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A STUDY OF COLLOID-ENHANCED ULTRAFILTRATION

FINAL REPORT

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COLLOID-ENHANCED ULTRAFILTRATION FOR WATER PURIFICATION

SUMMARY OF RESULTS OF PROJECT FROM 1984-1993

Our research group has been funded for nine years to study colloid-enhanced ultrafiltration processes for water clean-up by the Office of Basic Energy Sciences. The following is a short summary of what we have achieved in these nine years in developing this technology and the underlying scientific principles which govern its application.

Micellar-Enhanced Ultrafiltration

Removal of Dissolved Organics

The initial project funded was to study the use of micellar-enhanced ultrafiltration (MEUF) to remove dissolved organics from water. This involves adding surfactant to the polluted water under conditions in which micelles (aggregates of approximately 50 to 100 surfactant molecules) are formed. Organic pollutants dissolve in the hydrophobic core of the micelles (solubilization). The solution is then treated by ultrafiltration with membrane pore sizes small enough to block the micelles (and solubilized organics) from passing into the permeate.

The feasibility of this technology has been established for removal of a number of organic molecules (e.g., phenolics, cresols, benzene, chlorinated volatile organics) [1-8]. First, it was established that micelles can be effectively blocked from passage through membrane pores of up to 50,000 MWCO (no leakage is observed for a 20,000 MWCO membrane and a small level of leakage is observed for a 50,000 MWCO membrane) [1,2]. The second important principle to be established was that the organic solute concentration in the permeate is equal to the unsolubilized organic concentration in the retentate except at extremely high surfactant concentrations- the separation is essentially at equilibrium under reasonable operating conditions [1-8]. This permits equilibrium solubilization data to be used to predict the efficiency of the separation (membrane rejection). As a result, extremely high rejections of solutes can be attained in MEUF - for example, tert-butylphenol shows rejections of 99.8 % [1,2].

A systematic investigation of the concentration polarization characteristics of MEUF showed the classical semilogarithmic plot of flux vs. retentate surfactant concentration commonly observed in ultrafiltration [1,2]. The surfactant concentration at which the relative flux becomes unacceptably low has been shown to be approximately 0.25 M for cationic [1,2] or anionic [8] surfactants. This is high enough to allow

high water recovery levels (permeate/feed) when the retentate is treated until this concentration is reached. However, nonionic surfactants cause worse flux reduction making these ineffective for practical separations [8]. There are advantages to the use of surfactant mixtures (anionic/nonionic surfactants) under some conditions [10].

Spiral wound ultrafiltration units have been shown to yield almost the same rejections and fluxes (per unit area of membrane) as a stirred cell unit [8,9]. This makes scale-up of MEUF straightforward so the substantial data base published based on stirred cell apparatus can be used for design of industrial spiral wound units. It also allows the faster and less expensive stirred cell experiments to be used to test the method on a particular waste water stream with confidence that the data can be used for scale-up.

Economic calculations have shown that the surfactant must be recycled for reuse in order for MEUF to be an economical separation. Therefore, much recent effort has gone to finding techniques to treat the retentate for surfactant recovery. In one specific application, we considered a problem where the trichloroethylene (TCE) concentration had to be reduced from a low concentration (ca. 10 ppm) by two orders of magnitude in polluted groundwater (to ca. 100 ppb) [8]. One characteristic of MEUF is that the separation efficiency does not become worse as more dilute streams are treated (as does some other methods such as bioremediation). In this case, vacuum stripping is the method used to remove the TCE from the retentate to allow recycle of the concentrated surfactant stream from the bottoms of the stripping column. The result of this is a process which yields only a pure TCE stream (for reuse or disposal) and a small level of surfactant in the permeate (about 20 ppm). Economic evaluations have shown that this process is approximately economically competitive with stripping the entire polluted groundwater stream. Since MEUF is a new technology, the potential for improvement is substantial compared to a mature technology such as vacuum stripping.

MEUF can be staged so that any degree of purification is possible. The more stages, the higher the capital cost, but the more pure the permeate or the higher the water recovery. For example, in the aforementioned example of 99 % of removal of TCE from water, four stages were found to be optimum [8].

As a result of the finding that equilibrium solubilization data can be used to predict rejections in MEUF, our group has spent substantial time in studying the phenomena of solubilization of a variety of organic solute types in a variety of surfactant solutions [11-25]. The ultimate goal of these studies is to permit a priori estimation of the solubilization equilibrium constant for solutes of arbitrary structure in several surfactant solutions. For example, we have developed a group contribution method for estimating solubilizations of compounds

in a model anionic surfactant (sodium dodecyl sulfate) and a model cationic surfactant (cetylpyridinium chloride) [33]. In addition to development of a large data base for solubilization data, one of the most significant contributions of this study of solubilization is the development of a new method of measuring solubilization as a function of solute activity or concentration called semi-equilibrium dialysis [11-15]. This method can be used to measure volatile or involatile solutes and other research groups have adopted the technique. Development of this analytical technique should help advance the knowledge of solubilization in the future. The co-PIs of this project are editing a book on "Solubilization in Surfactant Solutions", the first book on the topic in more than 20 years [26].

Removal of Dissolved Ionic Compounds

A major discovery made early in this project was the realization that the phenomena of counterion binding on micelles composed of charged surfactants could be used to remove charged target compounds from water. Counterion binding is the adsorption of oppositely charged ions to the surface of the charged micelles [27]. These ions are then retained in the retentate solution upon ultrafiltration [7,28-32]. Heavy metals with multivalent charge such as lead, copper, cadmium, or nickel have been shown to be removed with a 99.7% rejection with an anionic surfactant [28,29,31,32]. Metallic complexes with multivalent charge such as chromate can be removed using cationic surfactants [30,31]. We have modified the Oosawa model for counterion binding on polyelectrolytes to describe that on micelles and it shows an excellent capability of predicting rejection in removal of multivalent inorganic compounds by MEUF [30-32]. Flux behavior in this application is essentially the same as in organic compound removal (already discussed) [13].

