

# 2011 Annual Meeting Abstracts

## Surfactants and Detergents

### MONDAY

#### MORNING

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#### ANA 1.1 / S&D 1.2: Advances in Analytical Methods for Surfactants and Detergents

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Chair(s): D. Scheuing, The Clorox Company, USA; and K. Ma, Cognis Corp., USA

**Quantifying Adsorption of Surfactants and Polyelectrolyte Complexes at the Solid-Liquid Interface by Quartz Crystal Microgravimetry with Dissipation.** Mona Marie Knock, David R. Scheuing, Michael I. Kinsinger, Clorox Technical Center, Pleasanton, CA, USA

The suitability of quartz crystal microgravimetry with dissipation (QCM-D) for measuring the adsorption of surfactants and polyelectrolyte complexes at the solid-liquid interface is examined. The effect of sensor hydrophobicity on surfactant adsorption is investigated for sodium dodecyl sulfate (SDS), 'dioctyl' sulfosuccinate sodium salt (AOT), hexadecyltrimethylammonium bromide (CTAB), and dihexadecyldimethylammonium bromide (DHDAB). Surfactant solutions were studied above their respective critical micelle concentration (CMC) and Krafft point in the absence of added electrolyte. Surfactant adsorption at the hydrophobic octadecanethiolate sensor surface was compared with adsorption on hydrophilic gold and silicon dioxide sensor surfaces. The adsorption behavior of net anionic and cationic polyelectrolyte complexes on silicon dioxide was also characterized.

**Consumer-preferred Rheology of Surfactant-thickened Cleaning Products.** D. Fritter, The Clorox Company, Pleasanton, CA, USA

Surfactants are commonly used to thicken oxidant-containing cleaners through the formation of a viscoelastic network of cylindrical micelles. These systems can exhibit a range of flow properties that influence ease of use and consumer perception of the product. Relevant measures go beyond the traditional thin-to-thick scale of viscosity and include ease of dispensing, elasticity, and cling to vertical surfaces. Rheological characterization provides a way to quantitate flow behavior that allows definition of the consumer-preferred space for a particular application. Viscoelastic materials can be characterized by the zero-shear viscosity, relaxation time, and static shear modulus, as obtained from a Frequency Sweep. For surfactant-thickened formulations, the consumer-preferred rheology for a product that is squirted or sprayed onto a vertical surface is a relaxation time less than about 0.01 s and a zero-shear viscosity greater than about 100 cP. The low relaxation time ensures a smooth and fluid appearance as the product hits and covers the surface, while the zero-shear viscosity requirement ensures that the coating doesn't drain too quickly. This combination of parameters leads to a product with consumer-preferred cling to vertical surfaces.

**Applications of Fourier Transform Infrared Spectroscopy to Studies of Surfactant**

**Behavior.** David R. Scheuing, Clorox Services Company, Pleasanton, CA, USA

Liquid water is an intense absorber of infrared light and is thus commonly considered to interfere significantly in the analysis of aqueous systems via FT-IR. However, when the pathlength through the sample is restricted to below about 20 micrometers, a variety of analyses of surfactants in aqueous systems can be readily accomplished with FT-IR. Modern spectrometers, coupled with newer designs of optical accessories, can be used routinely and efficiently to characterize the behavior of surfactants or formulations on clean surfaces or on controlled dirty surfaces through the use of internal reflection (attenuated total reflectance or ATR) techniques. Due to the short effective pathlengths achieved with ATR and the excellent reproducibility of signals in the frequency domain with modern instruments, the elimination of the normally intense absorption due to water can be readily achieved via spectral subtraction or ratio techniques. Spectra of a variety of water-solid interfaces can be obtained, and hence the chemical analysis of these interfaces, including time-resolved changes is possible. The combination of FT-IR data with results from other surface analytical techniques can be used to probe formulation performance or more fundamental properties of phase separation of aqueous systems of practical interest.

**Application of LC-MS to Surfactant Analysis.** David Dabney, Stepan Company, Northfield, IL, USA

Mass spectrometry has taken an increasing role in all segments of analytical analysis over the last 20 years. From quantitative analysis related to biologics to structural elucidation of novel compounds, mass spectrometry continues to improve our understanding of the materials we use everyday. The application of mass spectrometry to the study of surfactants while not new has generally been limited to the identification of surfactants related to biologic matrices. Here we apply mass spectrometry to the analysis of surfactants for the purpose of understanding the composition and properties of the surfactant as a stand alone entity. By understanding the total composition of our materials we provide for the information necessary for regulatory, manufacturing, performance and quality of the surfactants. Mass spectrometry is well suited for this endeavor due to its dynamic range, ability to be coupled to various separation techniques and array of ionization and mass selection configurations as well as rapidly improving data evaluation techniques. In this talk, the basic principles of mass spectrometry will be reviewed along with examples of mass spectrometry being applied to the evaluation of various surfactant chemistries.

**Emerging Ambient Ionization Methods and Their Use to Characterize Substrate Modifications.** Ismael Cotte-Rodriguez, The Procter & Gamble Co., Global Analytical, Cincinnati, OH 45252, USA

Tools that allow rapid in-situ analysis of ambient surfaces with minimal or no sample preparation are ideal to monitor substrate modifications. This presentation focuses on the use of desorption electrospray ionization (DESI) as an imaging tool to understand substrate modification. DESI is a powerful ambient ionization method that combines features of desorption ionization with those of spray ionization. DESI allows mass spectrometry to be performed on samples that are in ambient environments. The method is based on directing a pneumatically-assisted electrospray

onto a given surface, from which small organics and large biomolecules are picked up, ionized and delivered as desolvated ions into the mass spectrometer. Increased selectivity is achieved both by MS/MS and by including additives in the spray solvent (Reactive-DESI). DESI has high sensitivity, is suitable for characterization of both large and small molecules, and allows the direct analysis of pure compounds and formulated mixtures deposited on surfaces or in tissue without sample preparation. Examples of applications in consumer product development will be covered including analyte-substrate interactions and quantitation approaches for selected analytes.

**Analytical Toolbox to Unveil Complex Mixtures of Surfactant-Based Systems.** Michele Mangels<sup>1</sup>, José Andrés Rojo<sup>1</sup>, Bob Strife<sup>2</sup>, Kevin Garber<sup>2</sup>, <sup>1</sup>The Procter & Gamble Co., Miami Valley Innovation Center, Cincinnati, Ohio, USA, <sup>2</sup>Mason Business Center - Analytical GCO, Cincinnati, Ohio, USA

The characterization of the complex mixtures found in many surfactant-based systems and detergent products poses unique analytical challenges. The surfactant raw materials themselves are often intricate mixtures of active molecules that generally need to be formulated into blends with other raw materials involving co-surfactants, functional polymers and many other organic and inorganic chemicals and solvents. A variety of analytical approaches are available for the characterization of these mixtures. Presented are a broad suite of analytical techniques currently in use for understanding various polar and non-polar surfactants with nonionic, cationic, or anionic functionalities. Chromatographic approaches discussed range from the use of gas and high pressure liquid chromatography, including the use of supercritical fluids and the so-called aqueous normal phase separation mode. Detection techniques discussed which prove useful in the characterization of these complex systems include flame ionization, evaporative light scattering, and both low and ultra-high resolution mass spectrometry with various types of ionization sources. Also discussed are some approaches used to help visualize the complex data sets generated by these techniques.

### **S&D 1: Emerging Technologies in Industrial Application of Surfactants**

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Chair(s): M. Dahanayake, Rhodia, Inc., USA; and U. Weerasooriya, The University of Texas, USA

**Advanced Microemulsion Systems for Subsurface Remediation: Laboratory and Field Results.** D.A. Sabatini, J.H. Harwell, B.J. Shiau, R.C. Knox, University of Oklahoma, Norman, OK, USA

Subsurface contamination by fuel (gasoline, jet fuel) and cleaning oils (chlorinated solvents) is a pervasive environmental problem that can also produce important health risks. Subsurface trapping of these oils by capillary forces renders water-only pump and treat remediation ineffective ? requiring hundreds to thousands of pore volumes be flushed through the subsurface to slowly dissolve the trapped oil. Surfactant micelles (Winsor Type I systems) have the potential to enhance the oil solubility but this is still a relatively inefficient approach requiring tens of pore volumes of flushing. Winsor Type III middle phase microemulsions achieve ultra-low interfacial tension which liberates the oil by mitigating the capillary forces trapping the oil and thus

achieving remediation within several pore volumes. While initially high concentration surfactant systems (3 to 5%) were used to achieve this liberation, recent advances in microemulsion systems have allowed surfactant concentrations to be reduced by as much as an order of magnitude, greatly improving system economics. This paper will present basic concepts as well as laboratory and field results demonstrating the important considerations and exciting potential of this novel technology.

### **Surfactant Formulations for Chemical Flooding under High Salinity Reservoir Conditions.**

B.J. Shiau<sup>1</sup>, T.-P. Hsu<sup>1</sup>, P. Lohateeraparp<sup>2</sup>, B.L. Roberts<sup>2</sup>, J.H. Harwell<sup>2</sup>, <sup>1</sup>School of Petroleum Engineering, University of Oklahoma, Norman, OK, USA, <sup>2</sup>School of Chemical Engineering, University of Oklahoma, Norman, OK, USA

This study describes novel surfactant formulation developed for a pilot single-well test and their potential field implementation for improving oil recovery at the target high salinity reservoirs. The blended surfactant mixtures can tolerate extreme high salinity conditions (e.g., > 185,000 mg/L of total dissolved solids, TDS, and calcium ion of 12,000 mg/L) without experiencing adverse phase separation and/or precipitation under the reservoir conditions for weeks (50 °C). The current approach involves optimizing the salt tolerance by blending surfactants with different characteristics while forming the middle phase microemulsions to achieve ultra-low interfacial tension (< 0.02 dyne/cm) between the crude oils and reservoir brines. Significant oil recovery was realized in laboratory one-dimensional sand-packed column and the sedimentary core flood experiments. A pilot single-well surfactant chemical flooding is scheduled for later part of 2010. Thus, initial success of our laboratory experiments indicate that this newly developed low surfactant and co-solvent system (both are less than 0.5 wt%) could overcome the challenging issues of high brine reservoirs and provide a viable alternative for chemical EOR.

**New and Novel Viscosifying Surfactants for Chemical Enhanced Oil Recovery.** G. Degré<sup>1</sup>, M. Morvan<sup>1</sup>, M. Dahanayake<sup>2</sup>, D. Pakenham<sup>2</sup>, J. Bouillot<sup>3</sup>, A. Zaitoun<sup>3</sup>, <sup>1</sup>Rhodia, Laboratory of the Future, Pessac, France, <sup>2</sup>Rhodia, Bristol Research & Technology Center, Bristol, PA, USA, <sup>3</sup>Poweltec, Rueil Malmaison, France

At present, worldwide oil recovery factor is @ 30% by the use of primary and secondary oil recovery techniques. In the recovery of the remaining oil Chemically Enhanced Oil Recovery (EOR) is the most promising technology. This paper will present the use of some novel viscosifying surfactant fluids to mobilise oil by much improved sweep and displacement efficiency that will provide an effective solution and advantage over rather complex EOR techniques that are being currently practiced by oil industry. The technology we have developed exhibits a viscous phase and low interfacial tensions at very low surfactant concentration in a broad range of temperature and salinity reservoir conditions. Detailed characterizations of the surfactant system have been carried out using micro and millifluidic devices. Significant viscosity is maintained by these surfactants at temperatures, as high as 80 °C, with excellent thermal stability in contrast to polyacrylamides (HPAM) that show degradation and loss of viscosity under the same conditions. Core flood experiments further substantiated the physico-chemical stability for the viscosifying surfactants with 10 to 20% of incremental oil recovery where as HPAM under the same conditions showing gradual mobility reduction and recovery of oil.

