micellar shape or whether the presence of CCl_4 modifies the mem-

TABLE 2
Solubilization of Carbon Tetrachloride in Aqueous Surfactant Solutions (T = 25°C and Surfactant Concentration = 0.1 M)

Surfactant	S = moles CCl_4/mole surfactant
CO-850 (nonionic)	3.1
CO-630 (nonionic)	3.2
DTAB (cationic)	0.8
SDBS (anionic)	1.3

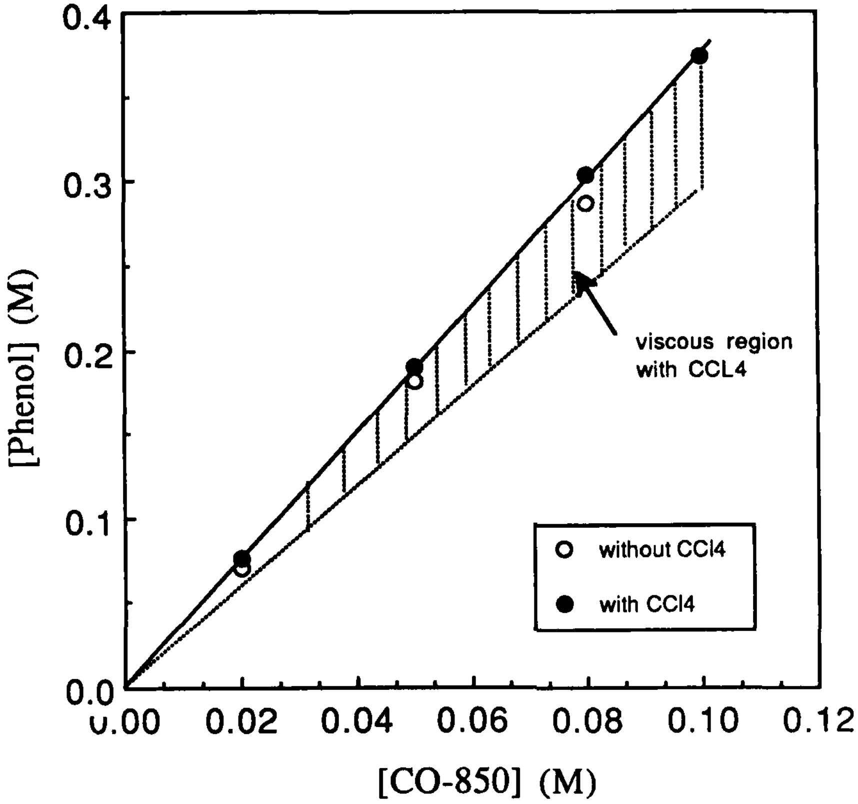


FIG. 14. Solubility diagram of phenol in CO-850 micellar solutions.

brane. Because of the relatively small improvement obtained using carbon tetrachloride, this question was not pursued further.

Cosolubilization of carbon tetrachloride did not greatly enhance the removal of phenol by MEUF. The cosolubilization of cyclohexane in the presence of phenol is substantially more than that of carbon tetrachloride, as shown by Fig. 17. This synergistic effect indicates that a core composed of cyclohexane and perhaps phenol exists at the center of the swollen micelles. Figure 17 shows that a maximum of slightly more than 8 moles of cyclohexane per mole of surfactant can be cosolubilized with phenol. When the overall phenol concentration is 0.351 *M*, $\alpha_p = 0.22$ in the absence of cyclohexane. This value decreases to 0.151 for $S = 7$ moles cyclohexane/

