SOLUBILIZATION AND MICELLAR-ENHANCED ULTRAFILTRATION OF o-CRESOL BY SODIUM DODECYL SULFATE MICELLES

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Abstract – The solubilization and the micellar-enhanced ultrafiltration (MEUF) of o-cresol were investigated by using an anionic surfactant, sodium dodecyl sulfate (SDS). In order to study the solubilization behaviour of the solute, the semiequilibrium dialysis (SED) method was employed and stirred-cell ultrafiltration experiments were performed for the test of MEUF. The analysis of the results supported that approximately two surfactant molecules provide a location for the solubilized solute within micelle. In the removal of o-cresol by MEUF, as long as high SDS concentrations in the retentate (>0.2 M) are avoided, relatively good rejection of o-cresol (85 %) could be obtained under the conditions used (initial concentration ratio:[o-cresol]/[SDS]=0.2 and 0.6). Furthermore, the ultrafiltration processes were nearly at equilibrium, so that the permeate concentrations of o-cresol could be predicted from the SED results. The separation efficiency was greater at lower o-cresol concentrations when the SDS concentrations were fixed in the feed, while the rejection increased with increasing the SDS concentrations at constant intramicellar mole fraction of the solute Xc. In addition, as the o-cresol loading of retentate increased, the less SDS in the retentate permeated through ultrafiltration membranes. On the other hand, the higher o-cresol loadings reduced the fluxes of MEUF runs.

INTRODUCTION

Micellar-enhanced ultrafiltration (MEUF) is a separation process using surfactants and membranes which can remove dissolved organic solutes or multivalent ions from water [Christian et al., 1988; Dunn et al., 1985, 1989; Hong et al., 1994; Scamehorn et al., 1989; Klepac et al., 1991]. In this process, surfactant is added to the aqueous stream containing organic solute or metal ions. When surfactants are present at concentrations above the critical micelle concentration (CMC), surfactants aggregate to form micelles, and the micelles solubilize organic solutes or adsorb multivalent metal ions. The solution is then treated in an ultrafiltration device with membrane pore sizes small enough to block the passage of micelles and the effective separations with high fluxes are attained.

In MEUF, the surfactant can be selected depending on the target material to be removed. For the separation of organics in aqueous solutions, either cationic or anionic surfactant may be used as long as the interior of the micelle contains the hydrocarbon chain and form a hydrophobic environment. Then, organic solutes dissolve or solubilize in micelles by hydrophobic association and interactions with the surfactant head groups.

In most of MEUF studies, however, cationic surfactants were employed for organics removal due to the disadvantages of using anionic surfactants; small micelle size, high CMC, and relatively low solubilization capacity [Dunn et al., 1985]. For example, a cationic surfactant hexadecylpyridinium chloride (CPC) was used for the removal of 4-tert-butylphenol [Dunn et al., 1985], phenol [Hong et al., 1994], cresols [Bhat et al., 1987] and benzene [Scamehorn et al., 1989]. On the other hand, for the removal of multivalent heavy metals, anionic surfactants must be employed due to the mechanism of separation. In other words, anionic micelles have a high negative electrical potential on the surface where the metal cations adsorb or bind due to electrostatic attraction. For these reasons, an anionic surfactant sodium dodecyl sulfate (SDS) was utilized in MEUF for the removal of Cu^{2+} [Scamehorn et al., 1986, 1989] and Zn^{2+} [Scamehorn et al., 1989].

In a number of industrial operations (including coal refining, textiles dyes, and synfuel processing), wastewater contains unacceptable concentrations of both dissolved organics and heavy metals. In order to remove dissolved organics and metal ions (cations) simultaneously, it is essential that we employ an anionic surfactant in MEUF. In fact, a study [Dunn et al., 1989] was performed to test the ability of MEUF for simultaneous removal of phenolics (phenol and o-cresol) and a divalent metal cation (Cu^{2+} or Zn^{2+}). According to the work, the removal of organic solute is not significantly affected by the presence of the metal and vice versa. This result is attractive since a single MEUF unit can replace two unit operations for removal of metals and organics. Unfortunately, however, systematic studies on MEUF using anionic surfactant for

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organics removal have not been reported yet.