**Non-alkaline Surfactant Formulations in Chemical EOR.** Upali P. Weerasooriya, Gary A. Pope, The University of Texas, Austin, Texas, USA

New Surfactant systems have been developed for use in Carbonate rocks and hard brine under non-alkaline pHs. These new formulations have been successfully tested in high temperature corefloods demonstrating their efficacies. Some of these formulations are under consideration for pilot scale testing.

**Effects of Alcohol Propoxy Sulfate Hydrophobic Structure on Performance, Applying the Net Average Curvature Model.** C.E. Hammond<sup>1</sup>, E. Acosta<sup>2</sup>, S. Congiundi<sup>1</sup>, G. Trahan<sup>1</sup>, <sup>1</sup>Sasol North America Inc, 2201 Old Spanish Trail, Westlake, LA, USA, <sup>2</sup>University of Toronto, Department of Chemical Engineering and Applied Chemistry, 200 College St., Room 131, Toronto, ON, M5S 3E5, Canada

In surfactant induced enhanced oil recovery there is a need to formulate the surfactant package to give optimum performance at specific reservoir conditions (i.e temperature, oil type, salinity, etc.). Anionic surfactants, especially those based on alcohol propoxy sulfates, are showing good oil recovery performance in core evaluation studies. In a 2009 AOCS presentation, the Hydrophilic-Lipophilic Deviation (HLD) equation was used to illustrate how to select an appropriate alcohol propoxy sulfate surfactant to match given reservoir conditions. This presentation now goes one step further to examine how the surfactant structure contributes to interfacial tension (IFT). The following equation has been proposed in the literature:  $IFT = E_r / (4 \xi^2)$ , where:  $E_r$  = Interfacial Rigidity,  $\xi$  = Characteristic Length (solubilization characteristic). Previously uncharacterized values for the rigidity of alcohol propoxy sulfates will be discussed for a series of homologous structures. This work also probes how the surfactant coalescence rate is related to the Interfacial Rigidity. Additionally, the Net Average Curvature (NAC) model will be used to predict the surfactants' ability to form microemulsions with alkanes or model oils.

### **S&D 1.1: Emerging Surfactant Applications**

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Chair(s): R. Masters, Stepan Co., USA; and E. Acosta, University of Toronto, Canada

**Nanoporous Materials Formed via Microemulsion Polymerization.** H.M. Cheung, University of Akron, Akron, OH, USA

This paper will describe the use of microemulsions as a precursor for the formation of nanoporous materials, mostly polymeric. Bicontinuous microemulsions when polymerized can give rise to nanoporous materials which mimic the nanostructure of the microemulsion. Depending on the composition of the precursor microemulsion either closed or open structures may be obtained with pore sizes in the few nanometer to few hundred nanometer range. Characteristics such as swelling behavior can be tuned via the precursor microemulsion composition. The formation, characterization, and potential uses of these materials will be described.

**Development of Functional Soft Materials from Surfactant/Biopolymer Mixtures.** Y. Lapitsky, University of Toledo, Toledo, OH, USA

Complexes between oppositely charged surfactants and polymers (polyelectrolytes) are used in numerous products, ranging from personal care and pharmaceutical formulations, to water-based paints. These mixtures have also attracted interest as building blocks for novel soft materials (e.g., micro- and nanoparticles, thin films and macroscopic gels) with well-defined macro- and nano-scale architectures. This talk discusses the design of these materials from bio-based feedstocks; specifically, from mixtures of chitosan-based polymers and fatty acid salts. We show how the microstructure and stability of surfactant/polyelectrolyte complexes can be predictably tuned through the rational selection of bio-derived surfactants and polymers. We also show how their stability can be dramatically enhanced through the covalent conjugation of the surfactant to the polymer, and how these materials can be utilized in medical and household applications.

**Delivery of Surfactant-stabilized Zero-valent Iron Nanoparticle (nZVI) Suspension for Soil Remediation.** Ziheng Wang, Edgar Acosta, University of Toronto, Toronto, ON, Canada

Zero-valent iron nanoparticles (nZVI) have been employed for the reduction of dense non-aqueous-phase liquids in contaminant sites since 2003. This type of nanomaterials showed core-shell structure with relatively high surface of area per mass, thus improving the surface reactivity compared with large-scale materials. One key problem encountered of this technique after the injection into the contaminated site is the limited transportability of nZVI. The main reason for the poor transportability is because the bare nZVI can aggregate rapidly due to their colloidal properties. Aggregation of nZVI also results the reduction of surface reactivity due to the decrease of relative surface area. A common objective in the development of this technique is to prepare stable nZVI suspensions to enhance the nZVI delivery and its reactivity in the contaminated field. In this presentation we discuss the mobility and the reactivity of various surface-modified nZVI suspensions based on column study. Characterization of nZVI suspensions with different coatings will be also introduced. DLVO predictions were applied to explain the stability of surface-modified nZVI suspensions. A comparative study based on iron oxide suspensions, which has the same component as the surface of nZVI, will be also included in this presentation.

**Admicelle Formation and Adsolubilization using Ethoxy Carboxylate Extended Surfactants.** Noulkamol Arpornpong<sup>1</sup>, Jirapat Lewlomphaisan<sup>1</sup>, Ampira Charoensaeng<sup>2</sup>, David A. Sabatini<sup>3</sup>, Sutha Khaodhiar<sup>4</sup>, <sup>1</sup>National Center of Excellence for Environmental and Hazardous Waste Management, Chulalongkorn University, Bangkok, Thailand, <sup>2</sup>Team Consulting Engineering and Management Co., Ltd, Bangkok, Thailand, <sup>3</sup>Schools of Civil Engineering and Environmental Science, University of Oklahoma, Norman, Oklahoma, USA, <sup>4</sup>Department of Environmental Engineering, Chulalongkorn University, Bangkok, Thailand

Surfactant modified adsorbents by anionic ethoxy carboxylate extended surfactants are evaluated. In this research, the adsorption of two anionic ethoxy carboxylate extended surfactants (C<sub>16-17</sub>-4PO-5EO-COONa and C<sub>16-18</sub>-4PO-5EO-COONa) and conventional surfactant (C<sub>12</sub> SO<sub>4</sub> Na) were measured and compared by virtue of the surface charge of the surfactant-modified aluminum. Adsorbed admicelles at solid/liquid interface are capable of solubilizing organic

solute from aqueous phase known as adsolubilization process. This study evaluated the adsolubilization enhancement of organic solute. In addition, due to surfactant loss from solid surface, desorption potential was determined to evaluate the stability of surfactants adsorbed onto surface. These results thus provide insights into the ethoxy extended surfactant based-admicellar systems with the aim of enhancing the ability of surfactant modified materials for industrial and environmental applications.

**HLD-NAC Theory for Real-world Use: Software and Database Development with High Throughput Methods.** S. Abbott<sup>1</sup>, A. Eady<sup>2</sup>, S. Van Loon<sup>3</sup>, E. Acosta<sup>4</sup>, <sup>1</sup>University of Leeds, Leeds, UK, <sup>2</sup>Syntopix, Bradford, UK, <sup>3</sup>Van Loon Chemical Innovations, Amsterdam, The Netherlands, <sup>4</sup>University of Toronto, Toronto, Ontario, Canada

HLD-NAC theory in principle allows the naïve user to formulate complex microemulsions with high predictability. Two barriers have existed up to now. First, there was no user-friendly software allowing exploration of the various predictions of the theory. Second, insufficient parameters have been available in the open literature to allow users to make intelligent choices from the large range of surfactants commercially available. The availability of an easy-to-use Optimal Surfactant package has addressed the first issue. And the use of a high throughput process for obtaining key parameters for the Optimal Surfactant database has shown how it is possible to provide a large amount of important data in a relatively short time and low cost. The use of the HLD-NAC in formulating drug delivery systems and other emerging applications will be discussed.

### **S&D 1.3: General Surfactants and Detergents I**

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Chair(s): S. Bolkan, Church & Dwight Co Inc., USA; and D. Hayes, University of Tennessee, USA

**Vegetable Oil Reverse Micelle Microemulsion as an Alternative Renewable Biofuel Using Extended Surfactant.** C. Attaphong, L. Do, D. Sabatini, The University of Oklahoma, Norman, OK, USA

Recently, vegetable oils are of interest as a source of renewable fuels. However, vegetable oils are problematic for long-term usage in diesel engines due to their high viscosity. Therefore, vegetable oil reverse micelle microemulsions have been evaluated as an alternative method of reducing vegetable oil viscosity while eliminating the trans-esterification reaction and avoiding the glycerol byproducts resulting and its environmental problems. Since it has been shown that extended-surfactants can form microemulsions with a high solubilization capacity and with a wide range of oils, extended-surfactant-based reverse micelle microemulsion systems have been evaluated. The objective of this research is to study phase behaviors of extended-carboxylate surfactant microemulsion systems with the goal of formulating optimized systems. It was found that extended-carboxylate surfactants were able to form reverse micelle microemulsions with no salt added. Therefore, the phase separation and precipitation which had been observed with extended-sulfate surfactants were avoided. In addition, fuel properties such as viscosities and combustion properties will be presented to provide useful information for design of surfactant systems for use in diesel engines.

**Surfactant Flushing for Aquifer Remediation at Ft. Drum, New York.** J.H. Harwell, B.J. Shiau, P. Lohateeraparp, T.P. Hsu, The University of Oklahoma, Norman, OK, USA

Surfactant flushing for aquifer remediation evolved from enhanced oil recovery. Application of surfactants for aquifer remediation occurs in a highly regulated environment, where public perception of risk often overrides economic-based decision making. In 2006 a major jet fuel spill was discovered at Ft. Drum, New York, the home of the US Army's 10th Mountain Division. An estimated 400,000 gallons of jet fuel had leaked from a hot-refueling depot and was floating on the aquifer over an area of approximately three acres. Surfactant flushing was selected by the US Army Corps of Engineers, on recommendation from the base environmental consultant, EA Engineering, for multiple reasons, including cost, speed to final cleanup, and the ability to re-use the recovered jet fuel. A pilot test, based on a treatability study performed at our labs, occurred in Fall 2009 and successfully remediated a 1/8th acre portion of the site. Based on these results, full scale implementation began in June 2010; installation of the remediation system began in July 2010, with surfactant injection beginning in September. The project is expected to be completed in late summer 2011.

**Changes in Bicontinuous Microemulsion Structure Caused by Encapsulated Proteins: A Small-Angle Neutron Scattering Study.** Douglas G. Hayes<sup>1</sup>, Javier A. Gomez del Rio<sup>1</sup>, Volker S. Urban<sup>2</sup>, <sup>1</sup>University of Tennessee, Knoxville, TN, USA, <sup>2</sup>Oak Ridge National Laboratory, Oak Ridge, TN, USA

The objective of this work is to understand the nature of the underlying driving force for the extraction of protein into the middle, bicontinuous microemulsion phase, of a Winsor-III (W-III) system, through observing the effect of protein on nano-structural changes via Small-Angle Neutron Scattering (SANS). We have selectively extracted proteins into the W-III middle phase microemulsions formed by mixing an aqueous protein solution with isooctane that contains a binary surfactant mixture: the anionic surfactant AOT and a 2-tailed 1,3-dioxolane alkyl ethoxylate: CK (>95% extraction). However, the yield and apparent driving force for extraction depends upon the protein type; moreover, hydrophilic proteins (e.g., chymotrypsin) are extracted by an electrostatic driving force. In contrast, hydrophobic proteins (e.g., cytochrome c) appear to be extracted by both electrostatic and hydrophobic driving forces. SANS analysis shows protein significantly affected the nanostructure of the middle phase, for instance decreasing or increasing the spacing between the surfactant monolayers of the biocontinuous microemulsions. SANS also demonstrated the presence of aggregates in the bottom W-III phase of the systems of cytochrome c, suggesting the formation of the aqueous micellar aggregates is a first step of extraction.

