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A STUDY OF COLLOID-ENHANCED ULTRAFILTRATION

Final Progress Report

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EFFORT OF PRINCIPAL INVESTIGATORS ON PROJECT

3/1/90 - 4/30/92

John F. Scamehorn

5% for 11 academic months
33.3% for 3 summer months

Sherril D. Christian

15% for 11 academic months
33.3% for 3 summer months

PUBLICATIONS AND PRESENTATIONS RESULTING
FROM WORK IN PREVIOUS PROJECT PERIOD

Books, Articles, and Book Chapters

Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "On the Terminology for Describing Thermodynamic Properties of Nonideal Mixed Micellar Systems", ACS Symp. Ser., In Press.

Dharmawardana, U.R., Christian, S.D., Taylor, R.W., and Scamehorn, J.F., "An Equilibrium Model for Ligand-Modified Micellar-Enhanced Ultrafiltration using a Water-Insoluble Ligand", Langmuir, In Press.

Tucker, E.E., Christian, S.D., Scamehorn, J.F., Uchiyama, H., Guo, W., "Removal of Chromate from Aqueous Streams by Ultrafiltration and Precipitation", ACS Symp. Ser., In Press.

Scamehorn, J.F., and Harwell, J.H., "Precipitation of Surfactant Mixtures", in Mixed Surfactant Systems (Ogino, K., and Abe, M., Eds.), Marcel Dekker, New York, In Press.

Christian, S.D., Scamehorn, J.F., Tucker, E.E., O'Rear, E.A., and Harwell, J.H., "Novel Colloid-Enhanced Separation Methods for Removing Heavy Metals from Water", in Handbook on Removal of Heavy Metals from Industrial Wastewater (Peters, R.W., Ed.), CRC Press, Boca Raton, Florida, In Press.

Amante, J.C., Scamehorn, J.F., and Harwell, J.H., "Precipitation of Mixtures of Anionic and Cationic Surfactants: II. Effect of Surfactant Structure, Temperature, and pH, J. Colloid Interface Sci., 144, 243 (1991).

Lee, B.H., Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "Effects of an Anionic Polyelectrolyte on the Solubilization of Mono- and Dichlorophenols by Aqueous Solutions of N-Hexadecylpyridinium Chloride, Langmuir, 7, 1332 (1991).

Klepac, J., Simmons, D.L., Taylor, R.W., Scamehorn, J.F., and Christian, S.D., "Use of Ligand-Modified Micellar-Enhanced Ultrafiltration in the Selective Removal of Metal Ions from Water", Sep. Sci. Tech., 26, 165 (1991).

Lee, B.H., Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "Substituent Group Effects on the Solubilization of Polar Aromatic Solutes (Phenols, Anilines, and Benzaldehydes) by N-Hexadecylpyridinium Chloride", J. Phys. Chem., 95, 360 (1991).

Uchiyama, H., Christian, S.D., Scamehorn, J.F., Abe, M., and Ogino, K., "Solubilization of 2-Phenylethanol by Dodecyltrimethylamine Oxide in Aqueous Solution", Langmuir, 7, 95 (1991).

Rathman, J.F., and Christian, S.D., "Determination of Surfactant

Activities in Micellar Solutions of Dimethyldodecylamine Oxide", Langmuir, 6, 391 (1990).

Sasaki, K.J., Christian, S.D., and Tucker, E.E., "Use of a Visible Spectral Displacement Method to Determine the Concentration of Surfactants in Aqueous Solution", J. Colloid Interface Sci., 134, 412 (1990).

Scamehorn, J.F., Christian, S.D., Tucker, E.E., and Tan, B.I., "Concentration Polarization in Polyelectrolyte-Enhanced Ultrafiltration", Colloid. Surf., 49, 259 (1990).

Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "Colloid-Enhanced Ultrafiltration Processes for Purifying Aqueous Streams and Reservoirs", American Environmental Laboratory, 13 (February, 1990).

Lee, B.H., Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "Solubilization of Mono- and Di-Chloro Phenols by Hexadecylpyridinium Chloride Micelles; Effects of Substituent Groups, Langmuir, 6, 230 (1990).

Sasaki, K.J., Christian, S.D., and Tucker, E.E., "Study of the Stability of 1:1 Complexes between Aliphatic Alcohols and β -Cyclodextrin in Aqueous Solution", Fluid Phase Equilibria, 49, 281 (1989).

Mahmoud, F.Z., Higazy, W.S., Christian, S.D., Tucker, E.E., and Taha, A.A., "Solubilization of Hydrocarbons by Surfactant Micelles and Effect of Added Salt", J. Colloid Interface Sci., 131, 96 (1989).

Presentations

Scamehorn, J.F., "Solubility of Anionic Surfactants: Effect of Number of Surfactant Components", 83rd Annual AOCS Meeting, Toronto (May, 1992).

Shiau, B., Harwell, J.H., and Scamehorn, J.F., "Precipitation in Anionic/Cationic/Nonionic Surfactant Mixtures", AIChE Annual Meeting, Los Angeles (November, 1991).

