

# The Institute for Applied Surfactant Research at the University of Oklahoma Celebrates its 20th Anniversary

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In 1986, five faculty in Chemistry and Chemical Engineering at the University of Oklahoma established the Institute for Applied Surfactant Research (IASR) to build on their collaborative efforts in surfactant-based research. As IASR celebrates its 20th anniversary, six faculty (including three of the founding members) collaborate in the institute from the fields of Chemical Engineering and Environmental Science (see photo of current faculty in Figure 1).

In 1987, an industrial consortium was established to support IASR research. Currently, the consortium consists of twelve industrial firms from major consumer product formulators, surfactant manufacturers, oil service and oil companies, and industrial and institutional (I&I) product formulators. IASR has also performed contract research for numerous companies in various industries including consumer products, pharmaceuticals, oil producers, surfactant suppliers, and environmental remediation. These projects permit our students to gain experience in industrial-based research and allow for interaction with company scientists, thereby better preparing our students for rapid start-up in an industrial environment. IASR graduates also hold faculty positions in the U.S. and abroad, and work in government laboratories.

Current IASR research focuses on the following broad topics: consumer product formulation—innovation and understanding; surfactant-enhanced environmental applications; the use of surfactant templates to form polymers; and fundamental surfactant science underlying these technologies.

## Consumer Product Formulation

### *Microemulsions*

Microemulsions are of growing industrial interest as an increasing number of consumer products are microemulsion-based systems. Significant research advances in our laboratories over the past 20 years have greatly increased our ability to form microemulsions under a wide range of conditions. Through the clever use of surfactant mixtures with a wide range of HLB val-



*Figure 1: Institute faculty: left to right: Tohren Kibbey, Jeffrey Harwell, John Scamehorn (Director), Brian Grady, David Sabatini (Associate Director), and Edgar O'Rear.*

ues, we have been able to microemulsify a wide range of oils. Further, using a new generation of surfactants known as "extended surfactants," we have been able to microemulsify triglyceride oils at ambient conditions without alcohol addition—to our knowledge, a first.

Significant progress has been made in the development of quantitative tools to formulate microemulsion systems for specific situations. For example, our zero curvature model describes microemulsion properties important to product formulation. A wide range of oils have been studied: vegetable oils, motor oil, chlorinated hydrocarbons, diesel fuel, gasoline, triglycerides, and cutting oils. We are one of the very few academic institutions in the world studying mechanisms of detergency and cleaning.

We have used microemulsion-based formulations to design laundry detergents for oily soil removal. Designing the detergent so that a microemulsion phase forms between the water and the soil leads to improved detergency and/or lower active levels as well as faster kinetics of cleaning.

We have also introduced a new class of molecules, called hydrophilic linkers, useful for formulation of microemulsions. Hydrophilic linkers are intermediate in hydrophilicity between surfactants and hydrotropes. They function within the surfactant membrane at an oil-water interface spreading the surfactant molecules and decreasing the membrane rigidity. The conse-

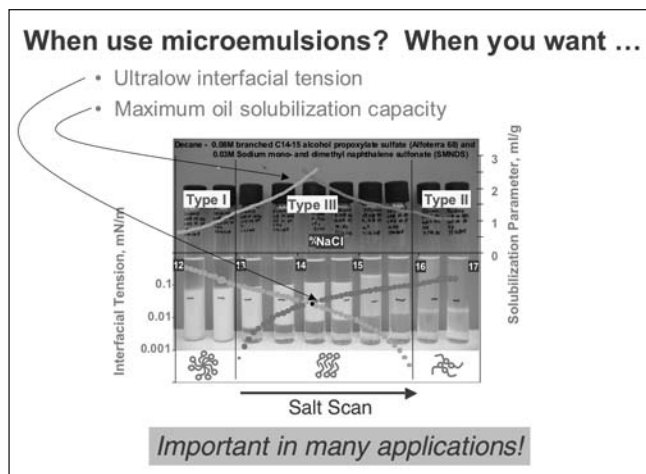


Figure 2: Microemulsion Salinity Scan.

quences of this are increased coalescence rates and increased rates of solubilization.