**Phase Behavior of Surfactant / Ethylene Glycol Distearate Systems.** Nicole Nguyen, Church & Dwight Co., Inc., Princeton, NJ, USA

Various physical methods and visual observations were used to study the solution behavior of model surfactant and ethylene glycol distearate compositions.

**Novel Anionic Extended Surfactant and Cationic Surfactant Mixtures for Maximizing Synergism (Solubilization and Adsolubilization) and Minimizing Precipitation.** D.



Panswad<sup>1</sup>, D.A. Sabatini<sup>2</sup>, S. Khaodhiar<sup>3</sup>, <sup>1</sup>National Center of Excellence for Environmental and Hazardous Waste Management (NCE-EHWM), Chulalongkorn University, Bangkok, Thailand, <sup>2</sup>School of Civil Engineering and Environmental Science, University of Oklahoma, Norman, Oklahoma, USA, <sup>3</sup>Department of Environmental Engineering, Chulalongkorn University, Bangkok, Thailand

Surfactant-modified mineral surfaces provide both hydrophobic coating for adsorbing organic contaminants and, in the case of ionic surfactants, a charged exterior for adsorbing oppositely charged species. This research is looking at the use of novel surfactant mixtures to form admicelles, specifically carboxylated-based anionic extended surfactants with pyridinium-based cationic surfactants. Precipitation phase boundaries of anionic extended surfactant and pyridinium-based cationic surfactant mixtures have been evaluated in order to define isotropic concentration regimes in which to conduct the adsorption studies. It is found that the precipitation phase boundary of this novel mixed surfactant system is smaller than the conventional mixed surfactant system. Moreover, the CMC of this novel mixed surfactant system is much lower than that of the individual surfactant systems. Furthermore, this research evaluates the adsorption and adsolubilization processes of these surfactant systems relative to their ability to act as an adsorptive media for plume management and groundwater treatment.

**Comparison on the Effect of Soda Ash and Sodium Bicarbonate on the Physico-chemical Properties of Green/Biosurfactants.** L. Del Rosario, Church & Dwight Co. Inc., Princeton, NJ, USA

Soda ash and sodium bicarbonate function as alkali builders in laundry detergents, maintaining high wash pH and promoting surfactant detergency. In this study, the effects of soda ash and sodium bicarbonate on green/biosurfactant properties such as critical micelle concentration, surface tension, and oil-water interfacial tension are evaluated. In particular, the effect of the electrolytes on surfactant properties was investigated as a function of salt concentration and pH. Selected green/biosurfactants include amino acid surfactants, alkylpolyglucosides, glycolipids, and lipopeptides.

**AFTERNOON**

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## **S&D 2.1: General Surfactants and Detergents II**

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Chair(s): B. Lin, Dial Corp./Henkel, USA; and M. Tsumadori, Kao Corp., Japan

**The Relationship between Mechanism of Hydrophilic and Hydrophobic Particle Removal in Laundry Detergency.** Sureeporn Rojvoranun<sup>1</sup>, Sumaeth Chavadej<sup>1</sup>, John F. Scamehorn<sup>2</sup>, David A. Sabatini<sup>2</sup>, <sup>1</sup>The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand, <sup>2</sup>The University of Oklahoma, Norman, OK, USA

The aim of this research is to investigate the mechanism of hydrophobic and hydrophilic particulate soil detergency in relation to various factors: surfactant concentration, surfactant type, fabric type, and solution pH. Carbon Black and Ferric Oxide are selected as a model of

hydrophobic and hydrophilic particulate soil respectively and two types of fabrics are used: pure polyester and pure cotton. The detergency experiments are carried out in a Terg-O-Tometer by using an anionic surfactant (Sodium Dodecyl Sulfate, SDS ) and a nonionic surfactant (octyl phenol ethoxylate, OP(EO)10). In order to gain a better understanding, the adsorption isotherms of the surfactants and the measurements of the zeta potential and the contact angle are carried out. From the results, for any given types of surfactant and fabric, detergency performance increased with increasing solution pH and the maximum performance was found at pH 11 for both types of soil. Additionally, the SDS exhibited a better detergency than the OP(EO)10 and the cotton fabric showed the highest detergency efficiency while the polyester gave the lowest performance for hydrophilic soil but for hydrophobic soil is vice versa. The results imply that the dominant mechanism for particulate soil detergency is well correlated to electrostatic repulsion force.

**LCA of Laundry Detergent Sheets vs. Traditional Products.** L. Bonvin, M. Spinatsch, Henkel Consumer Goods, Inc., Scottsdale, AZ, USA

Residential laundering process has traditionally encompassed three individual products: detergent, fabric softener and antistatic dryer sheet. Innovative new laundering products combined with heightened awareness of sustainable drivers are changing the way consumers consider the task of residential laundry. Using the lifecycle assessment (LCA) tool, we are able to demonstrate that Purex<sup>®</sup> Complete 3-in-1<sup>®</sup> Laundry Sheets , which deliver the benefits of all three traditional products, can make a positive impact on environmental parameters. Results including reduced CO<sub>2</sub> emissions, reduced impact on landfills and water consumption savings will be discussed.

**A Method of Standardizing the Removal Rate of Soils in Washing Tests using Probability Density Function.** M. Oya, R. Kurono, N. Nishio, Yokohama National University, Yokohama, Kanagawa, Japan

Removal rates of soils in washing tests tend to vary greatly even if those tests are performed under the same condition of temperature, mechanical power, type and quantity of soil, and so on. Therefore, removal efficiency of a detergent is compared to that of the standard detergent and judged only better than, equal to, or less than the standard. We previously proposed the method of expressing the absolute washing power of detergents using probability density functions assuming that initial soil adhesive power has a normal distribution[1]. In this study, washing tests were done varying concentration of surfactant and mechanical power in several stages, and confirmed the theory. Washing power parameter of individual washing condition was calculated from 4 removal rates obtained from 4-times repeated washing of artificial soiled cloths with Terg-O-Tometer. Then washing tests of combination of 2 different washing conditions were performed. The removal rates after the second washing procedure were calculated to compare with the experimental data, and good correspondence was observed. The results showed that this method could be used to express the absolute washing power.1) Y.Ishikawa, et.al., J.Oleo Sci., 55, 511 (2006), 56,163 (2007), 57,99 (2008)

**Understanding Cleaning Formulations Based on Microemulsion Phase Behavior.** M. Dreja<sup>1</sup>, A. Klemmer<sup>2</sup>, R. Strey<sup>2</sup>, <sup>1</sup>Henkel AG & Co. KGaA, Düsseldorf, Germany, <sup>2</sup>University of

Cologne, Cologne, Germany

Microemulsions are homogeneous, thermodynamically stable mixtures that contain water, oil and surfactants. It is common belief that microemulsions play a role in technically important processes. E.g. during the cleaning of clothes in the washing process or during the cleaning of dishes in the sink, microemulsions might form on a nanoscale while emulsifying oil in surfactant aggregates. The phase behavior of model systems made from pure oils like decane and pure nonionic surfactants of the C<sub>i</sub>E<sub>j</sub> type is well known. Detailed know-how of microemulsions with technically relevant surfactants and soil type oils is still lacking and of great interest in order to better understand the basic cleaning process and to tailor more effective cleaning products. We have investigated the phase behavior of microemulsions with commercial surfactants depending on concentration and temperature. The effects of water hardness, salt content and of mixtures with various surfactant types were studied. It was found that systems made with ionic surfactants are quite efficient, but show a high degree of temperature dependence. Using different types of nonionic surfactants, we identified large changes in solubilizing efficiency. Moving from decane to triglycerides reduced the efficiency of the surfactants significantly.

**Carboxymethyl Inulin: A Vegetable-based Ingredient for Liquid Laundry Detergents.** J. Kolpa<sup>1</sup>, S. Verrett<sup>1</sup>, G. Bonnechère<sup>2</sup>, <sup>1</sup>Thermphos USA, Anniston, AL, USA, <sup>2</sup>Thermphos International, Louvain-La-Nueve, Belgium

Due to consumer preference, liquid laundry products make up the largest share of the North American detergent market; therefore, there is a strong focus on liquid detergent innovation. Current trends include increased compaction, low temperature wash, and the introduction of high efficiency (HE) washing machines. These trends have created formulation challenges requiring innovative ingredients. Recent testing with carboxymethyl inulin (CMI) has demonstrated that its inclusion in HE compact liquid laundry formulations can significantly improve detergent performance. Detergents with CMI show improvement on bleachable and enzymatic stains. The cleaning capacity of liquid laundry detergents is enhanced due to CMI's ability to bind hardness ions and CMI's excellent compatibility with enzyme systems. Results also indicate that varying the inclusion level of CMI allows formulators to modulate the cleaning performance profile across a full product range from cost focused brands to premium brands. The vegetable origin of CMI, its exceptionally low toxicity, non persistent character and natural origin ensure that it has a low impact on the environment. Therefore, CMI is an ingredient of choice to reduce oil dependency and meet consumer aspirations for sustainable detergents without compromising on cleaning performance.

**Mixtures of Anionic Surfactants with Nonionic Surfactants from Renewable Resources.** L. Jackson, I. Pleasant, B. Grady, University of Oklahoma, Norman, OK, USA

Synergetic interactions between different types of surfactants may result in lower detergent usage. Further, the use of surfactants derived from petroleum-based sources is thought to be not as environmentally friendly as those from renewable resources. In this study, mixtures of alkyl N-methyl glucamines (MEGA) with linear alkyl carboxylic acid salts and alkyl glucopyranosides (glycosides/GPN) with linear alkyl carboxylic acid salts were investigated. Solutions at various concentrations and mixture ratios were tested and evaluated to determine critical micelle

concentration (CMC), surface tension at the CMC, surface tension reduction efficiency. These binary surfactant systems of anionics and nonionics headgroups reduce the electrostatic repulsion between ionic headgroups causing a reduction in the CMC vs. a simple pure entropically driven mixing rule. In previous investigation of alkyl sulfates by our group, a much greater interaction was seen between the sulfate headgroup and the methyl glucamine headgroup which was attributed to the more flexible nature of the glucamine headgroup relative to that of the glycoside headgroup. Similar synergetic effects will be evaluated and discussed through  $\beta$  parameter comparisons of linear alkyl carboxylic acid salts mixed micelle formation with defined MEGA and GPN ratios.

## **S&D 2: Surfactants and Performance Enhancers for Fabric Care: Polymers to Chelating Agents**

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Chair(s): S. Adamy, Church & Dwight Co Inc., USA; and R. Panandiker, The Procter & Gamble Co., USA

**Advances in More Sustainable Polymers.** A. Carrier, K. Rodrigues, M. Hazlewood, M. Vanderhoof, Akzo Nobel Surface Chemistry, Chattanooga, TN, USA

Petrochemical based polymers continue to experience wide fluctuations in both price and availability. We continue to focus on developing new polymers with a significant (> 50%) sustainable polymer content. In recent years, this research has taken the form of increased performance while keeping the sustainable polymer portion constant, and maintaining performance while increasing the level of sustainable polymer. The applications data from our work will be discussed.