A major advantage of MEUF is that both multivalent metals or metallic complexes and organics can be removed simultaneously. Since two processes would normally be required to attain this separation using traditional technologies (e.g., carbon adsorption and ion exchange), use of MEUF allows use of one unit operation instead of two.

Polyelectrolyte-Enhanced Ultrafiltration

One disadvantage of MEUF is that the unmicellized portion of surfactant (monomer) does leak through the membrane into the permeate. There are several solutions to this, such as using a low MWCO membrane for a polishing ultrafiltration on the permeate product [8], foam fractionation, or ion exchange.

If the only target solute is a multivalent ionic species, this whole problem can be avoided by using a water soluble

polyelectrolyte instead of micelle-forming surfactant. The target ion binds to the oppositely charged polymer and the molecular weight of the polyelectrolyte is chosen to be sufficient so that it is rejected by ultrafiltration membranes. This new separation technique is polyelectrolyte-enhanced ultrafiltration (PEUF). In PEUF, no leakage of the colloid into the permeate occurs as it does with surfactants. We have demonstrated that PEUF can remove either cationic divalent metals such as copper or divalent anions such as chromate using PEUF with rejections of 99.7% (approximately the same as with MEUF) [33-37]. Concentration polarization is very similar to that observed in MEUF as well [34]. As with MEUF, the separation is nearly at equilibrium under practical conditions [33]. Not only are we looking at wastewater/groundwater clean-up, but PEUF could be used in municipal or residential units for water softening [37].

In the practical application of PEUF, precipitation can be used for recycle of the polymer. For example, in clean-up of groundwater polluted with chromate, barium nitrate can be added to the retentate and after filtering the precipitating barium chromate, the resulting concentrated polyelectrolyte solution can be recycled for reuse [17].

The largest scale test of any colloid-enhanced ultrafiltration process was performed in spring of 1993. Polluted groundwater from a Coast Guard base in Elizabeth City, North Carolina was treated on-site by us using the PEUF/precipitation process to remove the chromate from the water. The pilot unit used was operated for 5 days with an average removal of >99% of the chromate from 750 gallons of water treated. A prefilter was needed to remove particulate matter from the feed water. This very successful test showed that this technology is not just a laboratory curiosity, but can be used to clean-up real world waters. We hope that subsequent work will involve more such field tests on the path to commercialization of the technology.

Ion-Expulsion Ultrafiltration

The two methods discussed so far, MEUF and PEUF, are direct methods in that the colloid attaches to the target solute and causes it to be retained behind the membrane. Another colloid-enhanced ultrafiltration developed in this project is ion-expulsion ultrafiltration (IEUF) [38,39]. In IEUF, a colloid (either micelle forming surfactant or polyelectrolyte) is added to the water containing a target charged solute of the same charge as the colloid. Repulsion between the similarly charged colloid and target solute causes the solute to become concentrated in the permeate relative to the retentate. This effect can be described at equilibrium by a Donnan equilibrium calculation [38,39]. Since the ion expulsion effect is being used, this is known as an indirect method. Unlike the direct methods, IEUF can be far from equilibrium because the target

solute must diffuse through the solution to the membrane to reach the permeate. Hence, pressure has a substantial effect on the separation efficiency as well as the ultrafiltration apparatus type (spiral wound vs. stirred cell) [39]. In fact, this effect can be taken advantage of in that either retention or repulsion can be observed, depending on operating conditions. Scenarios have been developed in which units can be configured so that this effect can be utilized in engineering design of a staged process. A major advantage of IEUF is that no downstream separation of colloid from target solute needs to be performed as in the direct methods since the target solute is both concentrated and separated from the colloid in the ultrafiltration step. A major disadvantage is that high ionic strengths of the solution reduce the effectiveness of the process substantially.

Ligand-Modified Micellar-Enhanced Ultrafiltration

A disadvantage of the colloid-enhanced ultrafiltration methods is that they show little selectivity other than the tendency of an organic solute to solubilize or the tendency of a ion to bind to a colloid. This latter tendency of the ion to bind is based almost solely on its charge. Therefore, calcium and copper are removed with almost the same efficiency in MEUF or PEUF [32]. Often, in real world applications, some ions need to be removed from water, but other ions of the same charge need not be removed. In order to introduce selectivity to MEUF, ligands with a large tendency to solubilize and to complex the target ion can be introduced with the surfactant. If the surfactant is of the same charge sign as the target ion, an infinite selectivity is attainable. For example in ligand-modified micellar-enhanced ultrafiltration (LM-MEUF), a cationic surfactant with a copper specific ligand can result in a rejection of copper in excess of 95% with calcium being expelled into the permeate [40]. In other words, the copper is concentrated in the retentate and calcium is concentrated in the permeate. We have successfully modeled this phenomena accounting for the various equilibria occurring as well as looked at several types of systems [41,42]. This work was mostly funded by NSF, but is an outgrowth of the early MEUF work funded by DOE on this project.

Polyelectrolyte/Surfactant - Enhanced Ultrafiltration

We have already mentioned the problem of surfactant leakage into the permeate in MEUF. If an organic is the target solute, surfactant must be present for solubilization to occur. If a mixture of surfactant and polyelectrolyte of opposite charge is added to solution, these can form complexes with as great an ability to solubilize organic solutes (per mole of surfactant aggregated) as micelles [43-45]. However, these complexes are in equilibrium with surfactant monomer which has a concentration

one to two orders of magnitude lower than that in equilibrium with micelles. Hence, by using the polyelectrolyte/surfactant complex, surfactant leakage can be reduced by at least an order of magnitude. Concentration polarization is even less severe than in PEUF or MEUF, so fluxes are high in these systems [44].