Among the new applications of our microemulsion research is a solvent-free process for producing vegetable oils from seeds. Under conditions where the volume of the microemulsion phase decreases towards zero, the recovered oil spontaneously separates to form a separate oil phase, allowing the surfactant to be recycled without a separate recovery step.

### Surfactant Precipitate Formation and Dissolution

IASR is a world leader in studies of the thermodynamics and kinetics of surfactant precipitation. Surfactant precipitation can dramatically decrease the effectiveness of a formulation. Precipitated surfactant is not available to perform other functions such as wetting, foaming, emulsification, solubilization, soil removal, and antiredeposition to name a few. The precipitate itself can be deleterious, as encrustation on fabric in laundry detergency for example. Recent projects include understanding the reduced rate of precipitation of surfactant mixtures compared to pure component systems and determination/modeling of phase boundaries of anionic/zwitterionic surfactant mixtures.

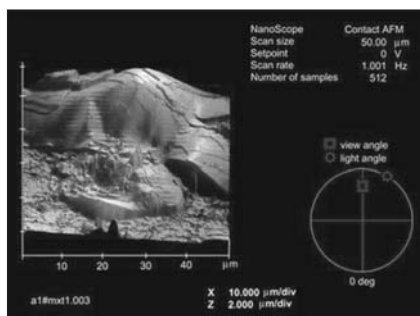


Figure 3: Atomic Force Micrograph of Anionic Surfactant Precipitated by Calcium.

Soap scum dissolution in hard-surface cleaners has been studied with an eye to understanding basic mechanisms. For example, recent research has evaluated the role of surfactants versus chelating agents in dissolving calcium stearate. In collaboration with a leading hard-surface cleaner manufacturer, both kinetic and thermodynamic studies have been performed, as well as scrub tests to combine fundamental understanding with practical results to improve formulations in this application. Soap scum is the calcium/magnesium precipitate of soap, so our work on understanding formation of surfactant precipitate is directly applicable to dissolving precipitate as the two research foci complement each other.

### Solubilization

The solubilization of oily soils by micelles can be an important phenomenon in detergency. Solubilization is a valuable tool in reducing the partial pressure of VOC's (volatile organic carbons) in such products as hard-surface cleaners. Solubilization can reduce the partial pressure of perfumes over a surfactant solution. We have developed methods to accurately measure solubilization of these kinds of compounds. We have also demonstrated that solubilization improves as a system tends toward a middle phase microemulsion (supersolubilization) and that maximum solubilization is realized within a middle phase microemulsion system. Solubilization rates are also improved by presence of hydrophilic linkers.

### Surfactant Adsorption on Solids

Adsorption of surfactant onto soils in clothes washing can be an important factor in their detachment from cloth and subsequent removal. The adsorption of surfactant onto solids is of obvious importance in hard-surface cleaning. A variety of techniques are available to measure adsorption of surfactants on surfaces. The goals of our research are to understand the forces causing adsorption and to quantify the factors enhancing or reducing adsorption. Our ability to predict the effect of changing surfactant structure in single surfactant systems or changing surfactant composition in

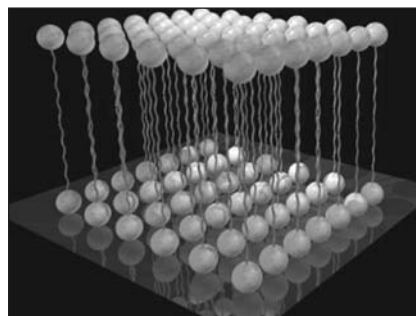


Figure 4: Schematic of an Adsorbed Surfactant Bilayer (Admicelle).

mixed surfactant systems on adsorption is continually being improved. Ultimately, this knowledge can be used with other detergency studies to design optimum detergent formulations.