**New Performance Additives for Fabric Care.** G.S. Miracle<sup>1</sup>, R.R. Dykstra<sup>1</sup>, B.J. Loughnane<sup>1</sup>, A. Chieffi<sup>2</sup>, A.T. Brooker<sup>2</sup>, <sup>1</sup>The Procter & Gamble Company, Cincinnati, OH, USA, <sup>2</sup>The Procter & Gamble Company, Newcastle upon Tyne, England

About 3000 B.C., garments were bleached in lye solutions formed from mixing wood ashes and water, then sun-dried. 5000 years later the materials are different but the challenge in the bleaching of laundered goods remains the same; delight the consumer with the benefits while caring for the garment. Oxygen based bleaches have been exploited more or less successfully following the discovery of hydrogen peroxide in 1818. Bleach activators gained prominence in the second half of the 20th century by virtue of their ability to achieve excellent bleaching in lower wash temperatures. Kinetic limitations imposed by three factors-lower wash temperatures, lower wash concentrations, and lower wash cycle times-continue to provide an impetus for pushing the barriers of oxygen based bleaches to ever more reactive and mass efficient forms to deliver consumer delight.

**Silicone Foam Control Technology Enables Sustainable Cleaning in High-Efficiency (HE) Machines.** S. Creutz<sup>2</sup>, K. Everaere<sup>2</sup>, B. Hénault<sup>2</sup>, J. Roidl<sup>3</sup>, M. Severance<sup>1</sup>, <sup>1</sup>Dow Corning Corporation, Midland, Michigan, USA, <sup>2</sup>Dow Corning S.A., Seneffe, Belgium, <sup>3</sup>Dow Corning GmbH, Wiesbaden, Germany

"High-Efficiency" (HE) home washing machines have increased in usage in North America in recent years as consumers look to reap the benefits of reduced energy and water consumption in their homes. This presents specific challenges for detergent producers to develop formulas which can effectively clean in reduced amounts of water while not causing unwanted side effects, especially excessive foam generation. High levels of foam often require extra rinsing steps and an extended washing duration, negating any environmental benefits from the use of the HE machine. Silicone foam control agents used in detergent formulations can deliver efficient foam control in HE machines, allowing the machine and detergent to work effectively to provide cleaning and other benefits to laundry. Silicones are therefore an important tool to enable the continuing trend of detergent producers providing sustainable solutions in laundry care for the future.

**Specialty Additives for Superior Performance and Sustainability.** M. Busby, I. Tomlinson, Dow Chemical, Midland, MI, USA

By the proper selection of specialty cleaning ingredients, such as surfactants, solvents, alkaline agents, and chelants, it is possible to formulate cleaners with a diverse property set, and the addition of hydrophilic or hydrophobic polymers can give unique protective functionality to the formulations. In the past, monoethanolamine has been used extensively as a chelant and alkaline agent in cleaners, but new VOC restrictions and toxicity and odor issues with MEA are forcing formulators to look for replacements. Potential replacements are being screened on the basis of cleaning performance and reduced environmental impact. Specialty alkanolamines which are low toxicity, readily biodegradable, and low or zero VOC. Incorporation of these materials into cleaners has produced some formulations which are effective at removing greasy soils while maintaining good filming and streaking performance. Various polymers can function in a variety of roles in cleaners such as processing aids, anti-redeposition aids, and soil dispersants. In addition, designed polymers can be used for surface protection. The use of specialty alkanolamines and polymers in cleaning formulations will be discussed.

**Improved Through-the-Wash Fabric Care Benefits by use of a New Polymer-Mineral Additive.** Carolina Rojas, AMCOL International, Hoffman Estates, IL, USA

Providing fabric care benefits through-the-wash is challenging since additives must deposit simultaneously with cleaning mechanisms. Layered aluminosilicates are crystalline anionic minerals of colloidal dimensions with chemically-reactive surfaces that are compatible with detergents and enhance fibers elasticity and smoothness. Layered aluminosilicates have also shown enhanced aesthetic and functional properties of powder detergents [1]. Unfortunately, low deposition efficiency and lack of additional fabric care attributes impair performance compared against rinse-added softeners. In this paper, surface modification of a model aluminosilicate with a specialized polymer was thoroughly characterized and optimized to achieve a synergistic effect. Additive deposition on fabrics was also quantified and correlated with fabric softness performance. A new polymer-mineral nanocomposite has thus been developed for 2-in-1 laundry detergents, which dramatically enhances fabric softening compared to traditional additives while providing fiber conditioning, loft, easier ironing and static energy reduction benefits.[1] Potential Benefits of Aluminosilicates as Partial Replacement for Sodium Sulfate in Powder Detergent Formulations. Carolina Rojas, Steve Azzarello. AMCOL International. 100th AOCs Annual

Meeting, 2009.

**Properties of EDTA Based Novel Carboxylate Anionic Gemini Surfactants.** Rashmi Tyagi, Jaypee University of Engineering and Technology, Guna, M.P., India

The properties of common anionics, in particular, of carboxylate surfactants are generally deteriorated by the presence of calcium and magnesium ions present in hard water. Accordingly, the development of surfactants that are stable in hard water is desired to reduce the use of softening agent while maintaining the surface activity. Present work is focused to develop cost-effective carboxylate gemini surfactants by simple synthetic route, based on commercial and cheaper raw materials and require lesser time in synthesis. Besides this, their higher stability and more solubility in hard water make them further attractive as compared to conventional anionic surfactants. Conventional surfactants have a single hydrophobic tail connected to an ionic group whereas a gemini has in sequence a long chain, an ionic group, a spacer, a second ionic group and another hydrocarbon tail. The structural features of geminis give extraordinary and better interfacial properties in comparison with their monomeric counterparts.

## TUESDAY

### AFTERNOON

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#### **S&D 3.1: Fundamental Principles and Applications of Surfactants Science: Special Session in Honor of Prof. Milton Rosen**

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Chair(s): J. Scamehorn, University of Oklahoma, USA; C. Choy, Seventh Generation, USA; and D. Sabatini, University of Oklahoma, USA

**Everything that You Always Wanted to Know about the Biodegradation of Surfactants: The What, the Why, and the How.** T. Federle, The Procter & Gamble Company, Cincinnati, OH, USA

Since the introduction of the first laundry detergent using a synthetic surfactant, biodegradation has become an important property of a surfactant to understand. Biodegradation combined with other processes (i.e. transport, sorption, volatilization, etc.) control the fate of surfactants released to the environment following use. Biodegradation reduces their dispersion, decreases their environmental concentration, prevents accumulation and results in higher and constant environmental safety factors. Various approaches are used to assess the biodegradability of surfactants, ranging from simple screening tests to environmental simulations. Analyses range from gas production as a simple end point to detailed mechanistic work involving sophisticated radioanalytical techniques. This seminar examines the role that biodegradability plays in making a surfactant safe and sustainable. It reviews various approaches for assessing biodegradability and describes the relevance of these approaches to the real world and their ability to predict exposure in the environment. It also touches on the characteristics of surfactants that affect their biodegradability and provides examples on how this knowledge can be used to design biodegradability into new molecules.

**Transforming Surfactant Art to Surfactant Science.** M.J. Rosen, Brooklyn College (CNY), Brooklyn, Brooklyn, NY, USA

This presentation will review my progress in surfactant research including synthesis, analysis, physical chemistry, and application.

**New and Novel Gemini Surfactants as "Sustainable" Amphiphiles for the 20's; Chemical Structure/Fundamental Property/Performance Relationships.** M. Dahanayake<sup>1</sup>, D. Tracey<sup>2</sup>, R. Reiersen<sup>3</sup>, M. Rosen<sup>4</sup>, <sup>1</sup>Rhodia, Inc., Bristol, PA, USA, <sup>2</sup>Tracy Consulting, Amelia, OH, USA, <sup>3</sup>Rhodia, Inc., Cranbury, NJ, USA, <sup>4</sup>Surfactant Research Institute, Brooklyn College, NY, USA

Gemini surfactants are a novel class of surfactants that, with the growing demand for "sustainable" chemistry in the formulation of consumer products, have recently generated much interest. They are distinguished from conventional surfactants by having two hydrophobic and two hydrophilic groups per molecule. This feature has given them distinctive surface properties that would not have been easy to predict. For this study, examples of amphoteric, anionic and cationic gemini surfactants have been designed for optimum surface activity based on their fundamental/performance properties and synthesized by industrially feasible processes. Results have shown high surface activity and effectiveness at concentrations 2 to 3 orders of magnitude smaller than corresponding conventional surfactants. This high surface activity, coupled with mildness, especially the mitigation of irritancy of the anionic surfactants, give gemini surfactants the potential for being the next generation of "sustainable" surfactants.

**Anionic and Cationic Surfactant Mixtures: Admicellar Modified Surfaces and Microemulsion Formation.** D.A. Sabatini<sup>1</sup>, J.F. Scamehorn<sup>1</sup>, S. Khaodhiar<sup>2</sup>, <sup>1</sup>University of Oklahoma, Norman, OK, USA, <sup>2</sup>Chulalongkorn University, Bangkok, Thailand

While anionic and cationic surfactant mixtures have the potential for great synergism in terms of CMC reduction, achieving this synergism requires avoiding the precipitation which occurs in these mixtures - the use of surfactant ?asymmetry? can help in this regard. Mixed anionic and cationic surfactants can also be used to achieve surface modification while reducing the amount of surfactant in solution to achieve maximum surfactant adsorption. Finally, titrating anionic and cationic surfactants can be used to transition between Winsor Type I, III and II systems. Examples of these processes will be presented for a range of surfactant systems.

**Thirty Years of Experience and Challenges with Emulsifiers' Preparation and Applications - Full Spectrum Thinking and Performance.** N. Garti, Casali Institute for Applied Chemistry, Hebrew University, Jerusalem, Israel

We are modifying reverse hexagonal and cubic mesophase for the solubilization and delivery of bioactives. In this study four different aroma molecules (phenylacetaldehyde, melonal, linalool and trans-4-decenal, t-4-d) were solubilized in a binary mixture of GMO/water. The aroma compounds with some amphiphilic characteristics were quantitatively solubilized and surprisingly acting as stabilizing agents for a room temperature formation of reverse hexagonal mesophases that otherwise are stable only at elevated temperatures. By entrapping the aroma compounds in the inner channels (the hydrophilic molecules), at the interface (the amphiphilic)

or in-between the fatty acids tails (the lipophilic molecules) a good chemical aroma protection was achieved. It was also detected that all examined guest molecules except phenylacetaldehyde, if entrapped at their maximum solubilization capacity, promoted a transformation from lamellar or cubic mesophase to the HII mesophase. Lattice parameter increases with water content and decreases with an increase in temperature and/or oil content. The tendency of different aroma compounds to induce phase transition was explained in terms of thermodynamic and geometry aspects (CPP).

**Biobased Surfactants from Renewable Resources.** M.R. Infante, L. Perez, IQAC-CSIC, Barcelona, Spain

Biocompatible surfactants from renewable raw materials such as amino acids will be described. Our multidisciplinary approach include design, synthesis, adsorption at interfaces and self-assembling behaviour, antimicrobial activity, study of biocompatibility including ecotoxicity, biodegradability and irritation effects. Considering the green chemistry principles the synthesis contemplates the preparation of more efficient and safer surfactants using chemo-enzymatic methodologies and designing for biodegradation.

**An Experimental Study of Wetting Behavior and Surfactant EOR in Carbonates with Model Compounds.** Yongfu Wu, Missouri University of Science & Technology, Rolla, MO, USA

This study focuses on the mechanisms responsible for enhanced oil recovery (EOR) from naturally fractured and oil-wet carbonate reservoirs by surfactant solutions, and methods to screen for effective chemical formulations quickly. One key to this EOR process is the surfactant solution reversing the wettability of the carbonate surfaces from oil-wet or mixed-wet to water-wet condition. This effect allows the aqueous phase to imbibe into the matrix spontaneously and expel oil bypassed by a water flooding. This study used different naphthenic acids (NA) dissolved in decane as a model oil to render calcite surfaces as oil-wet condition. Because pure compounds are used, trends in wetting behavior can be related to NA molecular structure as measured by solid adsorption, contact angle and a novel, simple flotation test with calcite powder. Experiments with different surfactants and NA-treated calcite powder provide information about mechanisms responsible for sought after reversal to a more water-wet state. Results indicate this flotation test is a useful rapid screening tool to identify better EOR surfactants for carbonates. The study considers the application of surfactants for EOR from carbonate reservoirs. This technology provides a new opportunity for EOR, especially for fractured carbonate where water flooding response typically is poor and the matrix is a high oil-saturation target.

