Miceliar-Enhanced Ultrafiltration Using a Twin-Head Cationic Surfactant

Stéphanie Gélinas; Martin E. Weber

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Micellar-Enhanced Ultrafiltration Using a Twin-Head Cationic Surfactant

STÉPHANIE GÉLINAS and MARTIN E. WEBER*
DEPARTMENT OF CHEMICAL ENGINEERING
McGILL UNIVERSITY
3610 UNIVERSITY STREET, MONTRÉAL, QUÉBEC H3A 2B2, CANADA

ABSTRACT

A twin-head cationic surfactant was used in micellar-enhanced ultrafiltration of aqueous solutions of benzoic acid. The surfactant, a tertiary amine with two polyoxyethylene head groups and an alkyl tail of 18 carbons, had a critical micelle concentration of 0.06 mM (0.05 g/L). Semiequilibrium dialysis measurements gave a maximum solubilization capacity of 1 mole of acid per mole of surfactant. The ultrafiltration was performed in hollow fiber units having molecular weight cutoffs of 5K and 30K at transmembrane pressures up to 138 kPa. The permeate flux was independent of the concentration of surfactant at concentrations below 4 g/L and decreased at higher concentrations. The flux was independent of the concentration of benzoic acid. At a fixed benzoic acid concentration, the rejection of acid increased with increasing concentration of surfactant, passed through a maximum, and then decreased. For surfactant concentrations above about 2 mM and below 20 mM, the rejections of the surfactant and benzoic acid were functions only of the ratio of surfactant to solute. The best ratio was 1.2 moles of surfactant per mole of benzoic acid, where the rejections were 0.89 for the acid and 0.95 for the surfactant.

INTRODUCTION

Micellar-enhanced ultrafiltration (MEUF), first demonstrated by Leung (1), has been shown by Scamehorn, Christian, and coworkers (2–4) and others (5, 6) to be an effective method of removing dissolved organic contaminants from aqueous solutions. The process is based on the tendency of surfactant

* To whom correspondence should be addressed.

micelles to solubilize organic solutes, thus increasing their effective size. The micelles and their solubilized contaminants can then be rejected, with high permeate flux, by an ultrafiltration membrane having a molecular weight cut-off (MWCO) much larger than the molecular weight of the contaminant. In MEUF, the surfactant is added to the contaminated aqueous stream at a concentration above the critical micelle concentration (CMC), so that sufficient micelles are formed to solubilize most of the organic contaminants. Ultrafiltration is usually performed using synthetic membranes with MWCOs of 10K and above. High rejections of contaminants and surfactants may be obtained. Ultrafiltration of micellar solutions containing solubilized organics may also be used to remove contaminants from the solutions produced by soil cleanup operations using surfactant flushing (7).

Table 1 summarizes the best results of the MEUF experiments reported in the literature. The experiments involved cationic surfactants, with cetylpyridinium chloride being used in every case but one. This material has a CMC of approximately 0.9 mM or 0.3 g/L (8). Dosages of surfactant, expressed as a ratio of surfactant to solute, were generally 5–10 on a molar basis or 15–30

TABLE 1
Experimental Results for Micellar-Enhanced Ultrafiltration of Organic Solutes[a]

| Surfactant | Solute | Ultrafiltration membrane | | Ratio: surfactant/solute | | Percent rejection | | Ref. |
		MWCO	Material	Mol/mol	Wt/wt	Solute	Surfactant	
CPC	TBP	1K	CA	10	23.9	99	99	2
CPC	TBP	1, 2, 5, 10, 50K	CA	10	23.9	95	96	3
CPC	Hexanol	10K	CA	10	35.1	79	99	
CPC	Heptanol	10K	CA	2, 5, 10	6.1, 15.4, 30.9	90	99	4
CPC	Octanol	10K	CA	5, 10	13.8, 27.5	97	98	
CPC	Phenol	3, 10, 30K	PS	5	19.0	75	99	5
CTAC	Phenol	3, 10, 30K	PS	5	17.0	83	94	
CPC	Decane	5K	PES	N/A	N/A	99	N/A	6
Rhodameen	Benzoic acid	5, 30K	PS	1.2	7.8	89	95	This work

[a] CPC = cetylpyridinium chloride; CTAC = cetyltrimethyl ammonium chloride; TBP = 4-tertiary butylphenol; CA = cellulose acetate; PS = polysulfone; PES = polyethersulfone.
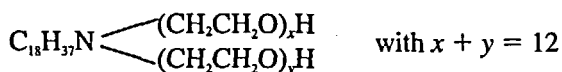
on a weight basis. Rejections above 85% were usually achieved for the solute and above 95% for the surfactant.