## Surfactant-Enhanced Environmental Applications

### *Surfactant-Enhanced Aquifer Remediation*

Our group has made a series of advances in surfactant-enhanced aquifer remediation (SEAR) over the past fifteen years, often resulting from the coupling of laboratory and field studies with economic considerations. An early advance looked at surfactant-enhanced solubilization versus mobilization and developed supersolubilization and gradient systems that realized higher removal efficiencies, and thus improved system economics, while avoiding vertical migration concerns for oil phases denser than water. System economics also motivated development/adaptation of separation processes for surfactant recovery and reuse, which is especially important for multiple pore volume (> 3 to 5 pore volumes) surfactant flushes. More recently, alcohol-free low surfactant concentration systems (< 1 wt%) have been developed to reduce surfactant purchase costs and the operating expense of recovering/reusing the surfactant. By combining SEAR with an aggressive polishing step (e.g., chemical oxidation), it is possible to further reduce groundwater concentrations toward closure goals in a timely manner. A spin-off company, Surbec Environmental, has now used this technology to remediate nearly 30 contaminated aquifers.

### *Colloid-Enhanced Ultrafiltration*

IASR members have developed several new membrane separation methods, involving the addition of surfactants and other water-soluble colloids to contaminated aqueous streams. These colloid-enhanced ultrafiltration processes can be used to remove both organic and metal impurities from water. In micellar-enhanced ultrafiltration (MEUF), surfactant is added to the water forming micelles to solubilize the pollutant. When the solu-

tion is passed through an ultrafilter having pore sizes small enough to block passage of the micelles, the resulting permeate contains greatly reduced concentrations of the contaminants. In variations of the MEUF method, other colloids (including polyelectrolytes and mixtures of water-soluble polymers and surfactants) are used to remove both ionic and organic pollutants.

### *Plastics Deinking*

One significant factor inhibiting extensive reuse of plastics, especially plastic film, is the existence of printing inks in plastic after re-extrusion. Development of effective methods for deinking of plastics offers tremendous economic and environmental benefits to manufacturers and consumers alike. IASR research staff has been developing a fundamental understanding of the deinking of plastic films. IASR researchers have examined a number of surfactants for deinking plastics and analyzed properties of the re-extruded material to assess its value for reuse. Deinking of plastic packaging is fundamentally a laundering process: detachment of inks from the plastic packaging film by a chemical mechanism, and separation of the detached soil from the substrate and dispersion of soil in a washing bath by mechanical action. IASR research has tested the deinking potential of a variety of surfactant systems using commercial plastic packaging film supplied by a major manufacturer. These IASR experiments clearly demonstrated that cationic surfactant is the most effective in removing printing inks from plastic film.

## Thin Films

### *Admicellar Polymerization*

A new, three-step process for the formation of ultrathin films has been developed by IASR as illustrated in figure 7. In the first step, aggregates of surfactant molecules are formed on the solid substrates by contacting the substrate with a surfactant solution. These surfactant aggregates can be formed on a great variety of surfaces in such a way as to result in coverage of the entire surface with surfactant.

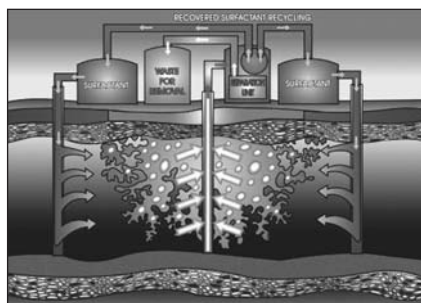


Figure 5: Schematic of a Surfactant-Enhanced Aquifer Remediation Operation.

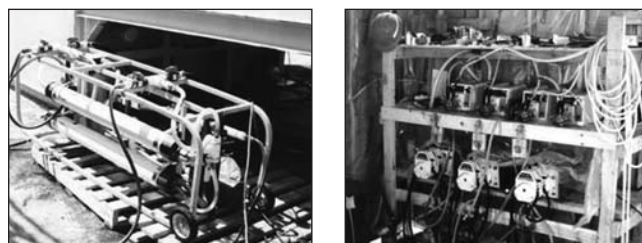


Figure 6: Micellar-Enhance Ultrafiltration Unit Used for Field Tests of Groundwater Remediation.

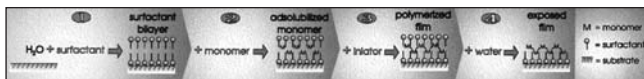


Figure 7: Strategy to Use a Surfactant Template to Form a Polymeric Thin Film.