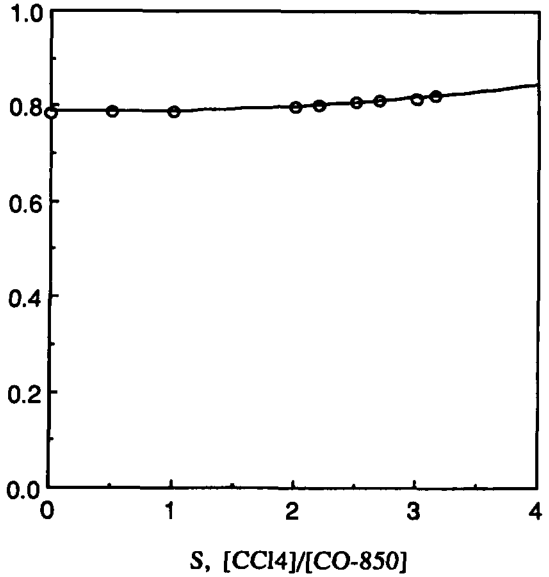


FIG. 15. Change of fraction of phenol in micelle with *R*: [Initial phenol] = 0.5%.

mole surfactant. Thus, an increase in the fraction of phenol partitioning into the micelle is observed.

It is of interest to estimate the fraction of the solubilized phenol actually residing within the core of the micelle. Assuming that all of the solubilized cyclohexane is contained within the micelle core as a bulk phase (very unlikely), and then knowing the partition coefficient, K_D (= concentration of phenol in cyclohexane/concentration in water), the amount of phenol associated with the cyclohexane can be estimated. Measurement of K_D over a wide range of conditions has shown $K_D = 0.14 \pm 0.003$. The concentration of phenol in water is given by $N_p\alpha_p$, where N_p is the overall phenol concentration. Thus, the concentration of that part of the solubilized phenol residing in the core is $K_D N_p \alpha_p$, and for $\alpha_p = 0.15$ and $S = 7$, 5.58×10^{-4} mol phenol per liter solution is found to be in the core. The increase in phenol solubilization in the presence of cyclohexane is 2.46×10^{-2} mol phenol per liter solution. Thus, very little (less than 2.3%) of the increase in phenol solubilized resides in the core. It is believed that the solubilization of cyclohexane increases the area per amphiphile, thus making more of the ethylene oxide chain available for phenol binding. This mechanism

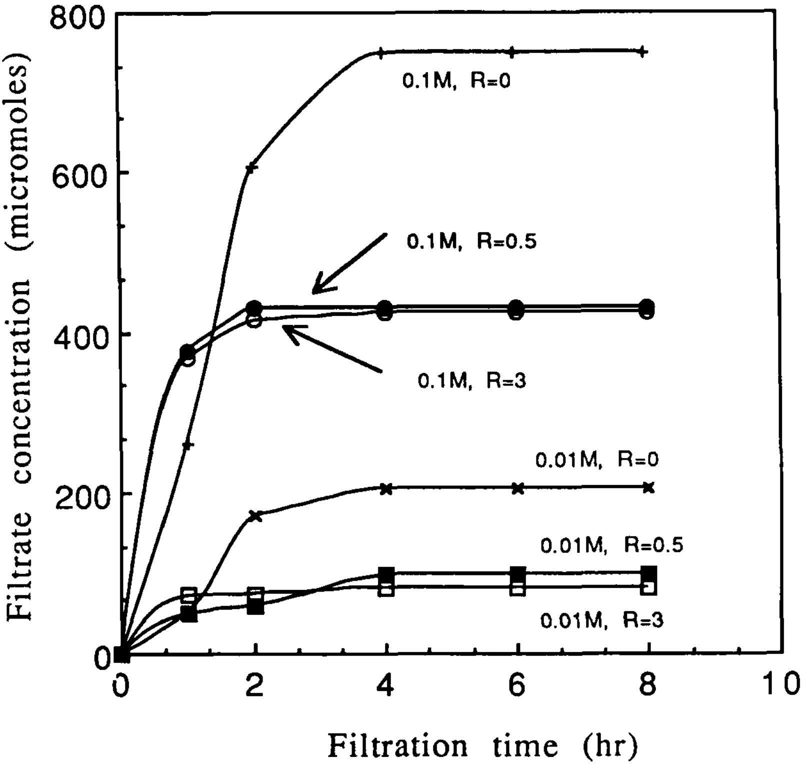


FIG. 16. Effects of carbon tetrachloride on filtrate concentration of CO-850 in ultrafiltration by YM-5 membrane.

does provide a means of increasing the solubilization of phenol and making the process more efficient. However, the increase is marginal since α_p only decreases from 0.22 to 0.15 when cyclohexane is added.