Kachelmyer, C.R., Krehbiel, D.K., Christian, S.D., Scamehorn, J.F., and Tucker, E.E., "Ion-Expulsion Ultrafiltration to Remove Multivalent Ions from Water", AIChE Annual Meeting, Los Angeles (November, 1991).

Roy, R.N., Christian, S.D., Taylor, R.W., Scamehorn, J.F., and Uchiyama, H., "Solubilization of 2,3-Dihydroxynaphthalene by Aqueous Solutions of N-Hexadecylpyridinium Chloride and the Removal of Pb^{2+} from Aqueous Streams by Ligand-Modified Micellar Enhanced Ultrafiltration", Midwest Regional ACS Meeting, Wichita (November, 1991).

Scamehorn, J.F., and Christian, S.D., "Removal of Dissolved Organics and Ionic Species from Water Using Colloid-Enhanced Ultrafiltration Methods", Engineering Foundation Conference on Separation Technology, Kona, Hawaii (October, 1991).

Scamehorn, J.F., "Surfactant Precipitation in Mixed Surfactant Systems", 65th Annual ACS Colloid and Surface Science Symposium, Norman, Oklahoma (June, 1991).

Shiau, B., Harwell, J.H., and Scamehorn, J.F., "Effect of Nonionic Surfactant on Precipitation of Mixtures of Anionic and Cationic Surfactants", 65th Annual ACS Colloid and Surface Science Symposium, Norman, Oklahoma (June, 1991).

Lopata, J.J., and Scamehorn, J.F., "Partial Molar Volumes of Mixed Surfactant Systems as a Measure of Nonideality of Mixed Micelle Formation", 65th Annual ACS Colloid and Surface Science Symposium, Norman, Oklahoma (June, 1991).

Lee, B.H., Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "Solubilization Isotherms for Chlorinated Phenols in Aqueous Solutions Containing a Cationic Surfactant and Excess Concentrations of an Anionic Polyelectrolyte", 65th Annual ACS Colloid and Surface Science Symposium, Norman, Oklahoma (June, 1991).

Shadizadeh, S.B., Schovanic, A.L., Scamehorn, J.F., Taylor, R.W., and Christian, S.D., "Use of Ligand-Modified Micellar-Enhanced Ultrafiltration to Selectively Remove Dissolved Metals from Water", 65th Annual ACS Colloid and Surface Science Symposium, Norman, Oklahoma (June, 1991).

Arshad, S.A., Scamehorn, J.F., and Christian, S.D., "Removal of Chlorinated Hydrocarbons from Water using Micellar-Enhanced Ultrafiltration", 65th Annual ACS Colloid and Surface Science Symposium, Norman, Oklahoma (June, 1991).

Krehbiel, D.K., Scamehorn, J.F., Christian, S.D., and Tucker, E.E., "Ion-Expulsion Ultrafiltration - A Novel Separation for Heavy Metal Removal from Water", 65th Annual ACS Colloid and Surface Science Symposium, Norman, Oklahoma (June, 1991).

Roberts, B.L., Scamehorn, J.F., and Christian, S.D., "Scale-up of Micellar-Enhanced Ultrafiltration for the Recovery of Multivalent Ions from Aqueous Process Water", 65th Annual ACS Colloid and Surface Science Symposium, Norman, Oklahoma (June, 1991).

Simmons, D.L., Taylor, R.W., Scamehorn, J.F., and Christian, S.D., "Use of Alkyl-(Di-2-Picolylamine) in Ligand-Modified Micellar-Enhanced Ultrafiltration for the Selective Removal of Metal Ions from Water", 65th Annual ACS Colloid and Surface Science Symposium, Norman, Oklahoma (June, 1991).

Shiau, B., Harwell, J.H., and Scamehorn, J.F., "Effect of Added Nonionic Surfactant on Precipitation of Mixtures of Anionic and

Cationic Surfactants", 82nd Annual AOCS Meeting, Chicago (May, 1991).

Simmons, D.L., Taylor, R.W., Scamehorn, J.F., and Christian, S.D., "Use of Alkyl-(Di-2-Picolylamine) in Ligand-Modified Micellar-Enhanced Ultrafiltration for the Selective Removal of Metal Ions from Water", 201st National ACS Meeting, Atlanta (April, 1991).

Schovanec, A.L., Taylor, R.W., Scamehorn, J.F., and Christian, S.D., "Use of Ligand-Modified Micellar-Enhanced Ultrafiltration in the Selective Removal of Metal Ions from Water", Southeast/Southwest Regional ACS Meeting, New Orleans (December, 1990).

Krehbiel, D.K., Scamehorn, J.F., and Christian, S.D., "Ion-Expulsion Ultrafiltration - A Novel Separation for Heavy Metal Removal from Water", AIChE Annual Meeting, Chicago (November, 1990).

Lopata, J.J., Scamehorn, J.F., and Harwell, J.H., "Thermodynamics of Adsorption of Surfactant Mixtures on Alumina", AIChE Annual Meeting, Chicago (November, 1990).

Roberts, B.L., Scamehorn, J.F., and Christian, S.D., "Scale-up of Micellar-Enhanced Ultrafiltration in a Spiral Wound Unit", 200th National ACS Meeting, Washington (August, 1990).