In the present work, the equilibrium solubilization of organic solute in micelles formed by a typical anionic surfactant (SDS) was investigated using the semiequilibrium dialysis (SED) method. This study aims at obtaining the information on the performance of the MEUF when SDS is used for organics removal. Furthermore, on the basis of the present work, the investigation will be continued in our laboratory on MEUF for the simultaneous removal of organics and metal cations. Accordingly, as a target solute, o-cresol was chosen for making a comparison with the similar studies [Dunn et al., 1989: Bhat et al., 1985]. The study on the equilibrium solubilization is important since the information about equilibrium solubilization of solutes in micelles can be applied directly to predict the results of MEUF separations of organic solutes from water [Bhat et al., 1985, 1987; Morgam et al., 1994]. In addition, the solubilization results can play a major role to understand the properties or structures of micellar solutions. To evaluate the performance of MEUF when SDS is employed, stirred-cell ultrafiltration experiments were conducted and the results were also reported.

EXPERIMENTAL

1. Semiequilibrium Dialysis (SED)

SED experiments were performed as described previously [Christian et al., 1985; Smith et al., 1986; Bhat et al., 1987], using regenerated cellulose membranes (6000 dalton molecular weight cutoff) and ordinary 20-mL equilibrium dialysis cells (Fisher Scientific). The dialysis membranes were washed in distilled water for approximately 8 h before use and placed between the compartments to separate the solutions. Initially, an aqueous solution containing known concentrations of o-cresol and SDS is placed on one side of the membrane (the retentate side) and pure water was added to the permeate side. Sodium dodecyl sulfate (SDS) and o-cresol were obtained from Sigma Chemical Co. They were more than 99 % pure and were used as received. The cells were kept in a desiccator, submerged in a thermostated bath at 30 °C. After 24 h, the concentrations of o-cresol and SDS in the both permeate and retentate sides were determined. The concentration of o-cresol was measured by UV spectroscopy and the concentration of SDS was determined by employing an ethyl violet spectrophotometric determination method [Motomizu et al., 1982; Hirai and Tomokuni, 1985].

2. Ultrafiltration Experiments

The ultrafiltration experiments were performed in a 400 ml batch, stirred cell (Fisher Scientific). The ultrafiltration cell was wrapped in tubing containing circulating water to maintain temperature at 30 °C. Pressure was maintained by nitrogen gas at 414 kPa (60 psig). The membranes were acetate cellulose, 76 mm diameter, membranes (Molecular/Por Type C) from Spectrum. The molecular weight cut-off of the membranes used in the ultrafiltration runs were 10,000 and the flux of pure water through the membranes was 68.1 L/h-m^2 at 414 kPa (60 psig). Initially, the cell was filled with 300 mL of feed solution containing known concentrations of o-cresol and SDS. Agitation speed was held at ap-

proximately 840 rpm. The permeate flux was measured and samples were taken periodically throughout the run. A run was terminated after 200 mL of permeate had been collected. At any time, the permeate concentration was determined experimentally as described above, and the retentate concentration corresponding to the permeate concentration was calculated by a material balance. Viscosities of the solutions of SDS and o-cresol were measured using Cannon-Fenske Routine Viscometers at 30 °C.

SED DATA ANALYSIS

The analysis of the SED results is based on the pseudo phase equilibrium model, which treats the surfactant and dissolved solute in the micelle as a separate condensed phase, existing in thermodynamic equilibrium with monomers of both the organic solute and the surfactant in the bulk aqueous phase [Bhat et al., 1987; Christian et al., 1985; Smith et al., 1986]. In this work, the solubilization equilibrium constant of o-cresol in an aqueous SDS micellar solution (K) is defined as

$$K = X_C/C_C \tag{1}$$

where X_C is the mole fraction of organic solute (o-cresol) in the micellar phase, which is the ratio of the molar concentration of the solubilized solute to the total molar concentration of the surfactant (SDS) and organic solute in the micellar phase. C_C is the molar concentration of monomeric organic solute. Activity coefficients and compositions of the intramicellar solutions in the permeate and retentate compartment of the dialysis cell can be inferred by the equations developed previously [Bhat et al., 1987; Christian et al., 1985; Lee et al., 1990; Smith et al., 1986].