In the second step of the process, a monomeric species is introduced. The surfactant layer acts as a two-dimensional solvent to concentrate the monomer at the interface. In the third step of the process, polymerization is initiated by chemical, thermal, or photochemical means. The adsorbed surfactant layer serves to localize the polymerization reaction at the solution-solid interface. An optional fourth washing step can be added to produce a thin film with the polymer exposed as needed for some applications.

IASR researchers have successfully formed such films on high surface area  $\text{TiO}_2$ , and  $\text{Al}_2\text{O}_3$  powders, on single-crystal, molecularly smooth silica, mica and graphite, and on alumina-coated plastic chips. Measured films thicknesses have varied from 3 to 100 nm. Films have been formed from many monomers including tetrafluoroethylene, aniline, pyrrole, styrene, butadiene, isoprene, ethylene, propylene, and many others. Formation of a new type of polymer frequently can be achieved by adaptation of a system from the emulsion polymerization literature. Four U.S. patents have now been issued to IASR researchers on this process and on materials formed by this process.

### Template-Assisted Admicellar Polymerization

By combining admicellar polymerization with an already-formed template, nanoscale polymer patterns can be produced. The pattern in Figure 8 represents the results when monodisperse spheres are formed as a monolayer on a flat surface, and the interstitial sites are where polymer forms. Surfactant is required to localize the monomer in the interstitial sites; otherwise polymer forms in solution and the result is an unordered system. We are also working in collaboration with the Center for Nanomaterial Science at Oak Ridge National Laboratories on this process.

### Hydrophobic Cotton

Cotton is one of the most popular materials for cloth-

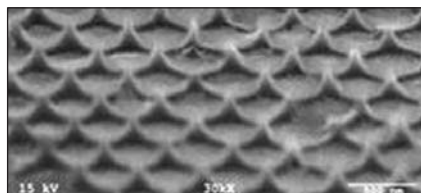


Figure 8: Nanoscale Polymer Patterns from Admicellar Polymerization.

ing because fabrics made of cotton breathe and exhibit a nice feel. However, these fabrics also readily soak up water that can be uncomfortable and, in some situations, even dangerous. With many of the techniques used to make textiles water-repellant, desirable properties of cotton can be lost. Admicellar polymerization has been applied to make a water-repellent cotton fabric that retains its positive attributes.

### Polymer-Matrix Composite Interface Modification

In polymer-matrix composites, the interface between the organic polymer and the inorganic filler determines many composite properties, in particular the tensile or flexural strength. Admicellar polymerization has been shown to improve the interface for many polymer/filler combinations including synthetic rubber/silica; epoxy resin/glass and polyethylene/glass. Because of the versatility of the admicellar process, we expect this process to be completely general for all possible combinations of fillers and polymers; it is only necessary to find the right type of admicellar polymer for a particular polymer/filler pair.

### Polymer-Surfactant Adsorption

Our laboratories have studied the adsorption of polymers on a variety of surfaces, and how that adsorption is modified by the addition of surfactant. We have found that the kinetics of adsorption are very different for the two systems; in the systems we have studied polymer tends to absorb faster than the surfactant, and over longer times surfactant will increase its surface concentration. This could be a displacement effect, or could be that surfactant is associating with polymer adsorbed at the surface (i.e. we have only measured relative changes). Ellipsometry, x-ray photoelectron spectroscopy, quartz crystal microbalance, contact angle measurements and chromatography are some of the methods have been applied to these systems.

### IASR Faculty

**John Scamehorn** is director of IASR. He served as associate director of IASR until the death of the founding director (Sherril Christian) in 2000. He is past chair of the Surfactants and Detergents Division of AOCS and has been active in the Society for over 20 years. He received his B.S. and M.S. at the University of Nebraska and his Ph.D. at the University of Texas, all in chemical engineering. He has worked for Shell, Conoco, and DuPont and has been on a number of editorial boards for journals in the area of surfactants



and of separation science. He has coedited five books and coauthored over 170 technical papers. In 2002, he was coauthor of the SDA's annual Outstanding Paper Award in *JSD* award and in 2001, he received an Annual Lectureship Award of the Division of Colloid and Surface Chemistry from the Japanese Chemical Society. His research interests include surfactant properties important in consumer product formulation and surfactant-based separation processes.