Supporting Research

We have already mentioned the large body of solubilization literature which our group has generated to support the work on micellar-enhanced ultrafiltration. One of the most promising methods of recovering surfactant from retentate streams is by precipitation [46]. We have investigated surfactant precipitation phenomena over the last decade [47-55] and this knowledge has helped us pursue this technological solution.

The funding of these colloid-enhanced ultrafiltration process studies by DOE have allowed us to establish ourselves as leaders in the area of surfactant-based separation processes. We have promoted these new important class of separations through book chapters, review articles and books [56-61]. These publications help get this new technological area accepted in the scientific/engineering community and will aid in ultimate commercialization.

Relation to Energy

Liquid phase membrane separations are generally low energy. Since flux has been shown to be high for colloid-enhanced ultrafiltration techniques, extraordinary means are not needed to maximize turbulence and reduce concentration polarization. Therefore, colloid-enhanced ultrafiltration methods involve very low energy consumption - really just the energy to pump the water through the membrane unit. The downstream separation processes to recover colloid from retentate or polish permeate are also generally low energy processes, such as precipitation/filtering. The one exception is the use of vacuum stripping for volatile organic solute treatment - however, the alternative here is to strip the entire polluted water stream. By first using MEUF to concentrate the pollutant, the stream to be stripped is reduced by about 80 % [8]. Therefore, the colloid-enhanced ultrafiltration methods can replace much more energy intensive techniques. Alternatively, a much lower volume of waste can be attained by the ultrafiltration techniques. To attain the same small volume of waste, the waste emitted from competitive techniques might have to be evaporated, for example, giving a great energy advantage to the ultrafiltration methods.

Summary

Over the past nine years of funding by DOE Office of Basic Energy Sciences, we have developed a whole family of methods under the umbrella of colloid-enhanced ultrafiltration techniques. These methods can be used for removal of either dissolved organics or multivalent ions from water or both simultaneously. We have gone from very fundamental studies of the ultrafiltration process to a field test using actual polluted groundwater.

The orientation of this research has been to ultimate development of a workable, economical process. To do this, we have tried to understand the underlying fundamental phenomena involved in the separation and in potential solutions to technological bottlenecks and developed new scientific knowledge in the process. However, the thrust of the investigations have been focused on bringing the technology to a successful adoption by industry. We feel that these methods are on the verge of commercialization as a result of the nine years of DOE support.

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58. Scamehorn, J.F., and Harwell, J.H., "An Overview of Surfactant-Based Separation Processes", in *Surfactants in Emerging Technologies* (M.J. Rosen, Ed.), Marcel Dekker, New York, 1987, p. 169.

59. Scamehorn, J.F., and Harwell, J.H. (Editors), *Surfactant-Based Separation Processes*, Marcel Dekker, New York, Surfactant Science Series, Vol. 33 (1989).

60. 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).

61. 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.

**PUBLICATIONS AND PRESENTATIONS RESULTING
FROM WORK FROM NOVEMBER, 1991 TO DECEMBER 1993**

Journal Articles and Book Chapters

Uchiyama, H., Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "Solubilization and Separation of p-tert-Butylphenol Using Polyelectrolyte/Surfactant Complexes in Colloid-Enhanced Ultrafiltration", J. Colloid Interface Sci., In Press.

Uchiyama, H., Tucker, E.E., Christian, S.D., Scamehorn, J.F., "Solubilization of Trichloroethylene by N-Hexadecylpyridinium Chloride Micelles", J. Phys. Chem., In Press.

Christian, S.D., Tucker, E.E., Scamehorn, J.F., and Uchiyama, H., "On the Interpretation of Solubilization Results Obtained from Semi-Equilibrium Dialysis Experiments", Colloid Polym. Sci., In Press.

Scamehorn, J.F., El-Sayed, D.A., Uchiyama, H., and Younis, S.S., "Removal of Divalent Metal Cations and Their Mixtures from Aqueous Streams Using Micellar-Enhanced Ultrafiltration", Sep. Sci. Tech., 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.

Uchiyama, H., Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "A Modified Semi-Equilibrium Dialysis Method for Studying Solubilization in Surfactant Micelles - Testing the Semi-Equilibrium Assumption", J. Phys. Chem., **97**, 10868 (1993).

Dharmawardana, U.R., Christian, S.D., Tucker, E.E., Taylor, R.W., and Scamehorn, J.F., "A Surface Tension Method for Determining Binding Constants for Cyclodextrin Inclusion Complexes of Ionic Surfactants", Langmuir, **9**, 2258 (1993).

Abe, M., Mizuguchi, K., Ogino, K., Uchiyama, H., Scamehorn, J.F., Tucker, E.E., and Christian, S.D., "Solubilization of Perfume Compounds by Pure Surfactants and Mixtures of Surfactants", J. Colloid Interface Sci., **160**, 16 (1993).

Kondo, Y., Abe, M., Ogino, K., Uchiyama, H., Tucker, E.E., Scamehorn, J.F., and Christian, S.D., "Stability of Surfactant Vesicles Formed from Cationic Didoecyldimehtylammonium Bromide", Colloid Surf. B: Biointerfaces, **1**, 51 (1993).

Kondo, Y., Abe, M., Ogino, K., Uchiyama, H., Scamehorn, J.F., Tucker, E.E., and Christian, S.D., "Solubilization of 2-Phenylethanol in Surfactant Vesicles and Micelles", Langmuir,

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, 1993, p. 283.