The total concentrations of organic solute and surfactant in either compartment of the SED cell can be expressed as

$$[C]_{tot} = \gamma_C \, X_C \, C_C^0 + (X_C/1 - X_C)[SDS]_{mic} \tag{2}$$

$$[SDS]_{tot} = \gamma_{SDS} \, (1 - X_C) \, C_{SDS}^o + [SDS]_{mic} \tag{3}$$

where $[SDS]_{mic}$ is the concentration of surfactant in the micelle, $[SDS]_{tot}$ denotes the total surfactant concentration, $[C]_{tot}$ is the total solute concentration, C_C^0 is a limiting concentration of the organic compound consistent with the pure component standard state (it is taken to be equal to the solubility of the solute), C_{SDS}^o is the concentration of monomeric surfactant in water (it is taken to be equal to the critical micelle concentration), and γ_{SDS} and γ_C are activity coefficients based on the pure micelle standard state for the surfactant and the pure component standard state for the solute.

If the values of γ_C and γ_{SDS} in Eqs. (2) and (3) are known, it is possible to solve these equations to obtain the values of X_C and $[SDS]_{mic}$. Although several forms have been used to express the relationship between the solubilization equilibrium constant and the mole fraction of organic solute in the micellar phase, it was reported that an excellent correlation can be provided by the equation

$$K = K_0(1 - B \, X_C)^2 \tag{4}$$

where K_O is the value of the solubilization constant in the limit as X_C approaches zero and B is an empirical constant [Lee et al., 1990]. In general, K often varies linearly with X when values of X is less than 0.2. If X is larger than 0.2, a higher order term should be included in the equation such as a general quadratic expression, $K \approx K_O (1+aX+bX^2)$. However, it has been reported that using eq. (4) provided an excellent fit of the solubilization data for numerous systems of polar aromatic solutes by ionic micelles without losing precision, compared to the general quadratic expression [Lee et al., 1990, 1991; Christian et al., 1994]. Therefore, the present study employes Eq. (4) to calculate the γ_C value. The activity coefficient, γ_C, is related by the equation

$$\gamma_C = 1/(K\ C_C^0) = a/(1 - B\ X_C)^2 \qquad (5)$$

where $a = 1/K_O C_C^0$.

If the micelle is assumed to be a pseudo phase, the activity coefficients of the two components can be related by the Gibbs-Duhem equation. By using the Gibbs-Duhem equation and Eq. (5), the activity coefficient of the surfactant, γ_{SDS}, can be expressed by

$$\ln \gamma_{SDS} = \frac{2}{1-B} \{B \ln (1 - X_C) - \ln (1 - B\ X_C)\} \qquad (6)$$

A nonlinear least-squares method [Christian and Tucker, 1982a, 1982b] is used to analyze SED data for each system by Eqs. (2)-(6). First, Eqs. (2) and (3) are solved simultaneously for X_C and $[SDS]_{mic}$, using analytical concentration data for the retentate solutions, trial values of the parameters a and B, known values of the standard concentrations C_{SDS}^0, C_C^0, and activity coefficients obtained from Eqs. (5) and (6). Second, $[SDS]_{mic}$ on the permeate side is estimated by employing a, B, γ_{SDS}, γ_C and eq. (3), assuming that X_C in the permeate solution is the same in the retentate solution. Eqs. (5) and (6) are used with the same values of a and B to predict values of the activity coefficients on the permeate solutions. Third, the predicted concentration of the solute in the permeate is calculated from Eq. (2) for each of the experiments. Finally, a and B are varied to minimize the root mean square deviation between the calculated and the experimental values of $[C]_{tot}$ to obtain the optimum values of the parameters (a and B).

Individual values of K are calculated from the equation [Christian et al., 1985]

$$K = (1 - X_C) \left\{ \frac{[C]_{ret.tot} - [C]_{per.tot}}{[C]_{per.tot} [SDS]_{ret.mic} - [C]_{ret.tot} [SDS]_{per.mic}} \right\} \qquad (7)$$

where the subscripts per and ret refer to the permeate and retentate compartments and the subscript tot indicates total concentration. $[C]_{ret.tot}$ and $[C]_{per.tot}$ are measurable values and X_C and $[SDS]_{ret.mic}$ can be calculated by solving Eqs. (2) and (3), using Eq. (5) and the least-squares value of B. Finally, $[SDS]_{per.mic}$ can be inferred by using Eq. (3), measurable values of $[SDS]_{per.tot}$, γ_{SDS} and B.
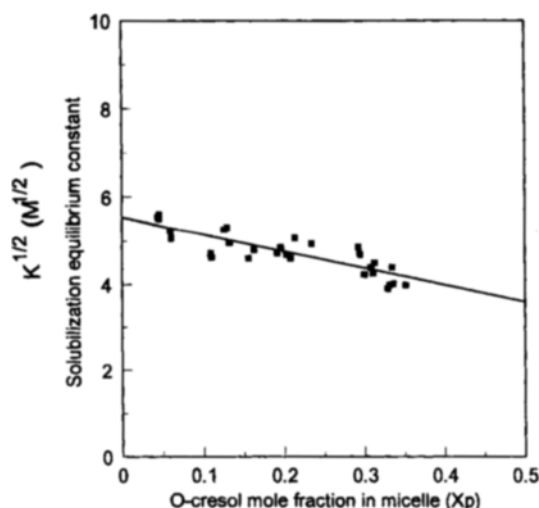