Recently, surfactants having two hydrophilic groups, twin-head surfactants, have been synthesized. These materials have low CMC values and high solubilization capacities for organic solutes (9, 10). The objective of this work was to determine the MEUF performance of a twin-head cationic surfactant having one hydrophobic tail.

EXPERIMENTAL

Materials and Methods

The surfactant used in this work was Rhodameen T-12 (Rhône-Poulenc, Mississauga, ON), a tertiary amine having one alkyl chain and two polyoxyethylene groups. The structure is

$$C_{18}H_{37}N \begin{cases} (CH_2CH_2O)_xH \\ (CH_2CH_2O)_yH \end{cases} \quad \text{with } x + y = 12$$

The surfactant was supplied as a 90% active liquid with the remainder being propylene glycol. The surfactant was used as received. Surfactant concentrations are expressed in terms of the active material, which has a molecular weight of 798. The CMC was determined by surface tension measurements using a platinum ring tensiometer (Fisher Scientific Co., Montreal, QC). A value of 0.06 mM (0.05 g/L) was obtained. The solute was benzoic acid of 99.9% purity (Aldrich Chemical Co., Toronto, ON).

The concentration of benzoic acid was measured by ultraviolet spectroscopy at a wavelength of 227 nm. The surfactant was analyzed by potentiometric titration using a surfactant electrode (Orion Research Inc., Boston, MA) with sodium lauryl sulfate (SLS) as titrant. For samples containing 0.01 to 0.1 mM surfactant, the titrant was 1 mM SLS; for samples containing 0.1 to 1 mM surfactant, the titrant was 5 mM SLS.

Solubilization Measurements

Solubilization tests were performed using the semiequilibrium dialysis technique devised by Christian, Tucker, Scamehorn, and coworkers (11, 12). The dialysis membrane allows solute molecules and surfactant monomers to pass, but retains surfactant micelles. The measurement of solubilization through semiequilibrium dialysis assumes that the solute achieves equilibrium in a relatively short time, usually 18–48 hours, and that equilibrium for the surfactant takes much longer to achieve.

Two compartment dialysis cells of 50 mL volume (Fisher Scientific Co., Montreal, QC) were used. The compartments were separated by a regenerated

cellulose membrane having a MWCO of 6K (Fisher Scientific Co., Montreal, QC). Each compartment was filled with the same volume of liquid. Initially, one compartment (Compartment A) contained an aqueous solution of the surfactant at a concentration above the CMC, while the other compartment (Compartment B) contained an aqueous solution of benzoic acid. Samples were taken from each compartment after 48 hours, a time which preliminary experiments indicated was sufficient for semiequilibrium to be attained. The initial concentrations were between 5.8 and 23 mM for the surfactant and between 4 and 16 mM for benzoic acid. Experiments were carried out at 23 ± 3°C.

The benzoic acid which diffuses across the membrane into Compartment A exists in two forms: dissolved material (free solute) and as material solubilized in surfactant micelles (solubilized solute). At semiequilibrium the concentration of free benzoic acid in Compartment A is equal to the concentration of benzoic acid in Compartment B, assuming that there are no micelles in Compartment B. We measured the concentration of acid in Compartment B, then using a mass balance and the fact that the volumes in each compartment were equal, the concentration of solubilized acid (averaged over the volume of the micelle-containing phase), $C_{A,S}$, was calculated from

$$C_{A,S} = C_A^0 - 2C_A \tag{1}$$

where C_A^0 is the initial concentration of acid in Compartment B, and C_A is the concentration of acid in Compartment B measured at semiequilibrium.

Ultrafiltration Apparatus and Procedure

Ultrafiltration was carried out in hollow fiber membrane cartridges (A/G Technology Corp., Needham, MA) containing polysulfone membrane tubes of 30 cm length. Two units were used; one with a MWCO of 5K containing 33 tubes (0.56 mm ID, 0.97 mm OD), the other with a MWCO of 30K containing 34 tubes (0.54 mm ID, 0.92 mm OD).