**EAT 3 / S&D 3: Film, Emulsions, and Foams**

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Chair(s): A. Wright, University of Guelph, Canada; D. Kim, Kraft Foods Inc., USA; and C. Rojas, AMCOL, USA

**The PIT Emulsification Process: Reality Versus Intuition.** S.E. Friberg, Clarkson University, Potsdam, NY, USA



The PIT (Phase Inversion Temperature) emulsification produce emulsions with a large fraction of oil drops that are significantly smaller than those obtained from traditional mixing process. The process is widely used, but its fundamentals have not been clarified. The emulsification is carried out in two stages: 1. A primary mechanical dispersion at the PIT, with three phases (water, an inverse micellar solution, and a bicontinuous microemulsion) in the emulsion. 2. Immediate cooling to application temperatures, reducing the number of phases to two; an O/W microemulsion and an inverse micellar hydrocarbon solution. A rational explanation for the smallness of the drops has assumed them to emanate from the colloiddally dispersed hydrocarbon in the original bicontinuous microemulsion. However, a quantitative analysis of the phase fractions in an emulsion of water, hexadecane and tetraoxyethylene dodecyl ether versus temperature revealed that the original water phase is not retained as the final aqueous phase. The final aqueous phase is instead formed by the microemulsion absorbing water during the cooling stage, gradually modifying the bicontinuous microemulsion structure to become water continuous. In the process a minor part of the original microemulsion is separated, forming the small oil drops.

**Design and Application of Functional Food-Grade Nanoemulsions.** D.J. McClements, Department of Food Science, University of Massachusetts, Amherst, MA 01003, USA

Nanoemulsions fabricated from food-grade ingredients are being increasingly utilized in the food industry to encapsulate, protect, and deliver lipophilic functional components, such as biologically active lipids (e.g.,  $\omega$ -3 fatty acids, conjugated linoleic acid) and oil-soluble flavors, vitamins, preservatives, and nutraceuticals. The small size of the particles in nanoemulsions ( $r < 100$  nm) means that they have a number of potential advantages over conventional emulsions: higher stability to droplet aggregation and gravitational separation; high optical clarity; ability to modulate product texture; and, increased bioavailability of lipophilic components. On the other hand, there may also be some risks associated with the oral ingestion of nanoemulsions, such as their ability to change the biological fate of bioactive components within the gastrointestinal tract and the potential toxicity of some of the components used in their fabrication. This presentation provides an overview of nanoemulsion formulation, fabrication, properties, applications, and biological fate with emphasis on systems suitable for utilization within the food and beverage industry.

**Fate of Oil-in-Water Emulsions Under Gastrointestinal Simulated Conditions: Evolution of Molecular and Supramolecular Lipid Structures.** H.B. Kenmogne Domguia, A. Meynier, C. Genot, INRA, UR1268 Biopolymères Interactions Assemblages, Nantes, France

The understanding of the fate of emulsified lipids within the gastrointestinal tract may assume particular interests for the design of functional foods. The purpose of this study is to set up the experimental conditions allowing assessment of the molecular and supramolecular fate of oil-in-water emulsions during *in vitro* digestion. Emulsions, with well-characterized droplet size distributions and stabilized by different emulsifiers were submitted to *in vitro* digestion conditions that simulate mouth, stomach and then upper small intestine environments. Supramolecular changes of emulsified lipids were monitored by microscopies and light scattering techniques, whereas, formation of lipids digestion products were assessed by liquid

chromatography. Other measures concern lipid oxidation. In stomach conditions, gastric juice composition and/or gastric pH led to profound modifications of lipid organization, characterized by different extent of flocculation and/or coalescence. In small intestine, structures smaller than  $\mu\text{m}$  containing lipids digestion products and biliary salts are evidenced. The results show the key impact of the digestion conditions on the fate of lipids and the interest to validate data obtained *in vitro* by *in vivo* studies

**Development of Thermodynamic Correlations to Predict the Stability of Emulsified Formulations.** S.K. Kiran, E.J. Acosta, University of Toronto, Toronto, ON, Canada

Emulsions are classified as micrometer-sized droplets of one medium dispersed throughout another with which it is naturally immiscible (i.e. oil and water). Being a thermodynamically unfavourable process, emulsification is facilitated by the presence of surfactants that act to reduce the interfacial tension and promote droplet formation and break-up during mixing. A critical design parameter in the formulation of emulsified systems is their stability. It has been reported that this property is strongly linked to the phase behaviour of its corresponding microemulsion formulations. Developing an understanding of the fundamentals governing this relationship is of great interest as it may potentially allow for the prediction of dynamic properties from equilibrium-based correlations. As an initial modelling attempt, the stability of well defined surfactant (sodium dihexylsulfosuccinate)-oil (toluene)-water systems will be predicted. Having done so, various industrially related processes will be characterized such as crude oil recovery from rag layers and vegetable oil extraction from oil seeds. All modelling results will be validated experimentally using an in-house designed multipoint turbidity meter.

**Physicochemical Properties of Lactoferrin-stabilized Oil/Water Emulsions: Effects of pH, Salt, and Heating.** T. Tokle, D.J. McClements, University of Massachusetts Amherst, Amherst, MA, USA

Lactoferrin (LF), a cationic bovine globular protein with a high isoelectric point ( $pI \sim 8$ ), may lead to novel functional properties in foods and other products. We investigated the influence of pH (2-9), NaCl/CaCl<sub>2</sub> addition (0-200mM), and thermal processing (30-90°C, 20min) on the stability of LF-stabilized o/w emulsions. At ambient temperature, emulsions were stable at  $pH \leq 6$  but exhibited some droplet aggregation from pH 7-9. The thermal stability of the emulsions depended on pH, holding temperature and thermal history. When LF-coated droplets were heated in distilled water and then their pH was adjusted from 2-9, they were highly unstable to aggregation at pH 7 and 8. On the other hand, when the pH was altered first and then heated, the droplets were highly unstable to aggregation at  $pH \geq 5$  when heated above 50°C. The stability of emulsions to salt addition depended on pH and salt type, which was attributed to counter-ion binding and electrostatic screening effects. For NaCl, emulsions were stable from 0-200mM at pH 3 and 9, but aggregated at  $\geq 100\text{mM}$  at pH 6. For CaCl<sub>2</sub>, emulsions were stable from 0-200mM at pH 3, but aggregated with  $\geq 150\text{mM}$  CaCl<sub>2</sub> at pH 6 and 9. These results have important implications in LF-stabilized emulsion-based products.

**A Study of Polyaphron (Biliquid Foam) Systems.** S.T. Adamy, Church & Dwight Co., Inc., Princeton, NJ, USA

Polyaphrons, or biliquid foams, are systems composed of relatively high volume fractions of oil dispersed in aqueous media. The volume fraction of oil in these systems is higher than that for systems of closely packed monodisperse spheres ( $\phi = 0.74$ ). Droplets are concentrated enough that they deform into polyhedral shapes. The droplets are separated and stabilized by thin films of the aqueous phase. In this way, these systems resemble gas-liquid foam systems, with the gas phase replaced by the oily phase. This paper will present findings on the preparation and characterization of polyaphron systems incorporating various alkanes and surfactants. Results of rheological measurements, optical microscopy, and Karl-Fischer titrations (for water) will be presented and used to discuss trends with changing composition.

**\*\*Cancelled\*\* Partial Coalescence Revisited.** Roja Ergun, University of Wisconsin-Madison, USA

## WEDNESDAY

### MORNING

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#### **BIO 4 / S&D 4: Biobased Materials: Surfactants, Polymers, and Enzymes in Green Cleaning**

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Chair(s): D. Solaiman, USDA, ARS, ERRC, USA; D. Hayes, University of Tennessee, USA; and G. Smith, Huntsman Performance Products, USA

**Enhanced Stabilization of Cloudy O/W Emulsions with a Blend of Gum Arabic/Whey Protein Isolate.** N. Garti, M. Klein, A. Aserin, I. Svitov, Casali Institute for Applied Chemistry, Hebrew University, Jerusalem, Israel

Cloudy emulsions are oil-in-water (O/W) emulsions normally prepared as concentrates which are diluted into the final beverages. The cloudy emulsions provide flavor, color and cloud (turbidity) to the soft drinks. These systems are stabilized by emulsifiers, by amphiphilic polysaccharides. Whey protein isolate (WPI) and gum Arabic (GA) are natural biopolymers. From previous work, we learned that mixing WPI and GA together in an aqueous phase may result in the formation of a charge complex soluble in water. The charge complex, we believe, has a potential to serve as natural emulsifier for cloudy emulsions. The aim of our work is to stabilize an O/W emulsions by the blend of the two natural biopolymers of WPI and GA at selected conditions (pH, oil type, preparation protocol, etc). These cloudy emulsions must be stable and should fulfill the requirements of the beverages. We concluded that stable emulsions were obtained from 3:1 wt ratio of WPI:GA. The emulsions shows better stability than emulsions stabilized by GA or WPI alone. The droplets size were smaller than 1  $\mu\text{m}$  and did not change significantly during a month of aging. The emulsion with the highest turbidity was composed of 3 wt% of WPI:GA (3:1) and 20 wt% Canola oil.

**Multifunctional Green Surfactants from Crops.** S.R. Jadhav, G. John, The City College of The City University of New York, New York, NY, USA

Sugars and fatty acids are ideal natural precursors to develop value-added chemicals and serve as sustainable alternatives to petroleum-based products. Current research exemplifies the approach by synthesizing novel amphiphiles, which are versatile oil gelators with varied industrial applications. Short chain fatty acids (C<sub>4</sub>-C<sub>10</sub>) and sugar alcohols (mannitol and sorbitol) were chosen as crop-based precursors. Enzyme mediated regioselective transesterification, was employed to obtain amphiphilic sugar dialkanoates. These non-toxic and biodegradable amphiphiles, specifically C<sub>8</sub>-derivatives, exhibited unprecedented gelation in crude oil fractions, edible oil and liquid pheromones. Structure-property relationship was thoroughly evaluated to fundamentally understand the gelation mechanism. The amphiphiles also exhibited preferential gelation of oil from oil-water mixture; such phase-selective gelation was utilized to demonstrate an environmentally benign method to clean-up oil spills. The vegetable oil gelation property was exploited as healthy alternative to existing oil structuring methods used in food industries. The amphiphiles were also utilized to compose gel-based controlled release devices for pheromones, which find application in agricultural pest management.

**Clickable Sophorolipid Surfactants.** J.A. Zerkowski, D.K.Y. Solaiman, USDA, ARS, ERRC, Wyndmoor, PA, USA

This presentation will report our recent progress in modifying the structures of sophorolipids to make them more water soluble. The methodology that we have been exploring includes the azide/alkyne "click" reaction and ruthenium-catalyzed olefin metathesis. Both of these routes can be used to attach hydrophilic groups to sophorolipids. The linkages that result are not readily hydrolyzable, which is a distinction from previous modified sophorolipids, where ester bonds were used to append charged units. Preliminary results suggest that hydroxyproline is a versatile moiety for introducing a zwitterion at the carbohydrate headgroup of a glycolipid. Progress toward constructing gemini sophorolipids using similar methods will also be described.