Fig. 1. Dependence of the solubilization equilibrium constant for *o*-cresol in SDS micelles of the intramicellar mole fraction of solute. Solid line calculated with least-squares parameters.

RESULTS AND DISCUSSION

Fig. 1 shows the relationship between the square root of the solubilization equilibrium constant $(K^{1/2})$ as a function of the mole fraction of *o*-cresol in SDS micelles. The model equation to relate K to X_C implies that a plot of the square root of K against X_C is linear with an intercept equals to $(K_O)^{1/2}$ and a slope equals to $-B(K_O)^{1/2}$. In Fig. 1, data are plotted in this way and the straight line is calculated from the least-squares values of B and K_O given in Table 1. As can be seen in the Fig. 1, Eq. (4) provides good representation of data for the system SDS/*o*-cresol.

In the previous studies [Lee et al., 1990; Morgan et al., 1994], it has been shown that the values of K_O and B can be related to constants in the Langmuir adsorption equation. Eq. (4) can be reduced approximately to $K=K_O (1-2BX_C)$ in dilute solutions of the organic solute in the micelle and this is consistent with Langmuir's equation in the form of

$$X_C = K_O\ C_C/(1+2B\ K_O\ C_C) \qquad (8)$$

where C_C is the concentration of monomeric organic solute in the bulk aqueous phase. Then, K_O relates to the strength of interaction of the organic molecule with the micellar surface and 2B is the number of molecules of the surfactant that constitute a "site" for binding the organic solute. The value of 2B for the system SDS/*o*-cresol is 1.68 and it can be inferred that one or two molecules of SDS provide a location for the attachment of a single *o*-cresol molecule. According to the solubilization study [Abe et al., 1993], the values of 2B for the system, 2-phenylethanol (PEA)/SDS and benzyl acetate (BA)/ SDS are 2.52 and 0.54, respectively. Since the smaller values of B are interpreted as indicating that the solute is less strongly bound in the head group region of surfactants [Uchiyama et al., 1994], it appears that *o*-cresol is less tightly anchored in the hydrophilic group re-

Table 1. Least-square parameter for o-cresol in sodium do-decyl sulfate at 30 °C

K_O, $(M^{-1})^a$	Parameter B^b	2B	$RMSD^c \times 10^4$ (M)	C_C^{od} (M)	C_{SDS}^{oe} (mM)
32.1±2.6	0.84±0.01	1.68	5.6	0.24	8.1

[a]Intercept of the plot of the solubilization constant $K^{1/2}$ vs the mole fraction of o-cresol in the celle, X_C.

[b]Parameter in Eq. (4).

[c]Root mean square deviation in o-cresol concentration in the permeate solution, fitted with model described.

[d]Solubility of o-cresol in pure water, defining activity coefficient of o-cresol.

[e]Critical micelle concentration of SDS in pure water defining activity coefficient of SDS.

gion of the SDS micelles than is PEA probably due to the existence of the methyl group in o-cresol. In PEA/SDS, hydroxyl group of PEA may exhibit strong hydrogen-bonding with the hydrophilic group of the micelle. On the other hand, the low value of 2B for BA system indicates that Langmuir's type adsorption model can not be applied to the system.