Roberts, B.L., Scamehorn, J.F., Christian, S.D., Tucker, E.E., and Uchiyama, H., "Use of Micellar-Enhanced Ultrafiltration with Vacuum Stripping to Remove Trichloroethylene from Polluted Water", *Proceedings of the International Membrane Science and Technology Conference* (Fane, A.G., Ed.), Centre for Membrane Science and Technology University of New South Wales, Sydney, Australia (1992) p. 163.

Simmons, D.L., Schovanec, A.L., Scamehorn, J.F., Christian, S.D., and Taylor, R.W., "Ligand-Modified Micellar-Enhanced Ultrafiltration for Metal Ion Separations: Use of N-Alkyltrialamines", in *Environmental Remediation: Removing Organic and Metal Ion Pollutants* (Vandegrift, G.F., Reed, D.T., and Tasker, I.R., Eds.), ACS Symp. Ser., Vol. 509 (1992), p. 180.

Tucker, E.E., Christian, S.D., Uchiyama, H., Guo, W., Scamehorn, J.F., and Puls, R.W., "Toxic Anion Removal from Aqueous Streams", 3rd Annual Conference on Groundwater Quality Research, Dallas, June, 1992, p. 271.

Krehbiel, D.K., Scamehorn, J.F., Ritter, R., Christian, S.D., and Tucker, E.E., "Ion-Expulsion Ultrafiltration to Remove Chromate from Wastewater", *Sep. Sci. Tech.*, **27**, 1775 (1992).

Scamehorn, J.F., and Harwell, J.H., "Understanding Krafft Point Variations in Mixed Surfactant Systems", *Proceedings of the 3rd International Surfactants Congress & Exposition*, Gardiner-Caldwell, Macclesfield, England, Section C (1992) p. 91.

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Tucker, E.E., Christian, S.D., Scamehorn, J.F., Uchiyama, H., Guo, W., "Removal of Chromate from Aqueous Streams by Ultrafiltration and Precipitation", in *Transport and Remediation of Subsurface Contaminants: Colloidal, Interfacial, and Surfactant Phenomena* (Sabatini, D.A., and Knox, R.C., Eds.), ACS Symp. Ser., Vol. 491 (1992), p. 84.

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*, **8**, 414 (1992).

**Presentations at Meetings Sponsored by National
and International Organizations**

Scamehorn, J.F., and Christian, S.D., "Surfactant Recovery from Remediation of Subsurface Contamination", 207th ACS Annual Meeting, San Diego (March, 1994).

Roberts, B.L., Scamehorn, J.F., Christian, S.D., Tucker, E.E., and Uchiyama, U., "Use of Micellar-Enhanced Ultrafiltration to Remove Trichloroethylene from Water", 8th International Conference on Surface and Colloid Science, Adelaide, Australia (February, 1994).

Haskins, C.J., and Scamehorn, J.F., "Modification of Krafft Temperatures of Surfactants Using Surfactant Mixtures", 8th International Conference on Surface and Colloid Science, Adelaide, Australia (February, 1994).

Haskins, C.J., and Scamehorn, J.F., "Modification of Krafft Temperatures or Solubility of Surfactants Using Surfactant Mixtures", 67th Annual ACS Colloid and Surface Science Symposium, Toronto (June, 1993).

Roberts, B.L., Scamehorn, J.F., Christian, S.D., Tucker, E.E., and Uchiyama, U., "Use of Micellar-Enhanced Ultrafiltration with Vacuum Stripping to Remove Trichloroethylene from Polluted Water", 67th Annual ACS Colloid and Surface Science Symposium, Toronto (June, 1993).

Haskins, C.J., and Scamehorn, J.F., "Modification of Krafft Temperatures or Solubility of Surfactants Using Surfactant Mixtures", 84rd Annual AOCs Meeting, Anaheim (April, 1993).

Tabatabai, A., Scamehorn, J.F., and Christian, S.D., "Water Softening Using Polyelectrolyte-Enhanced Ultrafiltration", 205th National ACS Meeting, Denver (March, 1993).

Roberts, B.L., Scamehorn, J.F., Christian, S.D., Tucker, E.E., and Uchiyama, U., "Use of Micellar-Enhanced Ultrafiltration with Vacuum Stripping to Remove Trichloroethylene from Polluted Water", International Membrane Science & Technology Conference, Sydney, Australia (November, 1992).

Christian, S.D., Uchiyama, H., Tucker, E.E., Roberts, B.L., and Scamehorn, J.F., "Solubilization of Several Chlorinated Hydrocarbons by Nonionic and Ionic Surfactant Micelles in Dilute Aqueous Solutions", 204th National ACS Meeting, Washington, (August, 1992).

Christian, S.D., Tucker, E.E., Scamehorn, J.F., and Uchiyama, H., "The Interpretation of Solubilization Results Obtained from Semi-Equilibrium Dialysis Experiments", 9th International Symposium on Surfactants in Solution, Varna, Bulgaria (June, 1992).

Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "Use of Polyelectrolyte/Surfactant Complexes in Colloid-Enhanced Ultrafiltration", 9th International Symposium on Surfactants in Solution, Varna, Bulgaria (June, 1992).

Harwell, J.H., and Scamehorn, J.F., "Understanding Krafft Point Variations in Mixed Surfactant Systems", 3rd International Surfactants Congress & Exposition, London (June, 1992).

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", 66th Annual ACS Colloid and Surface Science Symposium, Morgantown, West Virginia (June, 1992).

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

Guo, W., Tucker, E.E., Christian, S.D., and Scamehorn, J.F., "Removal of Anionic Surfactants from Aqueous Streams by Ultrafiltration using Soluble Cationic Polyelectrolytes", 83rd Annual AOCS Meeting, Toronto (May, 1992).