Uchiyama, H., Christian, S.D., and Scamehorn, J.F., "Solubilization of Phenethyl Alcohol in Alkylamine Oxide Micelles", 64rd Annual ACS Colloid and Surface Science Symposium, Lehigh University, Bethlehem, (June, 1990).

Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "Solubilization of Aromatic Solutes in Aqueous Solutions Containing Cationic Surfactants and Excess Concentrations of Anionic Polyelectrolytes", 81st Annual AOCS Meeting, Baltimore (April, 1990).

Scamehorn, J.F., and Christian, S.D., "Use of Micellar-Enhanced Ultrafiltration to Remove Dissolved Organics or Heavy Metals from Water", Bulgarian Academy of Sciences Conference on Membrane Separation Processes, Sofia, Bulgaria (March, 1990).

Scamehorn, J.F., "Surfactant-Based Separation Processes", Bulgarian Academy of Sciences Conference on Membrane Separation Processes, Sofia, Bulgaria (March, 1990).

Scamehorn, J.F., "Activities of the Institute for Applied Surfactant Research and Use of Micellar-Enhanced Ultrafiltration to Clean-up Wastewaters", Kerr-McGee Corp., Oklahoma City, (October, 1990)

Scamehorn, J.F., "Activities of the Institute for Applied Surfactant Research and Use of Micellar-Enhanced Ultrafiltration to Clean-up Wastewaters", Conoco Inc., Ponca City, Oklahoma (August, 1990)

Scamehorn, J.F., "Use of Micellar-Enhanced Ultrafiltration to Remove Dissolved Organics or Heavy Metals from Water", Case Western Reserve

University, Cleveland, Ohio (March, 1990).

Scamehorn, J.F., "Use of Micellar-Enhanced Ultrafiltration to Remove Dissolved Organics or Heavy Metals from Water", University of Sofia, Sofia, Bulgaria (March, 1990).

Scamehorn, J.F., "Use of Micellar-Enhanced Ultrafiltration to Remove Dissolved Organics or Heavy Metals from Water", Assen Zlatarov Higher Institute of Chemical Engineering, Bourgas, Bulgaria (March, 1990).

GRADUATE STUDENTS SUPPORTED DURING THIS PROJECT PERIOD

Dissertations and Theses Supported by this Grant

Lori L. Brant, M.S. thesis title: "Effect of Using Surfactant Mixtures on Micellar-Enhanced Ultrafiltration Performance", 4/91.

Mohammad Arshad, M.S. thesis title: "A Study of a New Method of Measuring Monomer-Micelle Equilibrium for Mixed Surfactants in an Aqueous Solution", 5/90.

Benjamin Shiau, M.S. thesis title: "Precipitation of Ternary Mixtures of Surfactants", 6/90.

Byung-Hwan Lee, Ph.D. dissertation title: "Effects of Substituents and Organic Additives on the Solubilization of Polar Aromatic Solutes by Aqueous Surfactant Systems".

Robert Tipton, M.S. thesis title: "Surface Properties of Aqueous Solutions of Cetylpyridinium Chloride", 12/89.

Erika K. Guzman, M.S. thesis title: "F-19 NMR of Fluorocarbon and Hydrocarbon Surfactant Mixtures", 10/89.

David K. Krehbiel, M.S. thesis title: "Ion-Expulsion Ultrafiltration to Remove Ions from Waste Water Streams", 7/90.

Students - Current Graduate Students who have been Supported on this Project.

Connie Keith - Ph.D. student in Chemistry.

Roxanne Ritter - M.S. student in Chemistry

Bruce Roberts - Ph.D. student in Chemical Engineering

ABSTRACTS OF PUBLICATIONS RESULTING FROM THIS PROJECT

In order to indicate in more detail the accomplishments of research during the past year on DOE project DE-FG05-87ER13678, we include verbatim copies of the abstracts of articles published during the past two years.

Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "On the Terminology for Describing Thermodynamic Properties of Nonideal Mixed Micellar Systems", ACS Symp. Ser., In Press.

The term 'regular solution theory' is frequently used to denote models for describing nonideality in aqueous mixed surfactant systems, particularly when activity coefficients of the components follow the Rubingh one-parameter symmetrical activity coefficient relationships. However, this usage is inconsistent with that commonly employed in thermodynamic studies of nonelectrolyte solutions. Although the Gibbs-Duhem equation can with some justification be used to interrelate partial molar quantities for the components of the intramicellar 'pseudophase', the mixture should not be termed 'regular' simply because certain equations relating solute activities to intramicellar mole fractions are observed to apply. The regular solution label should be reserved for systems in which the entropy of formation of mixed micelles at constant volume does approximate that of an ideal solution. Mixed surfactant systems and micellar mixtures containing a single surfactant with an added solute seldom meet the ideal entropy requirement of regular solution theory, so describing these solutions as regular is usually inappropriate.

Dharmawardana, U.R., Christian, S.D., Taylor, R.W., and Scamehorn, J.F., "An Equilibrium Model for Ligand-Modified Micellar-Enhanced Ultrafiltration using a Water-Insoluble Ligand", Langmuir, In Press.