In Fig. 2, the dependence of activity coefficients of SDS and o-cresol on X_C are given. The information about the activity coefficient of solubilized component and the dependence of γ_C on X_C are very useful since we can determine the environment of o-cresol within the micelles. For example, large values of γ_C indicate that compounds solubilize in environment less favorable than the pure solute state, and near unity values are characteristic of compounds that the environment of a solute is energetically similar to that of the pure component. In addition, values of γ_C less than unity indicate that the micelle strongly attracts the solute [Kondo et al., 1993]. As shown in Fig. 2, as intramicellar mole fraction X_C increases up to 0.4 the activity coefficient of o-cresol increases gradually from 0.13 to 0.3, while γ_C decreases from unity to about 0.7. From the results, it can be inferred that the SDS micelles strongly attract o-cresol. In the case of
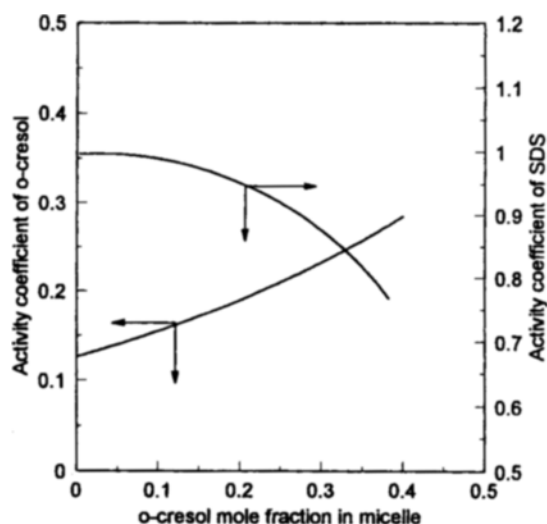
Fig. 2. Dependence of the activity coefficients for o-cresol and SDS on the composition of micelle.
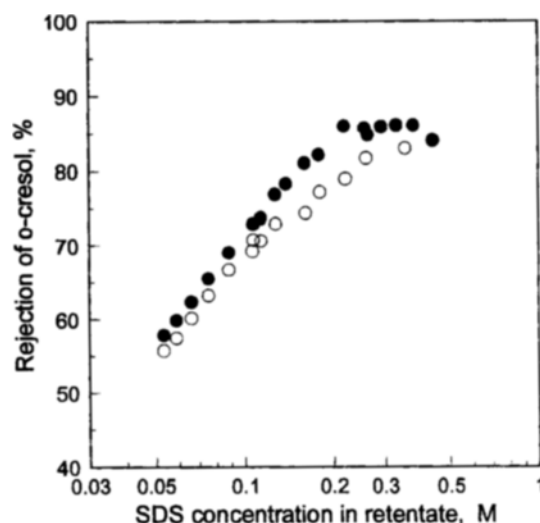
Fig. 3. Rejection % as a function of SDS concentration. Obtained from MEUF runs. Initial ratio of [o-cresol]/[SDS]; 0.2 (●), 0.6 (○).

nonpolar organic solute such as benzene and toluene, the activity coefficients are close to one [Christian et al., 1989]. On the other hand, the values of γ_S indicate that adding an organic compound to an micellar solution lower the activity of the surfactant-that is, decrease the concentration of monomeric or unbound surfactant. This phenomenon is important in MEUF because monomeric surfactant can leak from the retentate to the permeate. Therefore the decrease in monomeric surfactant concentration is favorable in MEUF since the impurity in the permeate can be reduced. When the dependence of K and activity coefficients on X_C are considered, the results of the equilibrium solubilization study support that the present solute, o-cresol, is intermediate in behaviour between a typical solute for Langmuir' type adsorption and a solute solubilized in the core of micelles.

Fig. 3 shows the percentage rejection of o-cresol in MEUF as a function of total SDS concentration in the retentate and the percentage rejection is defined as [Christian et al., 1989; Dunn et al., 1985; Hong et al., 1994]

$$Rejection = (1 - [solute]_{per}/[solute]_{ret}) \times 100 \tag{9}$$

The definition of intramicellar mole fraction gives

$$X_C = \frac{[o-cresol]_{mic}}{[SDS]_{mic} + [o-cresol]_{mic}} \tag{10}$$

and the following equation is also obtained with the definition of K

$$\frac{1-X_C}{K} = \frac{[o-cresol]_{free}}{[o-cresol]_{mic}} \times [SDS]_{mic} \tag{11}$$

where $[o-cresol]_{free}$ is the unsolubilized solute, i.e., the permeate concentration of the solute and $[o-cresol]_{mic}$ is the solubilized solute in the micelles. From the Eq. (11), it can be inferred that the ratio of the concentration of unsolubilized o-cresol to the concentration of o-cresol solubilized by the micelles is proportional to $(1 - X_C)/K$ at fixed SDS concentra-