Tucker, E.E., Christian, S.D., Scamehorn, J.F., Uchiyama, H., and Guo, W., "Removal of Chromate from Contaminated Groundwater and Industrial Process Streams Using Polyelectrolyte-Enhanced Ultrafiltration", 203rd National ACS Meeting, San Francisco (April, 1992).

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", 203rd National ACS Meeting, San Francisco (April, 1992).

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", ACS Meeting, San Francisco (April, 1992).

Theses and Dissertations

Bruce L. Roberts, Ph.D. dissertation title: "A Study of Surfactant-Based Separation Processes", 9/93.

Susan B. Shadizadeh, M.S. thesis title: "A Study of Ligand-Modified Micellar-Enhanced Ultrafiltration to Selectively Separate Copper from Wastewater Streams", 6/92.

Jeffrey J. Lopata, Ph.D. dissertation title: "A Study of the Thermodynamic Properties of Surfactant Mixtures: Mixed Micelle

Formation and Mixed Surfactant Adsorption", 4/93.

Dharmawardana, Udeni, R., PhD dissertation title: "An Equilibrium Model for Ligand-Modified Micellar-Enhanced Ultrafiltration Selective Separation of Metal Ions Using Iminoacetic Substituted Polyamins and a Theoretical Model for the Titration Behavior of Polyamines", 1/93.

Morgan, M., M.S. thesis title: "Solubilization of Pentanol By Cationic Surfactants and Binary Mixtures of Cationic Surfactants", 6/93.

Uchiyama, H., Tucker, E.E., Christian, S.D., Scamehorn, J.F., "Solubilization of Trichloroethylene by N-Hexadecylpyridinium Chloride Micelles", J. Phys Chem., In Press.

An automated vapor pressure method has been used to obtain solubilization isotherms for trichloroethylene (TCE) in N-hexadecylpyridinium chloride (CPC micelles, throughout a wide range of solute activities and at temperatures varying from 15°C to 45°C. The simple empirical expression $K + K_0(1 - \alpha X + \beta X^2)$ is used to correlate the solubilization equilibrium constant (K) with the mole fraction of TCE in the micelles (X) at each temperature. The solubilization equilibrium constant has a maximum value at approximately 30°C, the temperature at which the solubility of TCE in water is a minimum. Activity coefficients are also reported for TCE in the micelle; these values increase slightly with increasing mole fraction of TCE. The general solubilization behavior of TCE in CPC micelles resembles that of benzene or toluene in CPC, suggesting that TCE solubilizes in ionic micelles both within the hydrocarbon micellar interior and phenol derivatives, indicating that TCE is not as tightly anchored in the head-group region of the CPC micelles as are more polar solutes such as phenol and chlorinated phenols. With increasing temperature, the tendency of TCE to solubilize with the hydrocarbon core region of the micelles increases, relative to its tendency to solubilize in the micellar surface region.

Christian, S.D., Tucker, E.E., Scamehorn, J.F., and Uchiyama, H., "On the Interpretation of Solubilization Results Obtained from Semi-Equilibrium Dialysis Experiments", Colloid Polym. Sci., In press.

The interpretation of intramicellar solubilization data obtained from semi-equilibrium dialysis (SED) experiments is described, and methods are presented for determining equilibrium constants for the solubilization of organic species by aqueous surfactant within the micelle. The solubilization equilibrium, constant of an organic solute in an aqueous micellar solution (K) is defined as the ratio of the mole fraction of organic solute in the micellar 'pseudophase' (X) to the concentration of the unsolubilized monomeric organic solute in the aqueous phase (c_0). Expressions compatible with the Gibbs-Duhem equation are used to represent the concentration dependence of activity coefficients of both the solubilize and surfactant in the micellar pseudophase; the analysis leads to calculated values of the concentration of free and intramicellar surfactant and organic solute in both compartments of the equilibrium dialysis cell. Solubilization equilibrium constants for many amphiphiles are well correlated by the simple expression $K + K_0(1 - BX)^2$, where B is an empirical constant and K_0 is the limiting value of K as S approaches 0.

Scamehorn, J.F., El-Sayed, D.A., Uchiyama, H., and Younis, S.S., "Removal of Divalent Metal Cations and Their Mixtures from Aqueous Streams Using Micellar-Enhanced Ultrafiltration", Sep. Sci. Tech., In Press.

Micellar-enhanced ultrafiltration (MEUF) is a novel membrane based separation technique that can be used to remove multivalent metal cations from aqueous streams. In this technique an anionic surfactant is added to the aqueous stream containing the metal cations to be removed. The surfactant forms highly charged aggregates called micelles onto which the metal cations adsorb or bind. The aqueous stream is then passed through an ultrafiltration membrane with pores small enough to block the passage of the micelles and adsorbed metal cations. In this study, MEUF has been shown to remove divalent cadmium, zinc, copper, and calcium ions and their mixtures with recoveries of at least 96%. A previously developed equilibrium binding model describes the result successfully. Under reasonable conditions the flux rates are not substantially below that of pure water, indicating the feasibility of MEUF for industrial application.

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.

A new class of separation methods utilizing dissolved colloids has been developed to remove heavy metal ions from industrial wastewater. All of these methods exploit the tendency of moderately high molecular weight colloidal species (for example, micelles, admicelles, polyelectrolytes, and surfactant polymer complexes) to attract ions or molecules of certain types or alternatively to repel ions having a charge opposite that of the colloid. The present chapter describes the use of *indirect* ultrafiltration methods (micellar-enhanced ultrafiltration and polyelectrolyte ultrafiltration) in which impurities remain associated with colloid in the retentate, and an *indirect* method (ion expulsion ultrafiltration), in which ionic species are expelled by the charged colloid into the permeate. Included is a description of admicellar chromatography, in which admicelles (adsorbed micelles) that are reversibly formed on the surface of a packing material can bind metal ions from a contaminated aqueous stream.