The semi-equilibrium dialysis method has been used to investigate the ionic equilibria occurring in a ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) process. By attaching a C_{12} -hydrocarbon group to an iminodiacetic acid group and incorporating this ligand in a cationic micelle, it is possible to bind Cu^{2+} selectively to the ligand in the retentate and expel Ca^{2+} into the permeate. An ion equilibrium model has been developed to predict the concentrations of the divalent ions in the permeate from known concentrations in the retentate and known experimental parameters, including the binding constants of the divalent metal ion/ligand complexes. In contrast with other micellar-enhanced ultrafiltration processes, addition of salt increases the retention of the bound metal ion. The model explains both the enhanced retention of Cu^{2+} and variations in the extent of expulsion of Ca^{2+} caused by changing the added salt concentration.

Tucker, E.E., Christian, S.D., Scamehorn, J.F., Uchiyama, H., Guo, W., "Removal of Chromate from Aqueous Streams by Ultrafiltration and Precipitation", ACS Symp. Ser., In Press.

The present research seeks to establish an efficient and economic process for removing toxic anions such as chromate, arsenate, and selenate from aqueous streams without requiring addition of large quantities of chemicals. We have established a direct ultrafiltration process which is capable of removing over 99% of chromate ion (CrO_4^{2-}) from an aqueous feed stream. The ultrafiltration process using a cationic polyelectrolyte is also capable of recovering a large fraction of the input stream and producing it as permeate water of high quality under low operating pressures. The polyelectrolyte is separated from the toxic metal by a precipitation step and can be reused. The process should be particularly useful for treating ground water and wastewater streams contaminated with low concentrations of toxic metal anions.

Scamehorn, J.F., and Harwell, J.H., "Precipitation of Surfactant Mixtures", in Mixed Surfactant Systems (Ogino, K., and Abe, M., Eds.), Marcel Dekker, New York, In Press.

Precipitation of surfactants in aqueous solution is a phenomena of great practical importance in such applications as detergency and petroleum production using surfactants. In this chapter, precipitation of anionic surfactants by added monovalent cations and divalent cations or by decreasing temperature is discussed. The tendency of anionic surfactant to precipitate is reduced when nonionic surfactant is added to the system. The concentration of cationic surfactant required to precipitate an anionic surfactant (or vice versa) is shown to increase above the critical micelle concentration of the system. Addition of nonionic surfactant to these anionic/cationic surfactant mixtures reduces the tendency for precipitation to occur. In all of these precipitation reactions, the presence of micelles decreases the tendency for precipitation to occur, since precipitation can be viewed as a competition for monomeric surfactant between micelles and precipitate. Finally, the rate of precipitation is shown to be on the order of several minutes to reach equilibrium for pure anionic surfactant precipitated by calcium and on the order of thirty minutes for anionic/cationic surfactant mixtures. In both cases, there is a period of inhibition during which little precipitation occurs. The more supersaturated a system is, the faster the precipitation reaches an equilibrium level.

Klepac, J., Simmons, D.L., Taylor, R.W., Scamehorn, J.F., and Christian, S.D., "Use of Ligand-Modified Micellar-Enhanced Ultrafiltration in the Selective Removal of Metal Ions from Water", Sep. Sci. Tech., 26, 165 (1991).

Ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) is a membrane-based separation technique which can selectively remove specific ions from an aqueous solution containing several ions of like charge. In LM-MEUF, surfactant and amphiphilic ligand are added to the contaminated water. The surfactant forms aggregates called micelles, and the ligand is selected to complex the ion of interest and to solubilize strongly in the micelles. The result is micelles containing a high fraction of the ligand and the target ion. If the surfactant is chosen to have the same charge as the target ion, other ions in solution with this same charge will not associate with the micelles, making the retention of ions by the micelles very selective. The solution is then passed through an ultrafiltration membrane with pore sizes small enough to block the passage of micelles. In this study, divalent copper is the target ion in a solution also containing divalent calcium. A cationic surfactant is used with *N*-n-dodecyl-iminodiacetic acid as the copper-specific ligand. Rejections of copper of up to 99.2% are observed, with no rejection of calcium, showing that LM-MEUF has almost perfect selectivity, as well as high capacity in this case.

Lee, B.H., Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "Substituent Group Effects on the Solubilization of Polar Aromatic Solutes (Phenols, Anilines, and Benzaldehydes) by *N*-Hexadecylpyridinium Chloride", J. Phys. Chem., 95, 360 (1991).

Solubilization isotherms of polar aromatic solutes (phenols, anilines, and benzaldehydes) in *N*-hexadecylpyridinium chloride micelles have been determined at 25 °C by using the semiequilibrium dialysis method. Effects of various substituent groups (H, F, Cl, Br, CH₃O, NO₂, CH₃, Et, *i*-Pr, and CF₃) have been studied for the solubilization of phenol, aniline, and benzaldehyde derivatives in aqueous solutions of the surfactant. Both hydrophobic and electrostatic effects are shown to be important in influencing the solubilization behavior. The simple expression, $K = K_0(1 - BX)^2$, is used to correlate the solubilization equilibrium constant (K) with the mole fraction of solute in the micelles (X). Linear free energy relationships can be used to correlate the solubilization results for the different classes of compounds.