**David Sabatini** is associate director of IASR, having joined the School of Civil Engineering and Environmental Science in 1989. He received his B.S. from the University of Illinois, his M.S. from Memphis State University and his Ph.D. from Iowa State University, all in civil engineering. He has coauthored or coedited four books, over 110 refereed publications and book chapters, and more than 270 presentations. He received the AOCS SDA Distinguished Paper Award in 2003. He has served on National Research Council and industrial advisory panels. He is an associate editor for *Journal of Surfactants and Detergents* and *Journal of Contaminant Hydrology*. During 1997–1998, he was a senior Fulbright Scholar at the Universitaet Tuebingen, Germany. His research interests include microemulsion-based technologies for environmental remediation, solvent replacement, and consumer product formulation. He holds the Sun Oil Company endowed chair and is a David Ross Boyd Professor at OU.

**Jeff Harwell** joined the School of Chemical, Biological and Materials Engineering in 1982. He received his B.A. in chemistry and M.S. in chemical engineering from Texas A&M University and his Ph.D. in chemical engineering from the University of Texas. He has coauthored or coedited four books, nearly 140 refereed publications and book chapters, and more than 150 presentations. He received the AOCS SDA Distinguished Paper Award in 2003 and Outstanding Paper Awards from the American Institute of Chemical Engineers in 1993 and 1996. He served at the National Science Foundation in 1986–87, and co-organized and co-hosted the 1991 ACS Colloid and Surface Science Symposium. He received the ACS Victor K. LaMer award in 1984. His research interests include microemulsion-based technologies for environmental remediation, phenomena in surfactant mixtures, and the role of surfactants in processing and separations of single-walled carbon nanotubes. He holds the Conoco/DuPont Professorship of Chemical Engineering.

**Brian Grady** is active in the field of surfactants and colloids, especially as related to polymer science. He received his B.S. at the University of Illinois and Ph.D.

at the University of Wisconsin, both in chemical engineering. He also been a faculty member at the University of Oklahoma for twelve years, and previously spent two years working for Procter & Gamble. He is the winner of a prestigious CAREER Award and spent a sabbatical year in Germany at the Max Planck for Colloid and Interface Science with financial support from a Humboldt Fellowship. He has coauthored eight review book chapters, as well as over 60 peer-reviewed articles in archival journals. His research areas include surfactant/polymer adsorption at solid surfaces, emulsion polymerization, and structural characterization of surfactant phases.

**Edgar O'Rear** joined the School of Chemical, Biological and Materials Engineering in 1981. He received his B.S. in chemistry/chemical engineering from Rice University, his M.S. in organic chemistry from MIT, and his Ph.D. in chemical/biomedical engineering from Rice University. He has coauthored more than 110 refereed publications and book chapters. He served at the National Science Foundation in 1993–94, held the offices of secretary general, vice president, and president of the International Society of Biorheology, is a Fellow of the American Institute for Medical and Biological Engineers, and has worked at Hitachi Central Research Laboratory and the Institute for Physical and Chemical Research (both in Japan). His research interests include ultrathin films produced from an adsorbed surfactant template, surfactant-based separations, and hybrid surfactants containing both hydrocarbon and fluorocarbon tails. He is director of the University of Oklahoma Bioengineering Center and holds the Francis W. Winn Professorship of Chemical Engineering.

**Tohren Kibbey** joined the School of Civil Engineering and Environmental Science in 1999. He received his B.S.E. from The University of Michigan in mechanical engineering, and his M.S.E. and Ph.D. from The University of Michigan in environmental engineering. He received a prestigious NSF CAREER award in 2001, and has over 20 peer reviewed publications in areas covering many aspects of colloid and surfactant science. His research interests include mixed surfactant behavior, solvent replacement, wettability modification, and the influence of surfactants on unsaturated and multiphase flow and transport.

**For more information about IASR, including how to become an industrial sponsor, a list of publications, and detailed faculty vita, see our website: <http://www.cems.ou.edu/iasr/index.htm> or contact John Scamehorn at [scamehor@ou.edu](mailto:scamehor@ou.edu).**