The ultrafiltration flow loop is shown in Fig. 1. The feed stream containing the solute and the surfactant was fed by a peristaltic pump at a flow rate of 150 mL/min through a pulsation dampener to the inside of the membrane fibers. The reject stream leaving the cartridge was recycled to the feed reservoir. The permeate, which drained by gravity from the shell side of the cartridge, was also recycled to the feed reservoir. The pressure on the tube side of the cartridge was controlled manually using the backpressure valve on the reject stream; the pressure on the shell side was 1 atmosphere. The permeate flux was measured by collecting the permeate stream for 1 minute. Two 40 mL samples were taken for solute and surfactant analysis; one from the feed reservoir and the other by diverting the permeate stream. All experiments were carried out at 23 ± 3°C.
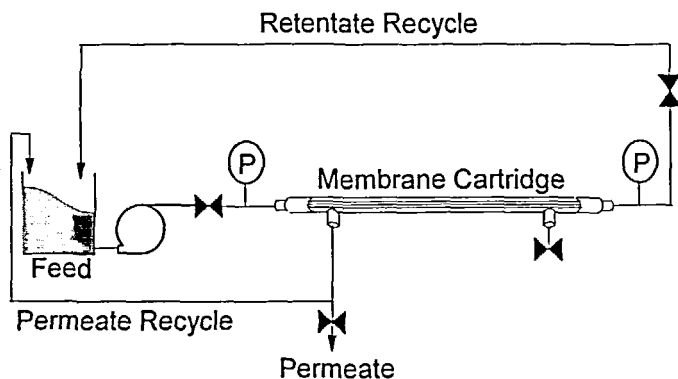
FIG. 1　Ultrafiltration apparatus.

The procedure for a run consisted of measuring the permeate flux for a distilled water feed at a transmembrane pressure of 69 kPa. If this flux was below 20 mL/min, the membrane was cleaned again. After this, the apparatus was drained and the feed reservoir was filled with 900 mL of solution having the desired concentrations of benzoic acid and the surfactant. The pump was started and the pressure adjusted to give the desired transmembrane pressure. When steady state was reached (less than 5 minutes), the permeate flux was measured and samples were taken. Preliminary experiments had shown that the permeate flux remained constant for times between 5 and 30 minutes. The pressure on the tube side was then increased and the procedure was repeated for a higher transmembrane pressure. After completion of a series of runs at different pressures with one feed solution, the cartridge was flushed with distilled water. The unit was then cleaned by circulating a solution containing 50 ppm chlorine in distilled water (1 mL of household bleach in 1 L of water) at 50°C through the tubes for 20 minutes. The cleaning solution was then flushed out of the cartridge with distilled water, also at 50°C. The cartridge was filled with distilled water and stored at room temperature until the next run. In a series of replicate runs, the 90% confidence interval for the permeate flux was determined to be about ±15% of the mean value.

The transmembrane pressure, ΔP, was determined from the pressures measured at the inlet and outlet of the cartridge, P_i and P_o, respectively, and P_p, the pressure on the permeate side, which was always 1 atmosphere:

$$\Delta P = \frac{P_i + P_o}{2} - P_p \tag{2}$$

The rejection was calculated from

$$R_i = 1 - c_i/C_i \tag{3}$$

where c_i is the concentration in the permeate and C_i is the concentration in the feed. For the surfactant, $i = S$. For the solute, benzoic acid, $i = A$, and C_A is the total concentration of acid in the feed:

$$C_A = C_{A,S} + C_{A,F} \tag{4}$$

where $C_{A,F}$ is the concentration of free benzoic acid and $C_{A,S}$ is the concentration of solubilized benzoic acid. The 90% confidence intervals for the rejections of surfactant and benzoic were approximately ± 0.04.

Other Measurements

The osmotic pressure of a 6.3 mM aqueous solution of the surfactant was measured at 30°C using a membrane osmometer (Genotec Model 090-B, UIC Inc., Joliet, IL). The membrane (UIC Inc.), which was regenerated cellulose, had a MWCO of 5K.

RESULTS AND DISCUSSION

Solubilization of Benzoic Acid by Surfactant Micelles

The results of the semiequilibrium dialysis experiments are plotted in Fig. 2 as moles of benzoic acid solubilized per mole of surfactant versus the concentration of free (unsolubilized) benzoic acid. Data are shown for surfactant concentrations ranging from 5.7 to 23 mM. Using the molar solubilization ratio removes most of the dependence on surfactant concentration, except for the highest surfactant concentration which gave a somewhat lower solubilization ratio. The maximum solubilization capacity was approximately 1 mole of benzoic acid per mole of surfactant, or 0.15 g benzoic acid per gram of surfactant. This high solubilization capacity is attributed to the fact that the surfactant is a tertiary amine which can be protonated easily by the hydrogen ion from the weak acid. The protonated amine can attract one ionized acid molecule, thus giving a one-to-one molar ratio of solute to surfactant.