tions. On the other hand, the ratio is inversely proportional to [SDS]$_{mic}$ under the conditions of constant mole fraction X$_C$. Now, K can be calculated with varying X$_C$ since K is obtained as a function of X$_C$ as shown in Fig. 1. In the case of the system SDS/o-cresol, the calculations revealed that the values of $(1-X_C)$/K increased about 23 % as X$_C$ increased from 0 to 0.5. Accordingly, the separation efficiency becomes greater at lower o-cresol concentrations when the SDS concentrations are fixed in the feed. In fact, it can be observed that the rejections are greater for the runs with lower initial concentration of o-cresol (20 mM) than that for the runs with higher one (60 mM) in Fig. 3. In addition, the relation (11) clearly show that the rejection increases with increasing SDS concentration at a constant X$_C$ as shown in the same plot. As can be seen in Fig. 3, the percentage rejections increase gradually with increasing concentration of SDS in the retentate from approximately 65 % to about 85 %.

Compared to the previous results, the rejections of MEUF by anionic surfactant SDS are lower than that by cationic surfactant CPC (by employing CPC, more than 97 % of rejection of o-cresol was reported [Bhat et al., 1987]). This can be explained by the difference in the charge of head groups between cationic and anionic surfactants. The degree of solubilization is known to be influenced critically by the type of head group of the surfactant [Hong et al., 1994; Lee et al., 1991; Lianos et al., 1984]. The higher rejection of the CPC micelles for o-cresol removal is largely due to the attractive interaction between π-electron cloud of arenes and positively charged surface of the aggregates (micelle). In addition, it should be also noted that the size of CPC is greater than that of SDS. As indicated by Mukerjee [1980], a solubilizate may provide greater stability on larger micelles than smaller ones because the former incorporate a relatively greater number of the solubilizate molecules. This effect may increase the average aggregation number of the surfactant. It has been reported that when the micelles are small, they usually exhibit a narrow size distribution, and the increase in the aggregation number on the addition of a solubilizate is relatively small [Mukerjee, 1980, 1972]. In addition, it can be also expected that the solubilization capacity of the bigger CPC micelles would be greater than that of the smaller SDS micelles by assuming that the solubilization location of the o-cresol is near the surface of the micelles as reported earlier [Lianos et al., 1984 and the present work]. Therefore, the separation performance could be expected to be better in MEUF using CPC rather than SDS due to the greater stability and capacity of CPC micelles.

The concentration of SDS in the permeate is plotted in Fig. 4 as a function of the total concentration of SDS in retentate. As can be seen in Fig. 4, the concentration of SDS in the permeate gradually increases as the retentate SDS concentration increases up to about 0.2 M. However, at retentate SDS concentrations above 0.2 M, the permeate SDS concentrations increase rapidly with the retentate concentrations. This abrupt increase in permeate SDS concentration has been attributed to passage of n-mer (for example, dimers, trimers, and etc.) [Dunn et al., 1985]. Accordingly, in order to prevent the penetration of excess surfactant through membranes,
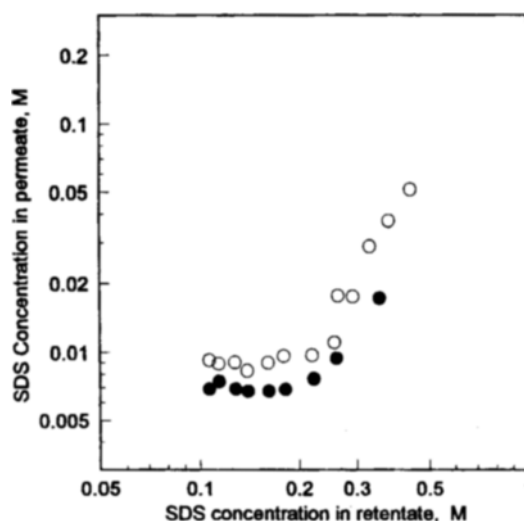

Fig. 4. SDS concentration in permeate obtained from MEUF runs. Initial concentrations: [SDS]=100 mM, [o-cresol]=20 mM (○), 60 mM (●).

it is recommended that SDS concentrations in the retentate should be lower than 0.2 M in practical MEUF runs. In Fig. 4, it can be also observed that the highly loaded system (i.e., at large X$_C$ with 60 mM initial o-cresol) gives lower permeate SDS concentrations than the system of low loading (small X$_C$ with 20 mM o-cresol). The reduction of permeate SDS concentrations for highly loaded system can be attributed to lowering the activity of the surfactant, i.e., decrease in the concentration of monomeric or unbound surfactant as mentioned in the equilibrium solubilization study. In Table 2, the results of MEUF and the predicted permeate solute concentrations are shown. The predicted values were calculated using the equilibrium model used in the present study. The difference between the predicted and the experimental permeate concentrations was about 10 %. These results indicated that the separation processes obtained using MEUF are closely related to equilibrium data. In other words, MEUF runs are performed under nearly equilibrium conditions.