Uchiyama, H., Christian, S.D., Scamehorn, J.F., Abe, M., and Ogino, K., "Solubilization of 2-Phenylethanol by Dodecyldimethylamine Oxide in Aqueous Solution", Langmuir, 7, 95 (1991).

The solubilization of 2-phenylethanol (PEA) was measured over a wide range of solute activities and pH values by using dodecyldimethylamine oxide (DDAO) as the surfactant. The DDAO in micellar form is all cationic (protonated) at low pH and all nonionic at high pH. At intermediate pH levels, the DDAO forms mixed micelles containing both the cationic and nonionic forms of surfactant. Thus, measurement of the solubilization of PEA as a function of pH produces solubilization data as a function of mixed micelle composition for this amphoteric surfactant. The solubilization equilibrium constant was found to decrease with increasing mole fraction of PEA in the micelle for all pH values and to be less in the mixed micelles than in either pure cationic or pure nonionic micelles. This latter effect could be due to the hydrophilic region of the mixed micelle being more compact than that of the single-component micelles.

Rathman, J.F., and Christian, S.D., "Determination of Surfactant Activities in Micellar Solutions of Dimethyldodecylamine Oxide", *Langmuir*, 6, 391 (1990).

The pseudophase separation model is used to describe pH and concentration effects on dimethyldodecylamine oxide (DDAO) solutions. If the protonated and neutral species are treated as separate surfactants, an amine oxide surfactant can be modeled thermodynamically as a binary mixture, the composition of which is varied by adjusting the solution pH. With the Gibbs-Duhem equation written for the micelle pseudophase, activities of the surfactant species at concentrations greater than the critical micelle concentration (cmc) can be calculated directly from experimental titration curves. It is not necessary to introduce an "apparent" pK_a for the surfactant in micellar form.

Sasaki, K.J., Christian, S.D., and Tucker, E.E., "Use of a Visible Spectral Displacement Method to Determine the Concentration of Surfactants in Aqueous Solution", *J. Colloid Interface Sci.*, 134, 412 (1990).

A substitution method in which phenolphthalein is displaced from the β -cyclodextrin cavity by the hydrocarbon moiety of a surfactant is used to determine the concentration of the surfactant. The 1:1 complex of phenolphthalein with β -cyclodextrin has an absorbance practically equal to zero in the region of the 550-nm band of the basic form of phenolphthalein. When solute molecules containing an alkyl moiety displace some of the phenolphthalein at a pH of approximately 10.5, the absorbance at 550 nm is significantly increased and serves as a direct measure of the concentration of the solute. The method is useful in determining concentrations of surfactants such as sodium dodecyl sulfate and *N,N*-dimethyl-*N*-dodecylamine oxide, which do not contain chromophores. © 1990 Academic Press, Inc.

Scamehorn, J.F., Christian, S.D., Tucker, E.E., and Tan, B.I., "Concentration Polarization in Polyelectrolyte-Enhanced Ultrafiltration", *Colloid. Surf.*, 49, 259 (1990).

Polyelectrolyte-enhanced ultrafiltration (PEUF) is a new method of removing ions from water. In PEUF, a polyelectrolyte of opposite charge to the target ion is added to solution and the target ion binds to the polymer. The polyelectrolyte is then removed from the water by ultrafiltration. The resulting permeate solutions are quite pure, with measured rejections in excess of 99%. In this work, a solution containing copper was treated using PEUF with poly(styrene sulfonate) as the anionic polyelectrolyte over a wide range of polymer concentrations. As the retentate becomes more concentrated in polyelectrolyte, the rejection decreases and the flux decreases. However, even with concentrated retentate solutions, the rejections remain high (96% was the lowest rejection observed here). Fluxes only decline sharply when the concentration in the retentate is quite high. Hence, classical concentration polarization behavior is observed in PEUF, but it is not severe in the operating range of practical importance, indicating the promise of PEUF as an industrial separation process.

Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "Colloid-Enhanced Ultrafiltration Processes for Purifying Aqueous Streams and Reservoirs", *American Environmental Laboratory*, 13 (February, 1990).

The ultrafiltration of aqueous solutions, to which surfactants or polyelectrolytes have been added, can produce effluent streams practically free from impurities. Micellar systems are effective in removing both molecular and ionic impurities, and polyelectrolytes can be used to remove ionic species. Direct methods, in which the impurities remain in the retentate in ultrafiltration, and indirect methods, in which species are actually expelled into the permeate, are described.

Lee, B.H., Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "Solubilization of Mono- and Di-Chloro Phenols by Hexadecylpyridinium Chloride Micelles; Effects of Substituent Groups, Langmuir, 6, 230 (1990).

Semiequilibrium dialysis measurements have been made to determine solubilization equilibrium constants and activity coefficients of mono- and dichlorophenols in aqueous solutions of hexadecylpyridinium chloride (CPC) at 25 °C. Solubilization equilibrium constants (which relate the concentration of solubilize in the micelle to the concentration of free organic in the "bulk solution") are well correlated by the expression $K = K_0(1 - BX)^2$, where B is an empirical constant, K_0 is the limiting value of the solubilization constant, and X is the mole fraction of the phenol present in the surfactant micelles. Values of B are reasonably well linearly correlated with $\ln K_0$, making it possible to predict entire solubilization isotherms from values of K obtained in the region of small X values. The effect of adding chloride groups is to increase the value of K at any value of X , although positional effects are also important. K_0 and B tend to be larger for compounds having chloro groups meta and para to the phenolic OH group.