**Production and Interfacial Characterization of New Types of Glycolipid Biosurfactants.** Dai Kitamoto, Tokuma Fukuoka, Tomotake Morita, Tomohiro Imura, AIST, Japan

Biosurfactants (BS) produced by a variety of microorganisms show unique properties compared to petroleum-based surfactants. Among BS, glycolipid-type BS such as mannosylerythritol lipids (MEL) and sophorose lipids (SL) are the most promising, due to the high productivity from vegetable oils or carbohydrates as renewable resources [1]. MEL are efficiently produced by *Pseudozyma* yeasts, and show versatile interfacial and biochemical actions. SL are produced by *Candida* yeasts, and now used as a washing agent. It is thus of interest to broaden the structural variety of these promising BS, and to clarify the structure-function relationship. Recently, we tried to synthesize new types of BS from di-acetylated MEL and SL, and obtained their deacetylated derivatives. We also obtained mono-acetylated glucose lipid and glucose lipid from di-acetylated SL. We then characterize the interfacial properties of these glycolipid BS. These new BS showed the similar surface activity to that of the starting materials, but indicated different aqueous phase behaviors. These results demonstrated that the acetyl group on the sugar moiety is likely to play more important role to direct the self-assembling manner of glycolipid BS.[1] D. Kitamoto et al., *Curr. Opin. Colloid Interf. Sci.*, 14, 315-328 (2009).

**Rhamnolipid Production and Purification.** M. Sodagari, Y. Chen, J. L. Lilly, N. M. Pinzon, L.-K. Ju, The University of Akron, Akron, OH, USA

Rhamnolipids are unique biosurfactants produced by bacteria. Rhamnolipids are extremely effective in emulsifying/solubilizing hydrocarbons, for clean-up of oil spills, bioremediation of petroleum-contaminated sites, and enhanced oil recovery. They have also been proposed as pesticides, as the source of rhamnose, and for several medical applications. Rhamnolipid production is complicated by the highly foaming nature of the fermentation broth when aerated to provide oxygen for cell respiration. We have investigated the rhamnolipid production by *Pseudomonas aeruginosa* fermentation under aerobic, microaerobic and anoxic denitrifying conditions. Effects of different carbon substrates have also been evaluated. The behaviors and challenges observed will be summarized in this presentation. About 70 g/L of rhamnolipids can be produced at 0.35 g/L-h. We have also been evaluating and developing purification methods for future large-scale operations at lower costs. The results from our recent and on-going work in rhamnolipid production and purification will be presented. If time permits, we will also briefly describe some new applications of rhamnolipids.

**Development of Bio-detergent using RSPO-certified Sustainable Palm Oil.** Yoshihiko Hirata, GlenLelyn Quan, Keisuke Igarashi, Taro Furuta, Saraya Co. Ltd., Kashiwara, Osaka, Japan

Biodiversity loss which accelerated in these years due to overexploitation of natural resources causes a rapid increase in the worldwide demand for bio-detergents, which are not only ready-biodegradable but also created from renewable and sustainable materials. In line with this, a certification system evaluated by a third-party organization has been in operation to help build a sustainable world. In the plant oil market, certified sustainable palm oil (CSPO) which is certified by Roundtable on Sustainable Palm Oil (RSPO) has been available since the end of 2008. On the other hand, we started the research of bio-based surfactants (biosurfactants, BS) for practical use as bio-detergents since 1998 and developed the automatic-dishwashing detergent containing sophorolipid, which is one of the glycolipid BSs. Sophorolipid may replace propylene oxide-ethylene oxide block copolymer surfactants which have low-foaming and high-washing ability but have poor or inconsistent biodegradability. Currently, ten bio-detergents are commercialized for domestic and industrial use and in healthcare facilities in Japan. This report contains our developed methods both for large yield fermentative production and simple purification of SL derived from CSPO resulting to a laundry bio-detergent marked with RSPO certification label.

**Improved Bioreactor Design and a Mathematic Model for Solvent-Free Lipase-Catalyzed Synthesis of Saccharide-Fatty Acid Ester in Suspension Media.** Ran Ye, Douglas G. Hayes, Department of Biosystems Engineering and Soil Science, the University of Tennessee, Knoxville, TN, USA

Saccharide-fatty acid esters, biodegradable, and nonionic biobased surfactants derived from cheap agricultural renewable sources, possess excellent properties for emulsification resulting in their wide use in foods, cosmetics, and pharmaceuticals. Previously, we have conducted esterification utilizing stable 10–200  $\mu\text{m}$  suspensions of saccharide in solvent-free media.

However, this approach has suffered from the stoppage of the recirculation to reform suspensions for several hours at a time. Recently, the operation and design of the bioreactor system have been improved, starting with the mixture of oleic acid/ fructose oleate 75/25 w/w, using the fed-batch addition of saccharide stirring at 65°C, containing an in-line filter to remove large suspended particles. After filtration, the suspension media is sent to a vessel where water is controlled at the optimal level of ~0.4 wt % via vacuum pressure and nitrogen gas bubbling and subsequently the effluent is sent to a PBBR, and recirculated to the stirred reservoir. The bioreactor system yielded a final conversion of 85% ( $0.195\text{mmol h}^{-1} \text{g}^{-1}$ ) with ~90% of monoester without further purification. A mathematical model is currently under development to describe the time course of reaction utilizing material balances and a Ping-Pong Bi Bi kinetic model.

**Interfacial Properties of Surfactant-like Extracts from Waste Biomass.** E.J. Acosta, F.Y. Garcia-Becerra, M. Baxter, D.G. Allen, University of Toronto, Toronto, ON, Canada

Surfactant-like materials extracted from waste biomass contain a wide range of chemical species that include proteins, polysaccharides, lipids, phospholipids and humic material. In this article we discuss how the composition and properties of the extract are impacted by the extraction pH and our current understanding of the relationship between composition of the extract and its ability to lower surface and interfacial tension. We will also discuss the impact of waste source/composition on the surface activity of the resulting extract. This discussion will lead to a series of scenarios where the extraction of waste biomass could be economical and might represent an advantage over petroleum-based products.

**\*\*Cancelled\*\* Synthesis and Properties of Esterquats Derived from Rice Bran Fatty Acids and Triethanolamine.** V.K. Tyagi, Harcourt Butler Technological Institute, India

**\*\*Cancelled\*\* Surface-active and Performance Properties of Alkyl Polyglycoside (APG) Surfactants Derived from Fatty Alcohols.** V.K. Tyagi, Harcourt Butler Technological Instit

**Recent Developments in Cleaning with Cellulase Enzymes.** N.J. Lant<sup>1</sup>, A. Calvimontes<sup>2</sup>, V. Dutschk<sup>3</sup>, S.G. Patterson<sup>1</sup>, <sup>1</sup>Procter & Gamble Technical Centres Ltd, Newcastle upon Tyne, United Kingdom, <sup>2</sup>Leibniz Institute of Polymer Research, Dresden, Germany, <sup>3</sup>University of Twente, Enschede, The Netherlands

Cleaning cellulases selectively modify the amorphous regions of cotton, resulting in durable laundry detergency benefits in the areas of soil release and anti-redeposition. In recent years, new cleaning cellulase enzymes such as Celluclean® and advances in formulation science have led to improved products with new consumer benefits and reduced dependence on commodity chemicals, for example in helping to enable the removal of builders such as sodium tripolyphosphate. Analysis of the morphology and topometry of fabric surfaces has improved our understanding of the effects of cleaning cellulase on textiles, helping to explain the observed detergency benefits as a function of changes in macro-, meso- and micro-porosity.

Carboxymethylcellulose (CMC) is currently used as an anti-redeposition agent in many laundry detergents, also acting through a surface modification mechanism, and this polymer is susceptible to hydrolysis by cleaning cellulases. Molecular optimisation of CMC to synergise with emerging cleaning cellulase technology has resulted in new enzyme/polymer fabric surface modification systems with improved performance.

**Breakthrough Enzyme Technology for Laundry Soap Bars.** Nelson Prieto<sup>1</sup>, Cheila Cavanholi<sup>1</sup>, Michael Bullock<sup>1</sup>, Christian Wieth<sup>2</sup>, Peter Klindt-Mogensen<sup>2</sup>, Yang Zaizhou<sup>3</sup>,  
<sup>1</sup>Novozymes North America, Franklinton, NC, USA, <sup>2</sup>Novozymes A/S, Bagsvaerd, Denmark,  
<sup>3</sup>Novozymes China, Beijing, China

Enzymes deliver unique cleaning benefits in various laundry applications but have not been used widely in laundry soap bars because it is difficult to stabilize them in a typical laundry soap bar matrix. An enzymatic breakthrough innovation has been developed for laundry soap bars that introduces a major performance advancement in this product category. Enzymes have been added and stabilized in diverse laundry soap bars enabling increased cleaning benefits without adversely affecting other key characteristics and delivering a product preferred by consumers. Results from diverse wash performance, physical properties, and stability tests were confirmed with consumer studies. The results will be presented demonstrating the benefits the breakthrough enzyme technology delivers in laundry soap bars.

#### **S&D 4.1: Surface Cleaning, Disinfection, Antimicrobials, and Odor Control**

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Chair(s): E. Szakeres, The Clorox Company, USA; and A. Taneja, BASF, USA

**The Disinfecting Effect of Metal Complex in Laundry.** Naoya Tamura, Kumiko Fujiwara, Ryo Hyodo, Hirohiko Tadenuma, Toshiaki Majima, Tomonari Suekuni, Hiromitsu Takaoka, Lion Corporation, Edogawa-ku Tokyo, Japan

Recently, consumers have come to pay much attention to environment conservation. This trend induces the laundry condition to the lower water temperature. Washing in cold water causes not only reduction of detergency but also inadequate removal of bacteria on the clothes. Therefore it is important for us to develop laundry detergents with superior disinfecting effect. We focused on the bleaching agents 'metal complexes' as disinfecting agents. We studied some combinations of metal ion and ligand from the point of view of the disinfecting activity and prevention of fabric damage. As a result, we found a new Cu complex which showed superior disinfecting activity to gram negative and gram positive bacteria even in small dosage, under the lower water temperature conditions. In addition, it is interesting that our complex had a deodorant effect for malodor caused by bacteria metabolism on the clothes. We think that the metal complex is the really effective ingredient to achieve both high disinfecting and bleaching performance under the eco-friendly laundry condition.

**Survey of Halamine Antimicrobials.** R.M. Broughton, H.B. Kocer, I. Cerkez, W. Liu, T.S. Huang, S.D. Worley, Auburn University, Auburn, AL, USA

Oxidative halogen antimicrobials have been universally applied in water treatment. The

disadvantages of this technology include: corrosion, reactions which produce toxic materials and the loss of halogen to the atmosphere. Halamine chemistry is an often used alternative and requires an amine, amide, or imide which reacts with a halogen (Cl or Br) to produce a halamine. The halogen is "stored" in a relatively noncorrosive, nonlabile state, and becomes active on contact with a bacterial cell, virus or any easily oxidized material. After exhaustion, the halamine can be regenerated by exposure to dilute household bleach. For 30 years, researchers at Auburn have worked on halamine chemistry. The work began with water purification, and has resulted in commercial products for that purpose. Recently the work has moved to antimicrobial surfaces and coating formulations. The surfaces include medical and consumer textiles (products commercially available) and coatings such as paints. The challenges include: 1. The balance between stability and reactivity, 2. Obtaining good contact with the halamine, 3. Bonding the halamine to a surface, 4. Minimizing UV degradation of the halamine, and 5. Maintaining substrate properties. Graduates from the program have also developed halamine products that are commercially available. The presentation will include both history and recent work.