We visualize the surfactant micelle to be composed of a spherical hydrophobic core containing a number of 18-carbon alkyl chains, with the amine nitrogen located at the surface of this core. The polyoxyethyene chains form an outer shell which extends into the aqueous phase. The locus of solubilization of benzoic acid is in this outer shell where the hydrogen from the acid can protonate the amine nitrogen. The presence of solubilized acid extends the polyoxyethylene chains, thus increasing the thickness of the shell and the size of the micelle. The radius of the micelle is bounded by the radius of the core (i.e., assuming that the polyoxyethylene chains are wrapped closely around the core) and the radius of the core plus the length of the fully extended
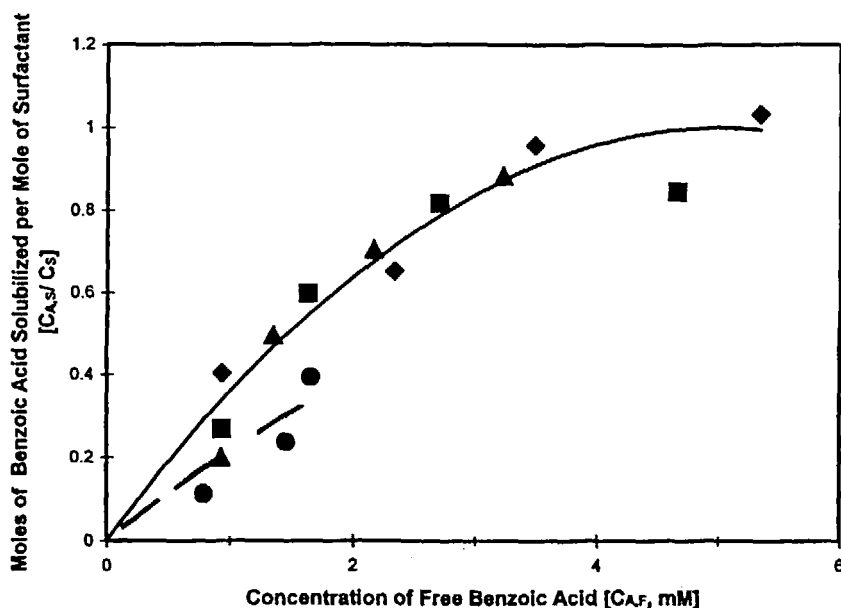
FIG. 2   Molar solubilization ratio as a function of the concentration of free benzoic acid (◆, C_S = 5.7 mM; ■, C_S = 8.5 mM; ▲, C_S = 12 mM; ●, C_S = 23 mM).

polyoxyethylene chains. Using these geometrical ideas and the chain dimensions of Tanford (13), we calculated an aggregation number of 117 as well as minimum and maximum micelle radii of 2.4 nm and 4.9 nm, respectively. Gélinas (14) gives details. The estimated aggregation number was in good agreement with a value determined from the measured osmotic pressure of a 6.3 mM solution of surfactant in water. Using the van't Hoff equation, the calculated molecular weight was 82.6K, corresponding to an aggregation number of 103.

Permeate Flux in MEUF

The permeate flux was measured at a fixed transmembrane pressure over a range of benzoic acid concentrations. Typical results are presented in Fig. 3 for the 30K MWCO membrane at a transmembrane pressure of 69 kPa. The flux was independent of the concentration of benzoic acid, but varied with the concentration of surfactant.

The variation of the permeate flux with transmembrane pressure up to 121 kPa is shown in Fig. 4 for the 30K MWCO membrane. The uppermost line represents the distilled water flux. As expected, the flux increased linearly
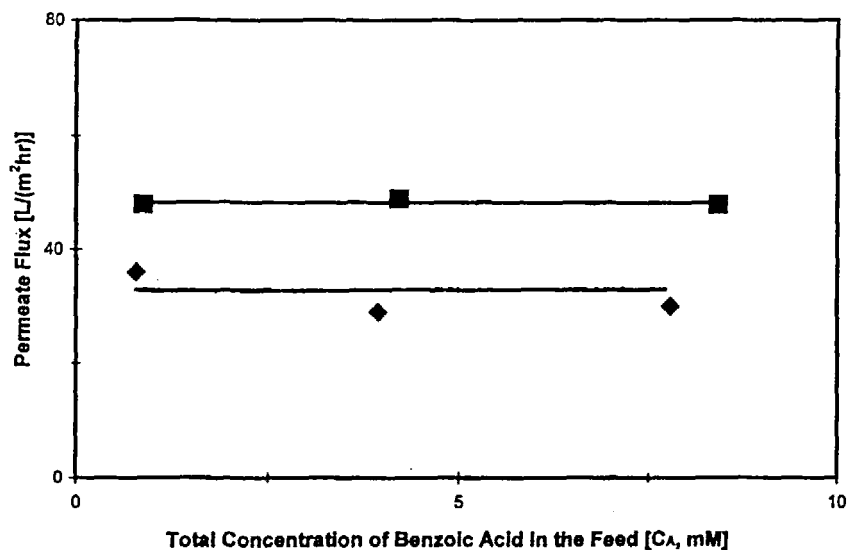
FIG. 3   Permeate flux as a function of the concentration of benzoic acid in the feed for MWCO = 30K and ΔP = 69 kPa (■, C_S = 4.8 mM; ◆, C_S = 20 mM).
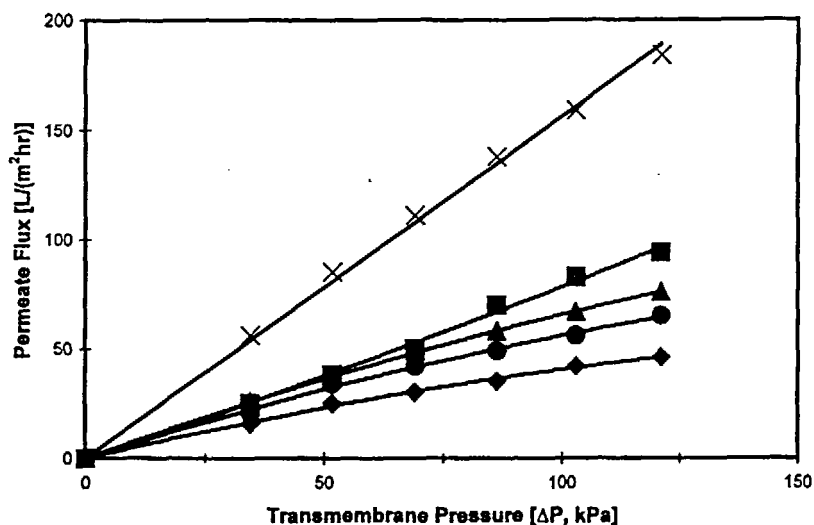