Fig. 5 shows the permeate o-cresol concentration as a function of the retentate SDS concentration. As was the case of SDS, at retentate SDS concentrations above 0.2 M, permeate o-cresol concentrations increase rapidly with retentate concentrations. This may be explained by the fact that some o-cresol is expected to solubilize in the n-mers. The n-mers may be able to penetrate through membranes, and eventually, the permeate o-cresol concentrations increase.

Relative fluxes are plotted in Fig. 6, as a function of SDS concentration in the retentate. As the retentate SDS concentration increases, the relative flux decreases nearly linearly with the logarithm of retentate SDS concentrations. This result indicates that the UF of these colloids obeys classical concentration polarization behavior. In solution concentrated enough for concentration polarization to occur, the flux is a linear function of log [SDS]. Extrapolation of this relationship to the concentration at which the flux becomes zero is the gel concentration. For the present system, the gel concentration is about 520 mM. Therefore, the concentration of

Table 2. Results of MEUF experiments for *o*-cresol in SDS at 30 °C

Intial solute concentration (mM)	Total retentate concentration (M)		Total permeate concentration (M)		Total predicted permeate concentration (M)
	[*o*-cresol]	[SDS]	[*o*-cresol]	[SDS]	[*o*-cresol]
20	2.127 E-02	1.064 E-01	0.435 E-02	1.024 E-02	0.599 E-02
	2.253 E-02	1.138 E-01	0.537 E-02	1.044 E-02	0.605 E-02
	2.476 E-02	1.274 E-01	0.558 E-02	0.900 E-02	0.584 E-02
	2.659 E-02	1.386 E-01	0.552 E-02	1.046 E-02	0.608 E-02
	3.008 E-02	1.600 E-01	0.572 E-02	1.046 E-02	0.609 E-02
	3.313 E-02	1.786 E-01	0.563 E-02	1.137 E-02	0.625 E-02
	3.945 E-02	2.173 E-01	0.593 E-02	1.046 E-02	0.612 E-02
	4.552 E-02	2.547 E-01	0.620 E-02	1.296 E-02	0.653 E-02
	6.005 E-02	3.450 E-01	0.732 E-02	1.509 E-02	0.682 E-02
60	6.358 E-02	1.067 E-01	1.956 E-02	0.690 E-02	1.861 E-02
	6.697 E-02	1.143 E-01	1.967 E-02	0.741 E-02	1.883 E-02
	7.313 E-02	1.284 E-01	1.979 E-02	0.690 E-02	1.854 E-02
	7.819 E-02	1.400 E-01	2.005 E-02	0.673 E-02	1.843 E-02
	8.788 E-02	1.623 E-01	2.013 E-02	0.673 E-02	1.835 E-02
	9.633 E-02	1.817 E-01	2.036 E-02	0.686 E-02	1.836 E-02
	1.138 E-01	2.216 E-01	2.089 E-02	0.762 E-02	1.863 E-02
	1.305 E-01	2.604 E-01	2.225 E-02	0.936 E-02	1.931 E-02
	1.702 E-01	3.531 E-01	2.745 E-02	1.710 E-02	2.253 E-02

Initial SDS concentration; 100 mM
Transmembrane Pressure; 414 kPa (60 psig)

SDS must be lower than 520 mM in operating MEUF runs when SDS is employed. In addition, as the micelles are highly loaded with *o*-cresol, the relative flux is greatly reduced. As Table 3 shows, the viscosity of solutions of *o*-cresol and SDS micelles is a function of solute concentration even at same SDS concentrations. Therefore, it appears that the reduction in flux is probably due to the difference in the solution viscosity since the flux is inversely proportional to the solution viscosity [Michaels, 1968; Mulder, 1995]. Second, the more concentrated solution provides the higher osmotic pressure on the permeate which can reduce a flux in ultrafiltrations. In addition, the higher loading of solute on micelles can lead to the increase in the size of micelles. Accordingly, the pore blocking effect may be pronounced by the micelles when the loading is very high. Therefore, the reduction in flux could be ascribed to the increases in solution viscosity, osmotic pressure and pore-blocking resistance.