Sasaki, K.J., Christian, S.D., and Tucker, E.E., "Study of the Stability of 1:1 Complexes between Aliphatic Alcohols and β -Cyclodextrin in Aqueous Solution", Fluid Phase Equilibria, 49, 281 (1989).

A substitution method, in which the 1:1 complex between β -cyclodextrin (cycloheptaamylose) and phenolphthalein forms competitively with a β -cyclodextrin-alcohol complex, has been used to obtain equilibrium constants for complexes of the C_4 to C_{16} alcohols and several other compounds containing aliphatic moieties. The logarithm of the complex formation constant is found to vary nearly linearly with the number of carbon atoms in a series of n -aliphatic alcohols. Similar results are obtained for β -cyclodextrin complexes of two C_{12} surfactants (sodium dodecylsulfate and hexa-ethyleneglycol monododecyl ether), cyclohexanol, and 1,10-decanediol.

Mahmoud, F.Z., Higazy, W.S., Christian, S.D., Tucker, E.E., and Taha, A.A., "Solubilization of Hydrocarbons by Surfactant Micelles and Effect of Added Salt", J. Colloid Interface Sci., 131, 96 (1989).

Highly precise vapor pressure/solubility measurements have been obtained for benzene, cyclohexane, and hexane in aqueous solutions of the cationic surfactant hexadecyltrimethylammonium bromide and the anionic surfactant sodium dodecanoate at temperatures varying from 25 to 45°C. The effect of added salt (NaBr for the cationic and NaCl for the anionic surfactant) has also been investigated at 35 and 45°C. The dependence of the solubilization equilibrium constant and of the activity coefficient of the solute on intramicellar composition has been inferred. © 1989 Academic Press, Inc.

SUMMARY OF PAST WORK

Colloid-enhanced ultrafiltration methods are a new class of water purification techniques which have been developed by our group at the University of Oklahoma¹⁻²⁷. The methods are designed to remove dissolved ions and/or organic molecules from water, in applications as diverse as industrial and home water purification units, wastewater and groundwater clean-up, and ship-board water treatment.

Leung²⁸ was the first to propose using surfactant micelles to enhance the ultrafiltration of organic compounds from water, but with the exception of one other publication in the literature²⁹, all other published reports of research on the use of this technique (for removing organic solutes from aqueous streams) have originated from our laboratories^{1,2,4-8,11-13,18,25}. The removal of multivalent ions, including metals, from water using MEUF as a chemical engineering unit operation was introduced by our research group and we have published all the papers on this application^{3,7-10,12,13,17,18,19-24,26}.

Figure 1 is a schematic diagram indicating how MEUF is used to remove both organic solutes and multivalent metal cations (either separately or simultaneously) from water. An anionic

Figure 1. Micellar-enhanced ultrafiltration (MEUF) for organic and metal ion removal.

surfactant is first added to the water at concentrations well above the critical micelle concentration (CMC) (i. e., the concentration level at which aggregates of surfactant molecules called micelles begin to form in significant amounts). For many surfactants in aqueous solution, the critical micelle concentration is in the range 0.00001 M to 0.01 M, and the micelles contain approximately 50 to 150 molecules of surfactant.

The interior of a micelle is a hydrocarbon-like environment. Organic solutes tend to dissolve or 'solubilize' within the micelles. When anionic surfactants are used in MEUF, the head group regions of the micelle are negative, and the micelle surface has a highly-negative electrical potential. Metals forming multivalent ions in solution (e. g., copper, lead, or aluminum) will preferentially bind to the oppositely charged micellar surface by electrostatic attraction. Conversely, when cationic surfactants are used, negative ions like chromate will bind to the positively-charged micellar surface. If a feed solution containing the added surfactant is forced through an ultrafiltration membrane having pore diameters small enough to block the passage of the micelles, the organic molecules and metal ions bound to the micelles are also prevented from entering the stream that passes through the membrane (the permeate). The concentrations of the organic molecules, metal ions, and surfactants in the permeate correspond very nearly to their uncomplexed species concentrations in the solution retained by the membrane (the retentate)^{1,2,6,7,9,11}.

In a properly-designed MEUF process, the permeate concentrations of all the target solute species will be quite small; the solute in the permeate can often have a concentration two orders of magnitude smaller than in the feed^{10,11}. The permeate stream can in many cases be discharged directly to the environment or reused in an industrial plant. The concentrated waste present in the retentate will contain almost all of the original solutes, in a volume which can be a small fraction of the original feed water. MEUF can be staged to attain any required degree of separation⁷.

Table 1 includes results obtained by using MEUF to remove both organic solutes and inorganic ions; anionic surfactants are used to remove the cations, cationic surfactants are used to remove anions, and either class of surfactant can be employed to remove neutral species. For

almost all of the solute species, low permeate concentrations and quite large rejections are observed. The organic solutes of low solubility tend to be removed most efficiently in MEUF.