Uchiyama, H., Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "A Modified Semi-Equilibrium Dialysis Method for Studying Solubilization in Surfactant Micelles - Testing the Semi-Equilibrium Assumption". J. Phys. Chem., **97**, 10868 (1993).

The detailed analysis of data obtained with the semiequilibrium dialysis (SED) method for studying solubilization in surfactant micelles requires accounting for the formation of micelles in the permeate compartment and for the presence of solubilized organic solute in these micelles. An extension of the SED method is proposed here, in which the concentration of surfactant is maintained well above the critical micelle concentration of surfactant is maintained well above the critical micelle concentration (cmc) in both compartments of the dialysis cell. Under these conditions, it is shown that the validity of the "semiequilibrium" assumption, viz., that the organic solute reaches equilibrium simultaneously, with both surfactant solution, can be demonstrated for solutions of small organic molecules and typical ionic surfactants. Agreement of the new results with those obtained in conventional SED results (obtained using a concentrated surfactant solution on one side of the dialysis membrane and pure water on the other) implies that semiequilibrium is ordinarily attained in SED studies of low molecular weight solutes such as phenol and its derivatives. It is also suggested that the new modification of the SED method has important mathematical and experimental advantages over conventional SED in inferring equilibrium solubilization results.

Dharmawardana, U.R., Christian, S.D., Tucker, E.E., Taylor, R.W., and Scamehorn, J.F., "A Surface Tension Method for Determining Binding Constants for Cyclodextrin Inclusion Complexes of Ionic Surfactants", Langmuir, **9**, 2258 (1993).

A new method has been developed for determining binding constants of complexes of cyclodextrins with surface-active compounds, including water-soluble ionic surfactants. The technique requires measuring the change in surface tension caused by addition of a cyclodextrin (CD) to aqueous solutions of the surfactant. Surface tension results are reported for three different surfactants (sodium dodecyl sulfate (SDS), cetylpyridinium chloride (CPC, and cetyltrimethylammonium bromide (CTAB)) in the presence and the absence of added β -CD. Data for CPC have been obtained at surfactant concentrations below and above the critical micelle concentration. Correlations between surface tension and surfactant activity are expressed by the Szyszkowski equation, which subsumes the Langmuir adsorption model and the Gibbs equation. It is observed that the surface tension increases monotonically as β -cyclodextrin is added to ionic surfactant solutions. At concentrations of CD well in excess of the surfactant concentration, the surface tension approaches that of pure water, indicating that neither the surfactant-CD complexes nor of the Szyszkowski equation and mass action constraints relating to the formation of micelles from monomers of the surfactant and the counterion. Evidence is given that two molecules of CD can complex the C-16 hydrocarbon chain of the cetyl surfactants.

Abe, M., Mizuguchi, K., Ogino, K., Uchiyama, H., Scamehorn, J.F., Tucker, E.E., and Christian, S.D., "Solubilization of Perfume Compounds by Pure Surfactants and Mixtures of Surfactants", J. Colloid Interface Sci., **160**, 16 (1993).

The solubilization of two perfume compounds, 2-phenylethanol (PEA) and benzyl acetate (BA), was studied by using an anionic surfactant (sodium dodecyl sulfate, SDS), a nonionic surfactant (hexadecyl polyoxyethylene ether, C₁₆POE₂₀), and mixed anionic-nonionic micelles (SDS/C₁₆POE₂₀). In order to study the distribution of perfume compounds between the micelle and bulk phases, the solubilization equilibrium constants (distribution constant) were determined as function of the intramicellar mole fraction of perfume compounds by using the semi-equilibrium dialysis method. The results of the present study show that (1) two or three surfactant molecules may on the average provide a location for the attachment of a PEA molecule in the single surfactant system, (2) BA molecules presumably bind somewhat more weakly to water and other polar groups in the hydrophilic group region of the single surfactant micelle, and (3) the solubilization equilibrium constant for the mixed surfactant system are smaller than predicted by linear or additive mixing rules applied to the single-component surfactant equilibrium constants, indicating that the compactness of the hydrophilic region of the mixed micelle may reduce the number of solubilization sites for the solutes in the micelle as a result of the hydrophilic interaction between the oxygen atoms of anionic surfactant and the ethylene oxide chains of nonionic surfactant.

Kondo, Y., Abe, M., Ogino, K., Uchiyama, H., Tucker, E.E., Scamehorn, J.F., and Christian, S.D., "Stability of Surfactant Vesicles Formed from Cationic Didodecyldimethylammonium Bromide", Colloid Surf. B: Biointerfaces, **1**, 51 (1993).

The solution properties of didodecyldimethylammonium bromide (DDAB) vesicles, including their relative stability, were estimated by measuring the vesicular diameter, the trapping efficiency of glucose, the aggregation number, and the ζ potential. DDAB vesicles with diameters in the range 17-40 nm were stable for long periods of time, However 50 nm vesicular solution were unstable and showed phase separation after 4 days. The stability of vesicles may be attributed to electrostatic repulsive forces between the vesicles. Also, the glucose trapping efficiency for the 17 nm vesicle solution was 0.57%, and increased with an increased in vesicular diameter up to 2%. The results indicate that DDAB vesicles with small diameters (17nm) have an inner phase. Further, the surface charge density calculation showed that 8-13% of DDAB molecules constituting the outside of the vesicles are charged, preventing the vesicles from fusing or flocculating in the aqueous solution and stabilized vesicle solution.

Kondo, Y., Abe, M., Ogino, K., Uchimaya, H., Scamehorn, J.F., Tucker, E.E., and Christian, S.D., "Solubilization of 2-Phenylethanol in Surfactant Vesicles and Micelles", *Langmuir*, 9 899 (1993).