**Readily Biodegradable Chelating Agent for Improved Detergent Efficiency.** P. Kincaid, W. Parry, Akzo Nobel Functional Chemicals LLC, Chicago, IL, USA

Chelating agents improve detergent performance by controlling multivalent ions. A strong chelate removes scale, controls hard water ions, improves surfactant efficiency and boosts biocide performance. EDTA has widely been used as the chelating agent of choice however there remains a need for greener alternatives. Monosodium glutamate (MSG) is produced via fermentation of sugars from renewable sources. MSG is modified to give the strong chelating agent glutamic acid, N,N-diacetic acid (GLDA). Chelating performance is comparable to EDTA and NTA with the added benefit that GLDA has a very high solubility at both low and high pH. GLDA is 53% biobased molecule as well as being readily biodegradable. Chelating agents boost biocides by depriving the organism of metals required for the membrane structure therefore improving efficiency. GLDA boosting properties are improved over common chelating agents currently in use. Added benefits of using GLDA could include: extended shelf life, reduction in preservative dose and reduction in water due to GLDA high solubility. The combination of strong performance, favorable toxicology and renewable sourcing make GLDA an ideal chelating agent for detergents.

**Dissolubility of Soap Scum by Surfactant in the Presence of Chelant.** Sawwalak Itsadanont<sup>1</sup>, John F. Scamehorn<sup>2</sup>, Sumaeth Chavadej<sup>1,3</sup>, <sup>1</sup>The Petroleum and Petrochemical College, Chulalongkorn University, Wangmai, Bangkok, Thailand, <sup>2</sup>Institute for Applied Surfactant Research, University of Oklahoma, Norman, Oklahoma, USA, <sup>3</sup>Center for Petroleum, Petrochemical, and Advanced Materials, Chulalongkorn University, Bangkok, Thailand

Dissolution of soap scum, or calcium salt of a long chain fatty acid, is a challenge for formulating hard surface cleansing agents since soap scum formed when soap is exposed to hard water has very low water solubility. In this research, the aqueous equilibrium solubility and dissolubility of soap scum or calcium octadecanoate (calcium stearate or  $\text{Ca}(\text{C}_{18})_2$ ) are measured as a function of pH from 4 to 11 under the presence of biodegradable chelating agent (Methylglycinediacetic acid or MGDA) and different surfactants. Methyl ester sulfonate (MES), alcohol ethoxylate with 9 ethylene oxide groups (OE9), and dimethyldodecylamine oxide



(DDAO) are selected in this study. At high pHs (9 – 11), the highest soap scum solubility (0.03 – 0.04 M  $\text{Ca}(\text{C}_{18})_2$ ) is observed with the DDAO, amphoteric surfactant. Under this condition, the amphoteric surfactant is in a zwitterionic form which forms mixed micelles well with the stearate anion while the chelant effectively bounds with calcium ions so the solubility of soap scum is high. Without the chelant, the solubility of soap scum is extremely low.

**Quick and Spotless Drying.** S. Gross<sup>1</sup>, A. Uner<sup>2</sup>, T. Albers<sup>3</sup>, <sup>1</sup>Cognis Corporation, Ambler, PA, USA, <sup>2</sup>Cognis Kimya A.Ş., Gebze/Kocaeli, Turkey, <sup>3</sup>Cognis GmbH, Dusseldorf, Germany

In this presentation, an amphoteric surface modification polymer (SMP) for application in manual dishwashing liquids is introduced. Its numerous benefits, such as faster drying time, spot-free drying and convenience for cleaning will be discussed. The convenience claim supported by inclusion of this amphoteric surface modification polymer in manual dishwashing liquids is: ?Quick & spotless drying without the need to towel dry the dishes.? Test methods for measurement of drying time and evaluation of water spots are presented along with results. A video showing faster drying of a half-treated ceramic plate is included, and guide formulations illustrating the usage of the SMP are also presented.

**Quantitative Stroke-by-Stroke Method for the Gardner Washability Apparatus: Application to DOE Optimization of Hard Surface Degreasers and Relation to Fundamental Wetting Properties of Formulations on Soiled and Unsoiled Surfaces.** R. Masters, W. Gorman, Stepan Company, Northfield, Illinois, USA

A digital camera system with controlled lighting has been constructed to provide quantitative analysis for Gardner cleaning test methods in Hard Surface Care. This system provides for a stroke by stroke analysis of cleaning speed. This system has been used to obtain detailed DOE data for hard surface degreaser formula optimization. Dynamic surface tension and contact angle measurements and on soiled and unsoiled surfaces will be presented for formulations across the DOE space, relating fundamental properties to observed speed of cleaning.

#### **S&D 4.2: Alternate Cleaning Methods: Solvents and Low Water Systems**

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Chair(s): J. Scheibel, The Procter & Gamble Co., USA

**Keynote Presentation: Sustainable Solutions in Laundry: Mass Efficient Formulation Approaches to Cleaning.** Jamie Danziger, The Procter & Gamble Co., Cincinnati, OH, USA

Today's detergent formulators are challenged by high commodity prices even for common ingredients. The challenge for consumer product companies is to build detergent formulations with highly weight efficient ingredients, which in combination with the common ingredients such as surfactants, can deliver far more than the sum of individual components in the formulators toolbox. This talk will present some of the tools and ways P&G has been able to provide mass efficient formulations for cleaning, reducing the level of the less efficient technologies such as surfactants.

**\*\*Cancelled\*\* Green Solvents and Ionic Liquids: Hard and Soft Cleaning Surfaces.** S.

Seelig, Waterless Cleaning, LLC, USA

**Critical Fluid Carbon Dioxide as a Cleaning Agent - Optimization and Use.** K. Srinivas, J.W. King, University of Arkansas, Fayetteville, AR, USA

Carbon-dioxide-based dry cleaning systems have for some time been an alternative option to replace solvent-based media for fabric cleaning operations. Success of this approach is partially witnessed by commercial dry cleaning operations that employ this principle. The efficacy of carbon dioxide as a solvent in fabric cleaning is frequently improved by using: co-solvents, surfactants, chelating agents and small quantities of water to solvate or physically remove soils from textile products. This presentation will focus on the optimization of the carbon dioxide based cleaning process in terms of the solubility parameter of CO<sub>2</sub> and water, its interaction with polymeric textile substrates, and integration of mechanical shear forces to affect better cleaning. The design of additive surfactants will be rationalized using Hansen 3-dimensional solubility parameter spheres and literature data, i.e., from inverse gas chromatography studies. Similarly, techniques and results from allied fields, such as the design of CO<sub>2</sub>-phillic chelating agents, can aid in the removal of metallic contaminants from the garment matrix. Finally examples will be given of using the above cleaning options in terms of contaminant - solvent-additive interaction with suggestions for "greening" the fabric cleaning process using oleophilic additives.

**Strategies for Eliminating Solvents in Hard Surface Cleaning Formulations.** E. Theiner, K. Yacoub, Air Products and Chemicals, Inc., Allentown, PA, USA

Solvents have long been a mainstay in hard surface cleaning applications because they are effective and historically cheap. Pressure from public perception, regulatory and licensing agencies, and economics have caused the term "solvent" to now be seen as negative, particularly for the more traditional high VOC solvents. Presented here are formulation concepts and methods utilizing commercial and developmental surfactants to reduce or remove solvents from hard surface cleaning formulations while maintaining a high level of performance.

## Surfactants and Detergents Posters

Chair(s): M. Wint, Amway Corporation, USA

**ASTM International Committee D12 on Soaps and Other Detergents.**

K. McClung<sup>4</sup>, B. Beckman<sup>1</sup>, T. Lynch<sup>2</sup>, A. Hardaway<sup>3</sup>, <sup>1</sup>Reckitt Benckiser, Montvale, NJ, USA, <sup>2</sup>Clorox Service Company, Pleasanton, CA, USA, <sup>3</sup>Whirlpool, Benton Harbor, MI, USA, <sup>4</sup>ASTM International, West Conshohocken, PA, USA

ASTM Committee D12 has over 80 members and 5 technical subcommittees with jurisdiction of 50 standards. These standards play a preeminent role in all aspects important to the industry. Some new activities are: Test Method for the Determination of Cleaning Efficacy of Hard Surface Cleaning Wipes The goal of this task force is to create a set of guidelines to evaluate the

cleaning performance of hard surface wet cleaning wipes intended for use on common household surfaces. These guidelines will be based upon cleaning industry practices that are compatible with the product type and reflect typical consumer usage. ? Test Method for Evaluating Cleaning Performance of Products Intended for Use on Kitchen Surfaces Found in the Home The withdrawal of a previous ASTM standard, ASTM D4488, Guide for Testing Cleaning Performance of Products Intended for Use on Resilient Flooring and Washable Walls, has inspired interest in this new method, which will be more specific to kitchen surface cleaning than the previous standard. ? Test Method for High Efficiency (HE) Detergent Sudsing Characteristics This test method provides guidelines for determining the suitability of laundry formulations to merit a HE designation. The test method measures the foam generation and stability of laundry formulations, both through a bench-top method and a washing machine method.

### **Biosurfactant Production by *Aureobasidium pullulans* with Alternatives Inducers.**

Betina Andréa Klafke Mahl, Rosana de Cassia de Souza Schneider, Valeriano Antonio Corbellini, Lucas Lengler, Santa Cruz do Sul University, Santa Cruz do Sul, Rio Grande do Sul, Brazil

The microbial biosurfactants are mostly from bacterial source. The bacteria most often reported for this purpose are of the genera: *Pseudomonas* sp. *Acinetobacter* sp., *Bacillus* sp. and *Arthrobacter* sp. However, most bacterial biosurfactants are not suitable for using in the food industry due to their possible pathogenic nature. Thus, the yeast may be an alternative, once some have already been studied for the production of emulsifiers. The *Aureobasidium pullulans* is a yeast that produces esters of arabitol and manitol under sucrose induction. This work aimed to use a strain of *A. pullulans* isolated from *Ricinus communis* L. phytoplankton in a medium containing alternative inducer (biodiesel, glycerol and kerosene) for production of biosurfactants. The production was evaluated by emulsification index, Thin Layer Chromatography, Gas Chromatography and Infrared Spectroscopy. The best inducer was the biodiesel with biosurfactant composition similar to that obtained with sucrose. FAP-UNISC, CNPq, PUI-UNISC

### **Bringing Performance to Green Formulations for the Home Care Market with Poly(sodium itaconate).**

Y. Durant, Itaconix, Dover, NH, USA

Poly(sodium itaconate) is produced from itaconic acid, an organic acid monomer fermented from carbohydrates. Itaconix™ Dispersant DSP2K is a low molecular weight poly(sodium itaconate) with primary utility found in home cleaning formulations. Its molecular structure provides unusually high binding capacity for metal ions such as calcium and magnesium, at neutral to elevated pH. For comparison, it has the equivalent binding capacity and binding constant for calcium as tri sodium polyphosphate (STPP). Since the phasing out of STPP in laundry and automatic dishwasher detergents, formulators have been using compromise alternatives such as sodium citrate, sodium polyacrylate, polyaspartic acid and other lower performance builders. DSP2K is inherently biodegradable according to test results of OECD301A, is made from sustainable bio-based resources, and is safe for the consumers and the environment. In addition to its ability to remediate performance issues found in numerous households with hard water,

Poly(sodium itaconate) additionally has unique soil anti-redeposition properties, antiscaling performance, and corrosion inhibition of soft metals. This polycarboxylic builder provides a cost effective solution to performance loss encountered by brands, particularly green brands, since the phasing out of STPP.