Table 1. Comparison of Permeate Concentrations of Organic and Metal Pollutants in MEUF

<u>Pollutant</u>	<u>Pollutant Concentration in Permeate (mM)</u>	<u>Rejection (%)</u>
Phenol	1.42	94.3
m-Cresol	0.526	97.9
4-Tert-Butylphenol	0.0767	99.7
Benzene	2.33	90.7
Toluene	0.80	96.8
n-Heptanol	0.323	98.7
n-Octanol	0.141	99.4
Zinc (II)	0.037	99.9
Copper (II)	0.037	99.9
Cadmium (II)	0.037	99.9
Chromate (-II)	0.030	99.9

Conditions: Retentate [Pollutant] = 25mM; Retentate [Surfactant] = 250mM; Pressure = 414 kPa; Membrane = 1 K to 20 K Molecular Weight Cutoff; Temperature = 30 °C; Rejection (%) = $100\{1 - [\text{Permeate}]/[\text{Retentate}]\}$

A major result of our studies of the use of MEUF in removing organic solutes is that the concentration of a solute passing from the retentate into the permeate is practically equal to the concentration of the monomeric or free solute - i. e., the concentration of the solute not bound to micelles. Therefore, we have been able to use information about the equilibrium solubilization of solutes by surfactant micelles to predict a priori the efficiency of MEUF in removing these solutes from aqueous streams^{1,2,5-7,11}. Our automated vapor pressure apparatus^{5,30-35} and a new general method, semi-equilibrium dialysis (SED)^{6,11,36-42}, as well as traditional head-space chromatography⁴³ have been used to determine reliable values of solubilization isotherms for organic solutes in several types of micellar systems. Several hundred solubilization isotherms have been obtained for various organic solutes, throughout wide ranges of solute activity, in anionic, cationic, and nonionic surfactant solutions at concentrations varying from 0.01 M to 0.6 M, at temperatures varying from 15 to 45 °C. Accurate and extensive solubilization results have been accumulated for numerous organic compounds, including many substances that are

dangerous pollutants in wastewaters⁴⁴. Our development of SED has made it possible routinely to investigate the solubilization of organics which are not volatile enough to be studied with the vapor pressure or head space chromatography methods.

We have used detailed mass action models to correlate and explain solubilization results for systems for which extensive results of sufficient accuracy are available^{33,34}. We have also applied the pseudo-phase equilibrium theory to describe complicated aqueous solutions containing surfactants and organic solutes and to understand the behavior of solubilization isotherms at various temperatures and various concentrations of surfactants^{1,2,5,6,11,30-42}. Finally, we have used this large data base to develop a group contribution method to predict the solubilization constants for organic solutes of arbitrary structure in anionic or cationic surfactant micelles^{11,45}. As a result, procedures are now available for estimating the efficiency of removal of organic solutes in actual MEUF separations, using only knowledge of the structural formulas of these compounds¹¹.

We proposed and subsequently demonstrated that MEUF can be used to remove either anionic or cationic multivalent ionic species that bind to surfactant micelles^{3,7-10,12,13,17,18,19-24,26}. For example, we have investigated the removal of a number of cations, including zinc, nickel, copper, lead, and calcium, and several anions, including chromate, and the cyano-complexes of iron and nickel. A new equilibrium model, combining the simple two-phase polyelectrolyte theory of Oosawa⁴⁶ with thermodynamic activity, material-balance, and charge-balance equations has been quite successful in predicting the ability of MEUF to remove dissolved cations and anions from aqueous streams^{9,10,18,20,26}. The equilibrium assumption mentioned above, which has been valuable in predicting the efficiency of MEUF in removing dissolved organic species, seems to apply equally well in estimating the concentrations of ionic species passing through the ultrafiltration membrane. Thus, semi-equilibrium dialysis experiments produce results in essential agreement with MEUF data for several aqueous ionic solute/ionic surfactant systems^{3,9,10}. Organic solutes and metal ions have been removed simultaneously in MEUF processes using anionic surfactants¹³.

Concentration polarization effects have been investigated in detail for stirred cell and

spiral wound ultrafiltration units, and gel points have been determined for anionic, cationic, and nonionic surfactants^{1,2,10,25,26}. In Figure 2 relative flux data are plotted as a function of colloid

Figure 2: Relative flux for MEUF and PEUF (5 000 MWCO membrane)

concentration in the retentate, for an anionic surfactant (sodium dodecylsulfate), a cationic surfactant (cetylpyridinium chloride), and a polyelectrolyte (polystyrenesulfonate)¹⁵. These results show that the relative fluxes remain large until the retentate solution becomes quite concentrated (> 0.3 M surfactant), that the concentration polarization obeys accepted gel polarization ultrafiltration models [i.e., flux vs. $\log(\text{retentate concentration})$ is linear], and that gel point concentrations are quite large (ca. 0.6 M colloid). Electrostatic repulsion between micelles or polyelectrolytes may help prevent coagulation in the gel layer next to the membrane, so that gel polarization is not severe in these systems. This observation is supported by the fact that somewhat poorer fluxes are obtained when using nonionic surfactants in MEUF separations²⁵.