CONCLUSION

The relationship between the solubilization equilibrium constant and the mole fraction of *o*-cresol in the SDS micellar phase could be correlated by the expression $K=K_o (1-B X_c)^2$. The analysis of the results from the solubilization equilibrium
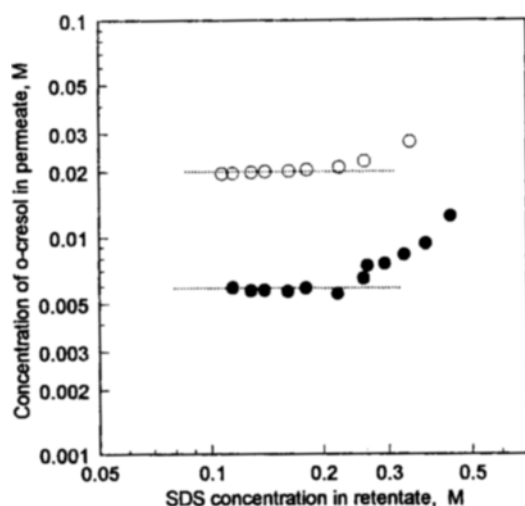

Fig. 5. *o*-Cresol concentration in permeate obtained from MEUF runs. Initial concentration: [SDS]=100 mM, [*o*-cresol]= 20 mM (●), 60 mM (○).
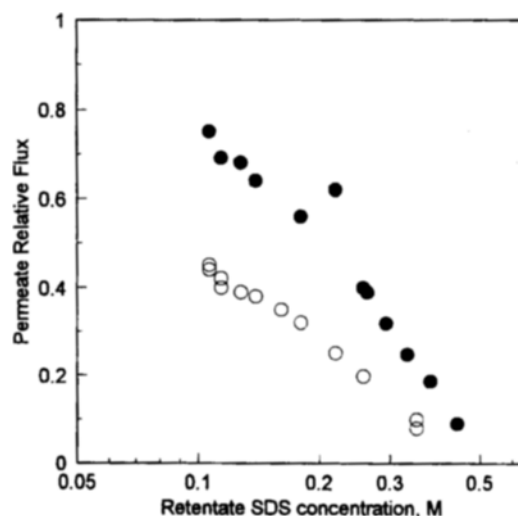

Fig. 6. Relative flux of permeate solution as a function of SDS concentration. Initial *o*-cresol concentration: 20 mM (●), 60 mM (○).

Table 3. Viscosity of solutions of *o*-cresol and sodium dodecyl sulfate micelles at 30 °C

Retentate SDS concentration, mM	Solution viscosity, cP	
	[*o*-cresol]=20 mM	[*o*-cresol]=60 mM
106	1.03	1.24
161	1.22	1.41
257	1.62	1.76
348	2.18	2.21

study supported that approximately two surfactant molecules provide a location for the solubilized solute within micelle.

In the removal of *o*-cresol by MEUF employing SDS micelles, the maximum rejection of 85 % could be attained under the conditions used (initial concentration ratio: [*o*-cresol]/[SDS]=0.2 and 0.6). Furthermore, the separation efficiency was greater at lower *o*-cresol concentrations when the SDS concentrations are fixed in the feed, while the rejection increased as the concentration of SDS increased with constant X_C. However, when SDS concentrations of the retentate was higher than 0.2 M, the performance of MEUF was greatly reduced in permeate purity.

In operating MEUF, the concentration of *o*-cresol in the permeate was nearly equilibrium-controlled, so that the permeate contained concentrations of *o*-cresol approximately equal to the equilibrium permeate concentrations determined by SED. In addition, as the *o*-cresol loading of retentate increased, the permeate concentrations of SDS decreased, i.e., the less SDS permeated through ultrafiltration membranes. On the other hand, when the *o*-cresol loadings were higher, the fluxes of MEUF runs decreased.

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NOMENCLATURE

a   : parameter in Eq. (5)
B   : parameter in Eq. (4)
CPC : hexadecylpyridinium chloride
K   : solubilization equilibrium constant $[M^{-1}]$
K_O : solubilization equilibrium constant in the limit as X_C approaches zero $[M^{-1}]$
MWCO : molecular weight cut-off
SDS : sodium dodecyl sulfate
X_C : intramicellar mole fraction of *o*-cresol

Greek Letters

γ   : activity coefficient
γ_C : activity coefficient of *o*-cresol
γ_{SDS} : activity coefficient of SDS

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