FIG. 4   Permeate flux as a function of the transmembrane pressure for MWCO = 30K for water (×) and for MEUF with C_S/C_A = 1.2 (■, C_S = 1.0 mM; ▲, C_S = 5.1 mM; ●, C_S = 9.9 mM; ◆, C_S = 20 mM).

with transmembrane pressure. For the 5K MWCO, the distilled water flux was about 50% smaller. The fluxes in MEUF are presented for a fixed ratio of 1.2 moles surfactant per mole of benzoic acid in the feed. The significance of this ratio is discussed subsequently. The surfactant concentrations were varied between 1 and 20 mM. At a fixed transmembrane pressure, increasing the concentration of surfactant decreased the permeate flux. At the highest surfactant concentration, 20 mM, the flux appeared to approach a plateau. These results are typical of those for the ultrafiltration of colloids, including surfactants (2–6).

Rejection of Surfactant and Benzoic Acid

The rejections for the ultrafiltration of benzoic acid and the ultrafiltration of the surfactant using both membranes are given in Table 2. Benzoic acid rejections were low, as expected. For a given membrane, the rejection of surfactant was lower at low concentration because a larger fraction of the surfactant was present as monomers or small aggregates. At high concentration, the surfactant rejections were 0.76 for the 5K MWCO and 0.54 for the 30K MWCO. When no benzoic acid is present, the surfactant micelles have their smallest size. This size corresponds to an effective molecular weight of 25–30K (a core of about 110 chains of $C_{18}H_{37}$). Some smaller micelles leak through the larger pores of each membrane.

Figure 5 shows the rejection of benzoic acid as a function of the molar ratio of surfactant to benzoic acid in the feed for the 30K MWCO membrane operated at a transmembrane pressure of 69 kPa. The data for the 5K MWCO membrane were similar. A molar ratio of zero corresponds to ultrafiltration of a benzoic acid solution, for which the rejection was 0.03 as shown in Table 2. When the molar ratio of surfactant to acid was less than about unity, there was insufficient surfactant to solubilize all of the acid. The acid which was not solubilized passed through the membrane. When the molar ratio was increased, the rejection increased because the benzoic acid was solubilized into micelles which were rejected by the membrane. The maximum rejection