It seems unlikely that cosolubilization will provide a substantial increase in the efficiency of MEUF. Thus, for practical purposes it will not be possible to reduce the concentration of hydrophilic solutes in a single stage. A multistage process will be required.

The MEUF Process

A multistage process for separating hydrophilic solutes will be necessary since such solutes do not reside entirely within the micelle but in-

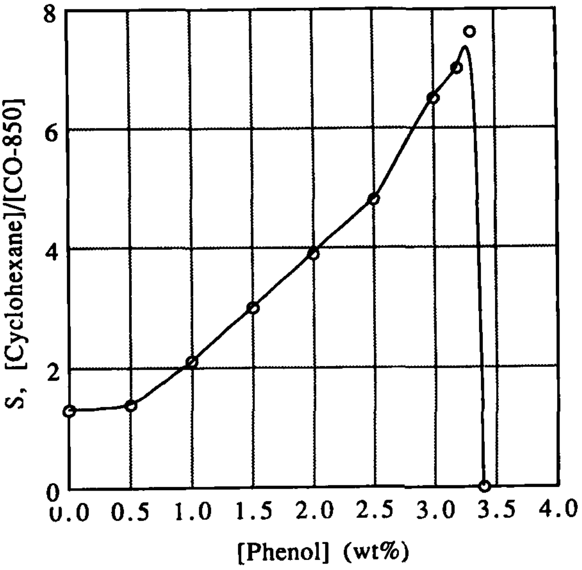


FIG. 17. Change of solubilization limit of cyclohexane with addition of phenol in CO-850 micellar solution: [CO-850] = 0.1 *M*.

stead partition between the micelle and the aqueous phase. Complete separation cannot, therefore, be effected in a single stage. One possible arrangement is shown by Fig. 18. Each stage can be thought of as a single tray in a distillation column with the vapor leaving a tray being equated to the filtrate passing through a membrane. The surfactant solution flows countercurrently.

Figure 19 shows an equilibrium curve which relates the total concentration of phenol in the micellar solution to that concentration which is presently molecularly dispersed. Assuming that the membrane rejects essentially all of the micelles, then the filtrate concentration is determined by the equilibrium curve. The filtrate leaving Stage I becomes, as shown in Fig. 19, the feed to Stage II, and the filtrate from Stage II is the feed to Stage III, and so on.

Clearly, this process is much like simple distillation, and the membrane performance is the important feature. If a membrane leaks, then, as in distillation, extra stages will be required to achieve a desired separation. Thus, a slightly "leaky" membrane may not be a real problem but will increase the number of stages. The membrane in the final stage is, however, crucial because surfactant permeating through this membrane will be lost