### **Saponification of Peanut Oil and its Cell Cytotoxicity.**

Moonsup IM, Sung Yeon Cho, Dae-kyeong Kim, John-hwan Lee, R&D Center, Amorepacific Corporation, Yongin-si, 446-729, Republic of Korea

A lot of people suffer from dermatitis or atopic skin disease because of environmental problems and external irritants. So, many companies launch products especially for sensitive skin or for atopic skin. Generally, these low irritant products are made of non-ionic and amphoteric surfactants. We focused on the carbon number of surfactants not on the charge of surfactants. Generally, palm kernel oil and coconut oil(their major component is lauric acid) are used as cleansing agent through saponification. However, we saponificate peanut oil(composed of oleic and linoleic acid) as a cleansing agent. We tested this sample with two cleansing products. One is made of non-ionic and amphoteric surfactants, for sensitive skin. The other is a soap-based cleanser made of potassium laurate and potassium myristate. To compare the irritation level of cleansers, we investigated in vitro cell cytotoxicity L929 agar overlay test. The test samples were loaded for 24h into cell medium and then we examined the decolorized area. As a result, two commercial products showed severe cytotoxicity, however, the saponificated peanut oil based cleaser did not have any cytotoxicity as a negative control. In conclusion, we found out that the carbon number of surfactants is a important factor of cell cytotoxicity and when the length of carbon chain gets longer, cell cytotoxicity would be lower.

### **Automatic Dishwasher Detergents, Challenges in the Builder System.**

H. Kola, Battelle, Duxbury, MA, USA

The purpose of this study was to assess the automatic dishwashing formulas produced by different manufacturers for both Western Europe and North American markets during 2008. State of the art analytical techniques were used to quantify and characterize the AEO/PO surfactant and other ingredients such builders, bleach, bleach activator, enzymes, polymers, etc. present in automatic dishwashing tablets, powders or gels. Some two phase tablets contain bleach in one phase and both enzymes and bleach activator in the other one. And there are also other two phase tablets that contain the exact same ingredients in each phase of the tablet. In the phosphate-free newly introduced products the phosphates where replaced by methylglycinediacetic acid, a readily biodegradable complexing agent or by sodium citrate. The study gives an overview of the different automatic dishwashing formulas on the market and illustrates the continuous effort of manufacturers to search for more ecologically acceptable ingredients while keeping the functionality and performance of the detergent.

### **Study of Interactions between Bentonite and Functionalized Polymers in a Simulated Wash Environment.**

Carolina Rojas, AMCOL International Corp., USA

The mineral montmorillonite, main constituent of bentonite clay, consists of layered

aluminosilicates of colloidal dimensions and chemically-reactive surfaces. Among its multiple applications, bentonite clay is widely used as fabric care additive and has recently shown to improve the properties and appearance of powder detergents [1]. Modifying the surface of bentonite nanoparticles with specialized polymers may enhance their through-the-wash fabric softening ability so that benefits are perceived after fewer wash cycles and/or at lower dosages. However, there are innumerable polymers available and their interactions with clay, detergent and fabric during the laundry process are crucial for success, but complex and unpredictable. A study was conducted to elucidate the interactions between certain polymer types and bentonite nanoparticles when dispersed under simulated wash conditions. The obtained data was correlated with fabric softening performance and served as basis to screen potential surface-modification polymers. The proposed methodology may lead to rapid discovery of new fabric care additives for 2-in-1 laundry detergents. [1] Potential Benefits of Aluminosilicates as Partial Replacement for Sodium Sulfate in Powder Detergent Formulations. Carolina Rojas, Steve Azzarello. AMCOL International. 100th AOCS Annual Meeting, 2009.

### **Silicone Polymers for Fabric Care.**

Smita Brijmohan, Robert Christie, Momentive Performance Materials, Tarrytown, NY, USA

Silicone polymers possess unique combination of chemical and physical properties. They provide clear, hydrophobic and soft feel to the treated substrates. Organic modification in silicone polymers renders improved properties such as affinity to substrate, enhanced feel and hydrophilicity. This poster demonstrates the delivery and application of organically modified silicone polymers in fabric care. The role of organic modification and its influence on the performance were studied. Special formulations were prepared for delivery through the washing machine.

### **Microemulsion Formation of Motor Oil by Using Alcohol Ethoxylate without Alcohol.**

Sanithad Issareenarade<sup>1</sup>, Sumaeth Chavadej<sup>1</sup>, John F. Scamehorn<sup>2</sup>, Veerapat Tantayakom<sup>3</sup>, <sup>1</sup>The Petroleum and Petrochemical Collage Chulalongkorn University, Bangkok, Thailand, <sup>2</sup>The University of Oklahoma, Norman, OK, USA, <sup>3</sup>PTT Chemical Company limited, Thailand

The aim of this research was to investigate the microemulsion formation of motor oil with alcohol ethoxylate (AEs), nonionic surfactant derived from plam oil, without adding alcohol. The alcohol ethoxylate with different ethoxylate groups (AE3, AE7 and AE9) were mixed with methylester sulphonate (MES) and sorbitan monooleate ( Span 80) for forming microemulsions with motor oil at various temperature (20°C, 30°C, 40 °C, and 50°C). Span 80 used as a lipophilic linker that was found to be crucial to the formation of these microemulsion systems. The mixed surfactant system between AE3, AE7 and Span 80 was found to form middle phase microemulsions (Winsor Type III) at relativity low surfactant concentrations. For all of the studied surfactant systems, temperature had a significant effect on the microemulsion phase transformation and the lowest values of the critical microemulsion concentrations were achieved at 50°C.

### **Detergency of Mixed Soils Using Mixed Surfactants of Methyl Ester Sulfonate and Alcohol Ethoxylate.**

Oranich Thiengchanya<sup>1</sup>, Sumaeth Chavadej<sup>1</sup>, John F. Scamehorn<sup>2</sup>, Veerapat Tantayakom<sup>3</sup>,

<sup>1</sup>Chulalongkorn University, Bangkok, Thailand, <sup>2</sup>The University of Oklahoma, Norman, OK, USA, <sup>3</sup>PTT Chemical Company limited, Thailand

The objective of this research is to investigate the detergency performance of mixed soil removal by using mixed surfactants. Methyl ester sulfonate (MES), anionic surfactant and alcohol ethoxylate (AE), nonionic surfactant are used in this study. Two types of fabric; pure cotton, and pure polyester are used in this study. For mixed soils, motor oil and kaolinite are chosen to use as a model of oily soil and particulate soil, respectively. All of washing experiments were performed in a Terga<sup>®</sup> Meter at 30 °C of different total surfactant concentrations. It found that the highest performance of mixed soils removal was performed at 0.3% of total mixed surfactant system. and this selected formulation was also gave the higher percentage of soils removal when compared with the single surfactant, MES or AE. Furthermore, the re-deposition of removed soils was also investigated. In addition, the selected formulation obtained from this study was also compared with a commercial detergent, It showed that the commercial detergent provided the higher percentage of mixed soils removal than the selected formulation because in the commercial detergent contains the other components which supports the soils removal such as enzymes, builder, polymer, and bleaches.

#### **Analysis of Brazilian Clays as Adsorbent for Surfactants.**

F.R. Valenzuela-Diaz<sup>1</sup>, A. Almeida<sup>2</sup>, E.A. Hildebrando<sup>1</sup>, J.B.A. Salgado<sup>2</sup>, S.G. Dantas<sup>2</sup>, M.G. Silva-Valenzuela<sup>1</sup>, <sup>1</sup>Poytechnic School, University of São Paulo, Sao Paulo, Sao Paulo, Brazil, <sup>2</sup>Pegmatech-Especialidades Tecnológicas Ltda, Joao Pessoa, Paraiba, Brazil

The adsorption of the sodium lauryl ether sulfate (SLES) (anionic) and cetyl trimethyl ammonium chloride (CTAC) (cationic) surfactants was analyzed by eight different layered (seven bentonites and one kaolin) Brazilian clays. The main was to investigate the behavior of these clays as adsorbent for surfactants. Clay samples were identified as P01-P08 and characterized by X-ray diffraction, IV spectrometry, electronic microscopy, and analyzed by Foster method to classify them in swelling and non-swelling clays. A series of six suspensions for each clay in surfactant solutions were prepared using concentrations in the range 100-10,000 µg/mL. The suspensions were shaken for 24 h at room temperature to maintain surfactant in solution and then centrifuged. The centrifuged clay was dried and characterized by X-ray. Adsorption isotherms were obtained by UV spectroscopy. Adsorption constants from Langmuir and Freundlich equations were used to compare adsorption of SLES and CTAC by different clay minerals studied. The X-ray difratograms indicated changes in the structure of clays caused by adsorption. Our results shown differences in the clay adsorption capacity, which were related to surfactant nature versus chemical composition and structure of clay mineral studied. These studies were used to formulate detergents and cosmetic oils.

#### **Micelle Formations in a Bio-compatible Surfactant Mixture.**

Zhongni Wang, Wu Zhou, Tonghao Wu, Min You, College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan, Shandong, China

For the purpose to be used as the carrier of functional food ingredients, the micelle formations for a biosurfactant sodium deoxycholate (NaDC) and a nonionic oleyed surfactant (Brij 97) mixture have been investigated through surface tension measurements at 30°C in both 0.1M

NaCl and the borate-sodium hydroxide buffer solution (pH 10) . The micellar molecular interaction parameter, activity coefficients, and free energy of micellization were calculated based on Clint, Rubingh&Rosen, Motomura and Maeda models. The results show that (1) The mole fraction of NaDC in mixed micelle is all less than 0.33 when the mole fraction of NaDC in the bulk solution varies from 0.17 to 0.95. (2) The mixed micelle formation shows a negative deviation to the ideal behavior and a  $\beta^M$  value in between around -4 and -9, which is much negative than that of the typical anionic/nonionic systems. (3) The two surfactants exhibit much stronger interactions in 0.1M NaCl solutions than in buffer solutions. Acknowledgments Financial support of this work by the Natural Science Foundation of China (31071603) is gratefully acknowledged.

### **Synthesis, Properties and Industrial Uses of Cationic Imidazolines.**

D. Bajpai, H.B.T.I., Kanpur, Kanpur, U.P., India

Imidazoline surfactants belong to the category of cationic surfactants. Present study based on the microwave synthesis of imidazolines based on cheap and easy available reactants using microwave irradiation, their properties and their applications. Along with their use as laundry detergent present study emphasize on their other industrial uses in pharmacy, oil industry, lubricant industry etc.

### **Effect of Palm Olein and Glycerol on Physicochemical Properties of Beverage Emulsion.**

Hamed Mirhosseini, Bahareh Tabatabaee Amid , Chin Pin Tan, University Putra Malaysia, Selangor, Malaysia

The main objective of present study was to investigate the effect of glycerol (0.5, 1 and 1.5% w/w) and palm olein oil (2, 3 and 4% w/w) on physicochemical properties of orange beverage emulsion. The addition of glycerol and palm olein to the basic emulsion formulation significantly ( $p < 0.05$ ) increased the stability of orange beverage emulsions. The increase of emulsion stability induced by palm olein oil may be attributed to the effect of vegetable oil on electrophoretic mobility. On the other hand, glycerol can alter the magnitude of the repulsive and attractive forces governing the stability and rheological properties of an emulsion. The addition of glycerol to the beverage emulsion led to enhance the emulsion viscosity, thereby increasing the emulsion stability. In general, the beverage emulsion formulations containing palm olein provided a lower turbidity loss rate than the glycerol-based beverage emulsion. This may be attributed to the more positive effect of oil phase concentration to enhance the turbidity of emulsion. The loss of turbidity of emulsions and beverages was due to the changes in refractive index of oil phase and aqueous phase. The results indicated that glycerol and vegetable oil can be used as supplementary emulsion components to modulate the physicochemical properties of beverage emulsion.