TABLE 2
Rejection in Ultrafiltration of Benzoic Acid and Surfactant

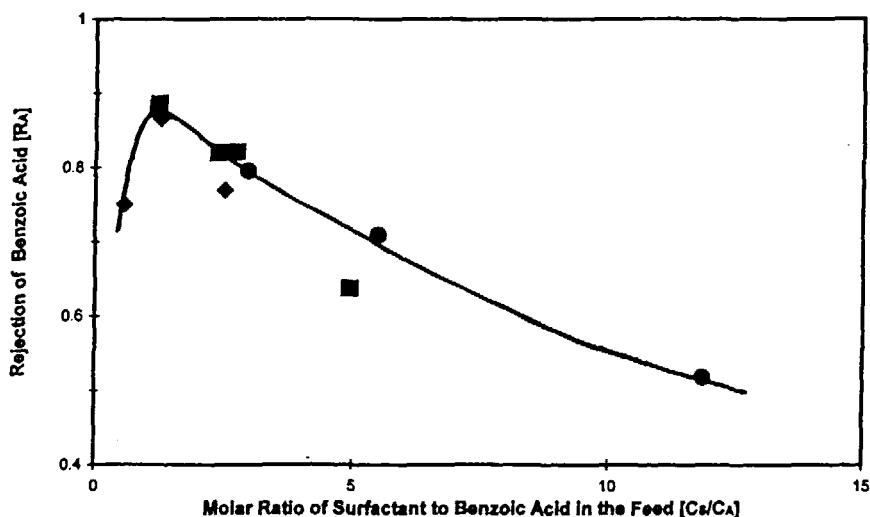| Solute	C_S (mM)	C_A (mM)	Rejection	
			5K MWCO	30K MWCO
Benzoic acid	0	0.8	0.18	0.03
Surfactant	4	0	0.66	0.35
Surfactant	20	0	0.76	0.54

FIG. 5   Rejection of benzoic acid as a function of the molar ratio of surfactant to benzoic acid in the feed for MWCO = 30K and ΔP = 69 kPa ($\bullet$, C_A = 0.8 mM; $\blacksquare$, C_A = 4.2 mM; $\blacklozenge$, C_A = 8.0 mM).

of acid was achieved at a ratio of approximately 1.2 moles of surfactant per mole of benzoic acid. As the ratio of surfactant to benzoic acid was increased further, the rejection of benzoic acid decreased. With increasing ratio, the amount of acid solubilized in each micelle decreased, the polyoxyethylene chains were less extended, and the micelles were smaller. Some of the smallest of the micelles penetrated the membrane, thus reducing the rejection of benzoic acid. At these higher ratios, the rejection of benzoic acid is even lower for the highest surfactant concentration where the solubilization ratio is lower.

The condition for the best rejection of solute is compared to the results of earlier workers in Table 1. The surfactant is very effective for removing benzoic acid. The optimum amount of surfactant per mole or per unit mass of solute is much lower than the amounts of surfactant required for other solutes shown in the table.

Figure 6 shows how the molar ratio of surfactant to benzoic acid in the feed affects the rejection of surfactant for the 30K MWCO membrane operated at a transmembrane pressure of 69 kPa. For surfactant to acid molar ratios less than about 3, the rejection of surfactant was approximately 0.95. This high rejection reflects the fact that most of the surfactant was in the form of micelles and each micelle contained appreciable benzoic acid, thus making large mi-

celles. With increasing molar ratio, the rejection of surfactant decreased. As the molar ratio of surfactant to benzoic acid increased, and as the feed surfactant concentration increased, the amount of benzoic acid solubilized in each micelle decreased, thus shrinking the micelle, as noted above. At high molar ratios, the rejection of surfactant was essentially the same as its rejection in ultrafiltration without acid, i.e., 0.55 as shown in Table 2.

The rejection of benzoic acid is shown in Fig. 7 as a function of the concentration of benzoic acid in the feed for a fixed ratio of surfactant to acid of 1.2. The concentration of surfactant increased from 0.48 to 9.6 mM as the concentration of benzoic acid increased. For benzoic acid concentrations of 4 mM and above, the rejection was essentially constant at 0.89 for the two MWCOs. At lower concentrations the rejection of benzoic acid decreased. The lowest benzoic acid concentration, 0.4 mM, is only 6.7 times larger than the CMC, hence about 15% of the surfactant was not in micellar form, and the fraction of the acid solubilized was less than the fraction solubilized at high surfactant concentration. If it is assumed that the rejection of benzoic acid is proportional to the difference between the surfactant concentration and the CMC and that the rejection at high surfactant concentration is 0.90,
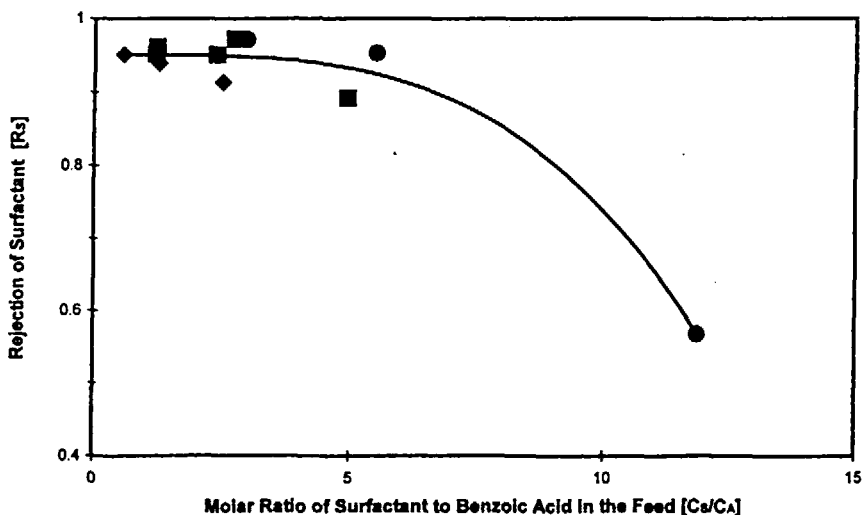