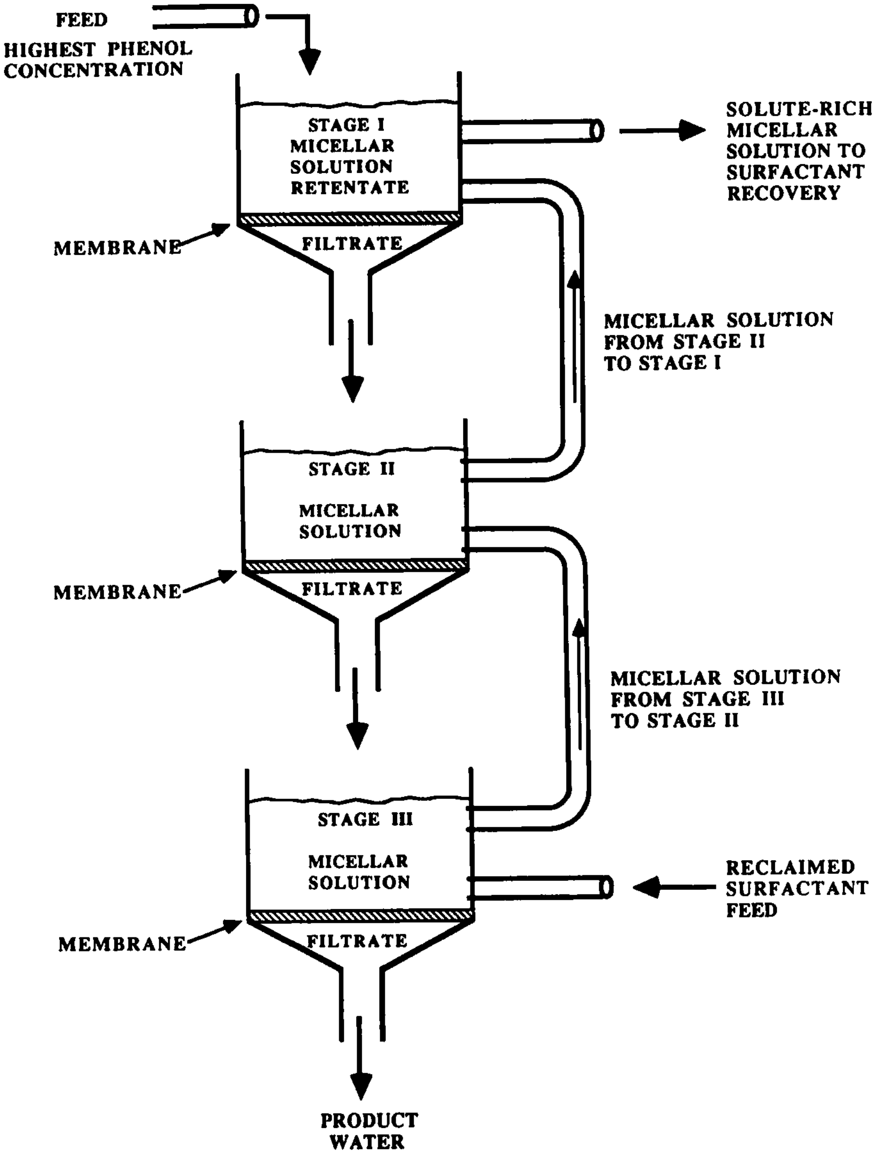


FIG. 18. Multistage process for solute removal.

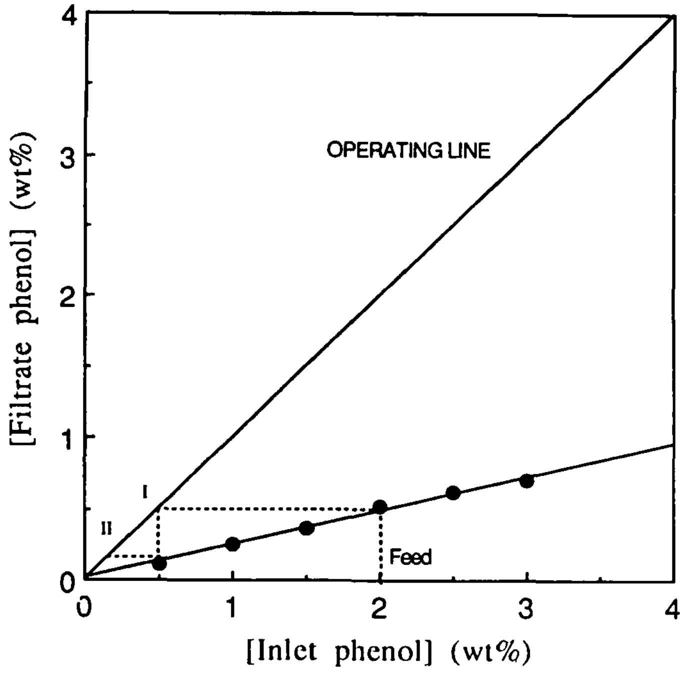


FIG. 19. Ultrafiltration of phenol by surfactant solution: [CO-850] = 0.1 *M*.

or require further treatment of the product water for its recovery. Thus, it is highly desirable that the last membrane reject essentially all surfactant molecules, not just micelles. While it appears, in principle, easier to find a membrane capable of rejecting surfactant molecules than finding one which will reject small organic solutes, no membrane capable of rejecting all surfactant molecules has been found. This remains a problem to be resolved.

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