The solubilization of 2-Phenylethanol (PEA) was measured over a wide range of solute activities using didodecyldimethylammonium bromide (DDAB) vesicles and dodecyltrimethylammonium bromide (DTAB) micelles. The solubilization equilibrium constant was found to be greater for DDAB vesicles than for DTAB micelles. At small values of X_p (the mole fraction of the solubilizate in an aggregate), the activity coefficient of PEA solubilized in the DDAB vesicle was much less than 1, and the value increased with increasing X_p . Further, the vesicular diameter increased with X_p and remained approximately constant from $X_p=0.3$ to $X_p=0.5$. It was found that PEA solubilized more strongly in DDAB vesicles than in DTAB micelles, and that it penetrates into the hydrophilic region of the vesicles as well as the micelles.

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, 1993, p.283.

Precipitation of surfactants in aqueous solutions 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 30 min 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.

Roberts, B.L., Scamehorn, J.F., Christian, S.D., Tucker, E.E., and Uchimaya, H., "Use of Micellar-Enhanced Ultrafiltration with Vacuum Stripping to Remove Trichloroethylene from Polluted Water", **Proceedings of the International Membrane Science and Technology Conference** (Fane, A.G., Ed.), Centre for Membrane Science and Technology University of New South Wales, Sydney, Australia (1992) p.163.

There are many industrial and government sites in the United States which have underlying groundwater polluted with trichloroethylene (TCE), a commonly used degreasing agent. Micellar-enhanced ultrafiltration (MEUF) involves the addition of surfactant to the water. The surfactant forms aggregates called micelles into which the TCE solubilizes. The water is then treated by ultrafiltration with membrane pore sizes small enough to block the passage of the micelles. An illustration of MEUF is shown in Figure 1. The retentate stream which does not pass through the membrane is then treated by vacuum stripping to remove the TCE from the surfactant. The permeate can be fed to subsequent stages in which further purification occurs. The process flow diagram for a four stage process is shown in Figure 2. As a result of the preconcentration due to MEUF approximately only 20 to 30 % of the volume of the solution needs to be vacuum stripped compared to the original polluted water stream. In this study, the effect of surfactant structure, surfactant concentration, number of stages, percentage of TCE ultimately removed, membrane pore size, and ultrafiltration device type (spiral wound vs. stirred cell) was investigated. A disulfonated surfactant (DOWFAX 8390) was found to be an excellent surfactant under these conditions since it has a high solubilization capacity, low tendency to precipitate, low leakage into the permeate, and concentration polarization only at high concentrations. Even though this surfactant is present in low concentration in the permeate from the MEUF process, it is still too high to be economically and environmentally acceptable. However, it has a high enough molecular weight to be able to be removed from the ultimate permeate with a rejection of 95% using a 500 MWCO ultrafiltration membrane. Approximately four stages are optimum to remove 99% of the TCE from the feed stream. Economic evaluations were performed to optimize the process configuration. The process shows promise to be less expensive than traditional clean-up techniques.

Simmons, D.L., Schovanec, A.L., Scamehorn, J.F., Christian, S.D., and Taylor, R.W., "Use of N-Alkyltrialamines in Ligand-Modified Micellar-Enhanced Ultrafiltration for Metal Ion Separations"; in **Environmental Remediation: Removing Organic and Metal Ion Pollutants** (Vandegrift, G.F., Reed, D.T., and Tasker, I.R., Eds.), ACS Symp. Ser., Vol. 509 (1992), p.180.

Ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) is a membrane-based separation technique that utilizes an amphiphilic ligand, solubilized in micelles, to selectively complex a target metal ion in a mixture of metal cations. The ligands tested were N-(n-dodecyl)-diethylenetriamine (DDIEN), N-(n-dodecyl)-di-2-picolyamine (DDPA), and N-(n-hexadecyl)-di-2-picolyamine (HDPa). These compounds were tested with the surfactants cetylpyridinium chloride (CPC), cetyltrimethylammonium bromide (CTAB), N,N-dimethyl-dodecylamine-N-oxide (DDAO), polyoxyethylene nonyl phenyl ether (NP(EO)₁₀), and sodium dodecyl sulfate (SDS). All three ligands solubilized readily into each type of surfactant. Solubilization parameters showed a strong dependence on the charges of the surfactant and ligand, and the length of the ligand alkyl chain. With HDPa, dialysis measurements with Cu²⁺/Ca²⁺ mixtures gave rejection values for Cu²⁺ as high as 99.8% (CPC), 99.7% (CTAB), 96.7% (DDAO) and 98.9% (NP(EO)₁₀), with no rejection of Ca²⁺. Addition of salt (NaCl) increased the retention of the bound Cu²⁺, but, when used with cationic surfactants, diminished the expulsion of Ca²⁺ into the permeate.

Tucker, E.F., Christian, S.D., Uchiyama, H., Guo, W., Scamehorn, J.F., and Puls, R.W., "Toxic Anion Removal from Aqueous Streams", 3rd Annual Conference on Groundwater Quality Research, Dallas, June 1992, p.271.

Polyelectrolyte enhanced ultrafiltration (PEUF) has been used to investigate the efficiency of removal of chromate and arsenate from aqueous streams. A cationic polyelectrolyte which complexes these anions is added to the stream. Subsequent ultrafiltration of the feed stream separates the stream into a retentate solution which contains enhanced concentrations of both polymer and anion and a permeate solution which contains substantially depleted anion concentrations. Laboratory solutions of chromate and arsenate have been tested under varying conditions of electrolyte levels. Several samples of ground water from a site contaminated with chromate have also been tested. Initial studies of a precipitation technique utilizing barium chloride to separate chromate as a solid waste and thus free the polymer for use in a cyclic process have been carried out. In several circumstances, it has been possible to produce large fractions of the feed solution (contaminated at ppm levels with toxic anions) as permeate water with less than 50 ppb levels of anions.