FIG. 6   Rejection of surfactant as a function of the molar ratio of surfactant to benzoic acid in the feed for MWCO = 30K and ΔP = 69 kPa ($\bullet$, C_A = 0.8 mM; $\blacksquare$, C_A = 4.2 mM; $\blacklozenge$, C_A = 8.0 mM).

the rejection of acid would decrease with surfactant concentration as follows.

$$R_A = 0.90 \left(\frac{C_S - \text{CMC}}{C_S} \right) \qquad (5)$$

The curve drawn in Fig. 7 was computed from this equation. The measured rejections were somewhat below the curve at low benzoic acid concentrations, and there was a small effect of MWCO. Another factor reducing the rejection is the size of the micelles. The micelles formed at surfactant concentrations near the CMC probably contained fewer surfactant molecules than the micelles formed at high surfactant concentrations, hence the rejection was lower and there was an effect of MWCO. For these reasons, data for surfactant concentrations below 2 mM are not included in Figs. 5, 6, and 8.

Figure 8 shows the relationship between the rejection of surfactant and the rejection of benzoic acid. Data are shown for three molar ratios of surfactant to benzoic acid in the feed. The equality of rejections is shown by the dashed line. The lines for the three ratios are drawn parallel to the equality line, indicating that the rejection of benzoic acid increased linearly with the rejection of surfactant. The rejection of the acid was below that of the surfactant because unsolubilized acid and, perhaps, small acid-containing micelles
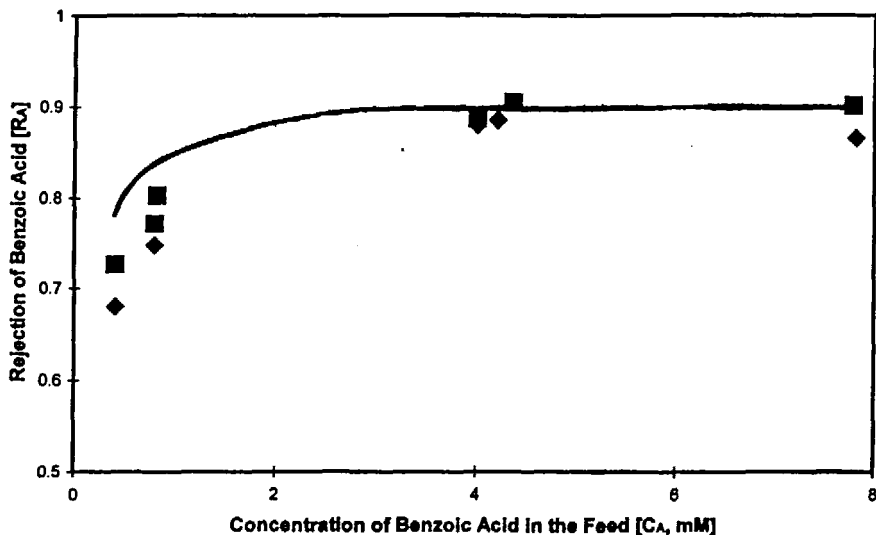

FIG. 7   Rejection of benzoic acid as a function of the concentration of benzoic acid in the feed for $C_S/C_A = 1.2$ and $\Delta P = 69$ kPa (■, MWCO = 5K; ◆, MWCO = 30K).
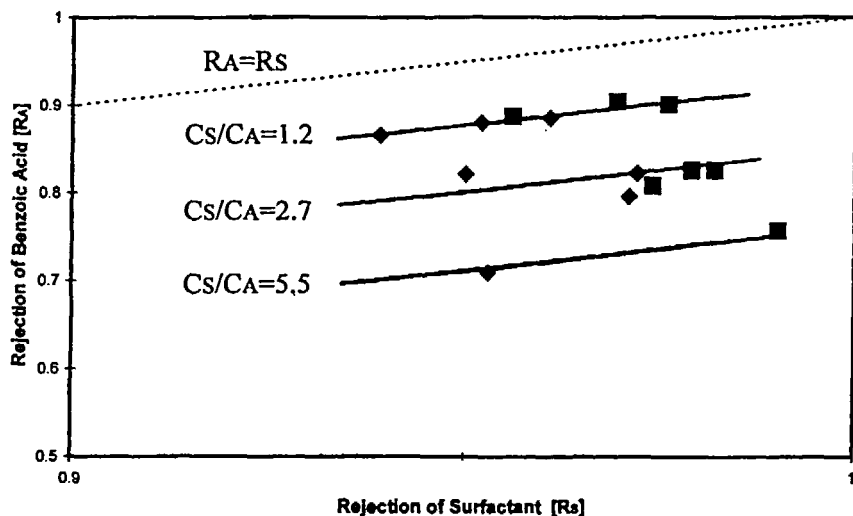
FIG. 8   Rejection of benzoic acid as a function of the rejection of surfactant for ΔP = 69 kPa (■, MWCO = 5K; ◆, MWCO = 30K).