One weakness of MEUF in some applications is that it does not remove ions selectively except on the basis of charge (e.g., Ca^{2+} is removed with approximately the same rejection as Cu^{2+}). Therefore, as a variation of MEUF, we have recently developed a technique (ligand modified micellar-enhanced ultrafiltration or LM-MEUF) which can be used to achieve

substantial selectivity in removing like-charged ions^{19,20,23}. In LM-MEUF, ligands chemically bound to hydrophobic groups are added to the aqueous stream, along with the surfactant, prior to the ultrafiltration step. The ligands become incorporated in the surfactant micelles through solubilization of their hydrocarbon groups. The modified micelles are capable of selectively removing particular metal cations, for example Cu^{2+} , Pb^{2+} , and Cd^{2+} , in the presence of other ions of the same charge which are not significantly complexed by the ligand. It has even been possible to use a cationic surfactant, containing a ligand that is selective for Cu^{2+} , to sequester copper in the retentate while expelling Ca^{2+} into the permeate stream by a Donnan effect, a phenomenon responsible for the operation of ion-expulsion ultrafiltration, IEUF (see later).

A diagram of polyelectrolyte-enhanced ultrafiltration (PEUF) is shown in Figure 3.

Figure 3. Schematic of Polyelectrolyte-Enhanced Ultrafiltration.

PEUF is similar to MEUF, but it uses a polyelectrolyte (instead of an ionic surfactant) as the colloid added to the aqueous stream to bind pollutants of opposite charge^{14,15,18,21,22}. In the subsequent ultrafiltration step, the ions bound to the polyelectrolyte will remain in the retentate solution. In using PEUF to purify aqueous streams, virtually none of the polyelectrolyte passes through the ultrafilter; therefore, there is no limiting lower concentration (such as the critical micelle concentration for aqueous surfactants) below which PEUF will become ineffective. An important advantage of PEUF, in comparison with almost all other separation methods, is that

it becomes more effective (gives a higher % rejection) as concentrations of the target ions and of the polyelectrolyte decrease. Thus, in PEUF separations using solutions containing a fixed mole ratio of an anionic polyelectrolyte to Cu^{2+} , the percentage removal of copper from the permeate stream becomes greater with increasing dilution, the relative separation efficiency continuing to improve even at very low polyelectrolyte concentrations. As is shown in Figure 2, the relative flux in PEUF can be even greater than in MEUF under comparable conditions. As a result, when the solution to be treated requires only the removal of multivalent inorganic ions, PEUF is preferred over MEUF because no colloid leaks through the membrane into the permeate.

Ion-expulsion ultrafiltration is a technique that we recently developed to remove ions (multivalent or monovalent) having the same charge as a polyelectrolyte or micellar species added to an aqueous stream^{16,18-20,27}. A flow diagram showing an IEUF configuration that could be used to purify an aqueous stream is shown in Figure 4. In this scheme, the charged colloid

Figure 4. Ion-expulsion Ultrafiltration Process.

exerts an 'ion-expulsion effect' on all ions having the same charge, thus causing these ions to pass through the membrane into the permeate stream at concentrations much greater than in the feed. If the system is well designed, a small fraction of the original feed solution passing

through the membrane will contain almost all of the target ion. When the remaining retentate solution is ultrafiltered in a second membrane unit, the permeate from the second stage will be practically pure water, and the retentate will contain almost all of the original colloid in concentrated form. An important advantage of IEUF is that the ion which is expelled into the first permeate solution is thereby removed from contact with the colloid, which remains in the final retentate solution, ready for reuse. In the example shown in Figure 4, an anionic colloid is used to expel cyanide ions (CN^-). In general, polyelectrolytes will be chosen in preference to surfactants in IEUF to avoid any leakage of colloid into the permeate.

Equilibrium separations attainable with IEUF (as determined by dialysis experiments) can potentially enhance concentrations of target ions to exceed feed concentrations by factors of tens or hundreds. However, the IEUF process is diffusionaly-limited, not equilibrium-limited as is the case with MEUF, LM-MEUF, and PEUF. These diffusional effects can limit dynamic UF-separations to efficiencies considerably lower than equilibrium separations^{16,18,27}. Therefore, the configuration of the ultrafiltration unit and operating conditions substantially influence separation results.

Figure 5 shows the dependence of separation efficiency in the removal of chromate by

Figure 5: Percent of Chromate Removed at Various Applied Pressures in a Batch Stirred Cell

IEUF, using polystyrenesulfonate as the colloid²⁷. At the higher applied pressures, the separation efficiencies are somewhat poorer, although the efficiency can be improved by using spiral-wound or hollow-fiber UF units instead of a stirred cell. When the applied pressures and fluxes are low, the process will operate nearly at equilibrium and separations will be best. For example, in an experiment with a stirred-cell UF unit at 10 psig applied pressure, when 10% of the feed solution volume had been removed as permeate, the permeate solution contained 18% of the total chromate originally present in the feed²⁷. In another experiment, with a hollow-fiber UF apparatus operated at 10 psig, using a sodium polycarboxylate polyelectrolyte, it was possible to remove 78% of the CrO_4^{2-} in a permeate containing a volume equal to 18% of the feed volume⁴⁷.

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