Krehbiel, D.K., Scamehorn, J.F., Ritter, R., Christian, S.D., and Tucker, E.E., "Ion-Expulsion Ultrafiltration to Remove Chromate from Wastewater", Sep. Sci. Tech., **27**, 1775 (1992).

In ion-expulsion ultrafiltration, a water-soluble colloid with the same charge as the target ion to be removed is added to water. This stream is then treated by ultrafiltration with membrane pores small enough to reject the colloid. In this study, chromate was removed from water using polystyrene sulfonate as the colloid in both batch-stirred cell and spiral-wound ultrafiltration devices. At very low pressures, Donnan equilibrium could be used to describe the permeate chromate concentration. As the pressure increased, diffusional effects caused the separation to become poorer. A spiral-wound unit resulted in a much higher separation efficiency than a stirred cell in this process.

Scamehorn, J.F., and Harwell, J.H., " Understanding Krafft Point Variations in Mixed Surfactant Systems", **Proceedings of the 3rd International Surfactants Congress and Exposition**, Gardiner-Caldwell, Macclesfield, England, Section C (1992) p.91.

The aqueous solubilities of surfactants are often expressed in terms of the Krafft Point Temperature. The Krafft Point will change, however, when electrolytes are added and when dissimilar surfactants are mixed. In this paper it is demonstrated that the apparently complex variation of the Krafft Point of a surfactant mixture in the presence of added electrolytes can be easily understood as a variation of precipitation phase boundaries. The effect of various parameters on the phase boundaries can be understood in terms of the interactions of several simple, well known aspects of surfactant behavior by simultaneously accounting for: (1) the solubility product constants of the monomers of the individual surfactant species, (2) the effects of added electrolytes on the critical micelle concentrations of the ionic surfactants, and (3) the formation of mixed micelles. Experimental results are presented which show that this approach can predict whether a given surfactant mixture will be above its Krafft Point even in mixtures containing anionic, nonionic, and cationic surfactants. This manner of looking at solubilities of surfactant mixtures can be very important in the design of modern high performance detergent formulations, in the design of high performance wetting agents.

Scamehorn, J.F., "Precipitation of Mixtures of Anionic Surfactants", ACS Symp. Ser., **501**, 392 (1992).

The tendency of an anionic surfactant to precipitate can be quantified in two different ways: (1) as a Krafft temperature or temperature below which surfactant precipitate appears, or (2) as a hardness or salinity tolerance - the minimum concentration of cation precipitating with the surfactant anion which is required to form any precipitate. Surfactants used in practical applications can contain many surfactant components, but these components are often similar enough so that they form nearly ideal mixed micelles. Yet precipitate initially formed from these mixtures contains only the one component most easily precipitated. As a result, the tendency of a multicomponent surfactant mixture to precipitate can be substantially less than that of a pure component typical of the mixture present at the same concentration.

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., **501**, 45 (1992).

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 (1) 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 equation 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.

Tucker, E.E., Christian, S.D., Scamehorn, J.F., Uchiyama, H., Guo, W., " Removal of Chromate from Aqueous Streams by Ultrafiltration and Precipitation", in **Transport and Remediation of Subsurface Contaminants: Colloidal, Interfacial, and Surfactant Phenomena** (Sabatini, D.A., and Knox, R.C., Eds.), ACS Symp. Ser., Vol. 491 (1992), p.84.

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 concentration of toxic metal anions.

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*, **8**, 414 (1992).

The semiequilibrium dialysis method has been used to investigate the ionic equilibria occurring in a ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) process. With attachment of a C_{12} hydrocarbon group to an iminodiacetic acid group and incorporation of this ligand in a cationic micelle, it is possible to bind Cu^{2+} selectively to the ligand in the redounded 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 redounded and known experimental parameters, including the binding constants of 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+} caused by changing the added salt concentration.

Lee, B., 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).

Solubilization isotherms for mono- and dichlorophenols in aqueous solutions containing N-hexadecylpyridinium chloride and an excess of anionic (dicarboxylate) polyelectrolyte have been determined at 25 °C by using the semiequilibrium dialysis method. The presence of the anionic polyelectrolyte greatly reduces the thermodynamic activity of the surfactant, but the surfactant-polymer complex can solubilize a large fraction of the dissolved chlorinated phenols in aqueous solutions. Implications of the results are considered in relation to the use of colloid-enhanced ultrafiltration methods; an added polyelectrolyte can greatly decrease the concentration of an oppositely charged ionic surfactant that will pass through the ultrafiltration membrane, while permitting removal of both nonionic organic and ionic solutes from contaminated aqueous streams.

Amante, J.C., Scamehorn, J.F., and Harwell, J.H., " Precipitation of Mixtures of Anionic and Cationic Surfactants", *J. Colloid Interface Sci.*, **144**, 243 (1991).

Precipitation phase boundaries for sodium alkyl sulfate/dodecylpyridium chloride were measured over a wide range of surfactant concentrations as a function of pH, temperature, and anionic surfactant alkyl chain length. Increasing temperature and decreasing surfactant alkyl chain length generally tend to decrease the tendency to precipitate. A previously developed model for predicting anionic/cationic surfactant precipitation phase boundaries described the experimental results very well except in some high surfactant concentration regions where coacervate and gels formed. This model uses a simple solubility product relationship, with regular solution theory, to describe mixed micelle formation. The environment of the alkyl chains favorable in the precipitate than in the micelles, from measured thermodynamic properties.

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