passed through the membrane. Since the surfactant concentrations in this figure were above 2 mM, there was no effect of MWCO.

CONCLUSIONS

A twin-head cationic surfactant was used successfully in micellar-enhanced ultrafiltration of benzoic acid. The surfactant was a tertiary amine with two polyoxyethylene head groups, each with an average of 6 oxyethylene groups and an 18 carbon alkyl tail. The CMC of this surfactant was 0.06 mM, which permitted its use at low concentrations. The maximum solubilization capacity for benzoic acid was 1 mole of acid per mole of surfactant. Ultrafiltration using hollow fiber membranes of 5K and 30K MWCO was carried out at pressures up to 138 kPa. The permeate flux was independent of the concentration of benzoic acid, and it was independent of the concentration of surfactant at concentrations below 4 mM. At low surfactant concentrations, the flux was larger for the 30K MWCO membrane. At surfactant concentrations above 2 mM and below 20 mM, the rejection of benzoic acid was a function only of the ratio of surfactant to benzoic acid in the feed. As this ratio increased, the rejection of acid increased, passed through a maximum, and then decreased. The maximum rejection was 0.89 at a surfactant-to-solute ratio of 1.2. The rejection of surfactant was 0.95 at this condition.

NOMENCLATURE

c_A	concentration of benzoic acid in the permeate
c_S	concentration of surfactant in the permeate
C_A	total concentration of benzoic acid (in the feed)
C	initial concentration of benzoic acid (in semiequilibrium dialysis)
$C_{A,F}$	concentration of free benzoic acid (in the feed)
$C_{A,S}$	concentration of solubilized benzoic acid (in the feed)
C_S	concentration of surfactant (in the feed)
P_i	pressure at tube (feed) inlet
P_o	pressure at tube (reject) outlet
P_p	pressure on shell (permeate) side
R_A	rejection of benzoic acid
R_S	rejection of surfactant

Greek Letter

ΔP transmembrane pressure

ACKNOWLEDGMENTS

REFERENCES

1. P. S. Leung, in *Ultrafiltration Membranes and Applications* (A. R. Cooper, Ed.), Plenum Press, New York, NY, 1979, p. 415.
2. R. O. Dunn Jr., J. F. Scamehorn, and S. D. Christian, *Sep. Sci. Technol.*, *20*, 257 (1985).
3. R. O. Dunn Jr., J. F. Scamehorn, and S. D. Christian, *Ibid.*, *22*, 763 (1987).
4. L. L. Gibbs, J. F. Scamehorn, and S. D. Christian, *J. Membr. Sci.*, *30*, 67 (1987).
5. J.-J. Hong, S.-M. Yang, and C. H. Lee, *J. Chem. Eng. Jpn.*, *27*, 314 (1994).
6. J. H. Markels, S. Lynn, and C. J. Radke, *AIChE J.*, *41*, 2058 (1995).
7. O. K. Gannon, S. Mukherjee, D. J. Mitchell, and D. J. Wilson, *Sep. Sci. Technol.*, *24*, 1073 (1989).
8. M. J., Rosen, *Surfactants and Interfacial Phenomena*, 2nd ed., Wiley, New York, NY, 1989.
9. J. D. Rouse and D. A. Sabatini, *Environ. Sci. Technol.*, *27*, 2072 (1993).
10. M. J. Rosen, *Chemtech*, *23*(3), 30 (1993).
11. S. D. Christian, G. A. Smith, E. E. Tucker, and J. F. Scamehorn, *Langmuir*, *1*, 564 (1985).
12. H. Uchiyama, S. D. Christian, E. E. Tucker, and J. F. Scamehorn, *J. Phys. Chem.*, *97*, 10868 (1993).
13. C. Tanford, *The Hydrophobic Effect*, 2nd ed., Wiley, New York, NY, 1960.
14. S. Gélinas, M.Eng. Thesis, McGill University, Montreal, QC, 1995.