

# 2010 Annual Meeting Abstracts

## Surfactants and Detergents

### MONDAY

#### MORNING

##### **S&D 1: Extended Chain Surfactants**

Chair(s): E. Acosta, University of Toronto, Canada; and D. Sabatini, University of Oklahoma, USA

**Extended Surfactants: A Fine-tuned Structure to Improve Interfacial Performance through a Gradual Polarity Transition.** Jean-Louis Salager, Ana Forgiarini, Cersar Scorzza, Laura Tolosa, Josmary Velasquez, Universidad de Los Andes, Columbia

Conventional surfactants exhibit well defined polar and apolar portions. The mixing of different surfactant species, as well as the introduction of additives like cosurfactants and linkers, allows to improve the performance as far as microemulsion solubilization and interfacial tension are concerned. However, such mixed components often fractionate, i.e., they partition between phases and interface in different ways; as a consequence, a hard-to-find optimum interfacial formulation is no longer insured when the surfactant concentration or water-oil ratio change, which is a very common occurrence in practice from laundry to enhanced oil recovery. Fastening together the mixture components in a single molecule that produces the same effect with no fractionation drawback, has been one of the goals of the so-called extended surfactant structure, which contains an intermediate polarity spacer between the head and tail groups. Recent investigations on different types and different applications such as detergency, cosmetics or crude demulsifying, indicate that these surfactants are likely to be particularly performant with problematical oils like high MW paraffin, triglycerides or asphaltenic crudes. Emerging trends are analyzed to correlate the structure to the properties and to guess about the next generation.

**Extended Chain Surfactants in Detergent Applications.** G.A. Smith, S. Sfamenos, Huntsman Corporation, 8600 Gosling Road The Woodlands, TX USA

Conventional surfactants have a hydrophobic tail attached to a hydrophilic head group. As the size of the hydrophobic group increases, the surfactant becomes more surface active but also less soluble in the bulk aqueous phase. To avoid the solubility paradigm, we introduce a linking group of intermediate polarity between the alkyl chain and head group. This new molecular architecture is called an extended chain surfactant. Different types of extended chain surfactants were prepared in the laboratory and the surface properties determined using a variety of experimental techniques. Nonionic extended chain surfactants (X-LAE) were prepared by adding propylene and ethylene oxide to detergent range alcohols using base catalyst. Different anionic extended chain surfactants were also prepared. Extended chain ether sulfates (X-AES) were prepared by sulfating the nonionic intermediate using chlorosulfonic acid (CSA) or sulfamic acid to give the sodium and ammonium salts respectively. Extended chain phosphate esters (X-PE) were prepared by reacting the nonionic intermediate with P<sub>2</sub>O<sub>5</sub> and neutralizing with sodium hydroxide. Extended chain ether carboxylates (X-EC) were prepared by reacting the nonionic intermediate with chloroacetic acid (CSA) and NaOH, neutralizing the resulting material with a strong acid, washing out the salts and drying the sample under vacuum to remove the water. The surface properties of the various extended chain surfactants were determined by a variety of experimental techniques. Surface tension and critical micelle concentration were determined using a Krüss K12 tensiometer. Interfacial tension against mineral oil and olive oil was determined by drop volume and spinning drop tensiometers. Results show that all of the extended chain surfactants require addition of electrolyte to achieve ultra low interfacial tension. Under optimum salinity conditions, extended chain surfactants give enhanced performance in hard surface and textile cleaning applications.

**Microemulsions with Extended-surfactants: Characterization and Applications.** D.A. Sabatini<sup>1</sup>, L.D. Do<sup>2</sup>, T.T. Phan<sup>1</sup>, <sup>1</sup>University of Oklahoma, Civil Engineering and Environmental Science, USA, <sup>2</sup>University of Oklahoma, Chemical Engineering and Material Science, USA

Extended surfactants contain an intermediate-polarity spacer, such as polypropylene oxide, between the head and the tail of a surfactant molecule. Owing to their unique properties, extended-surfactants show ultralow interfacial tension with highly hydrophobic oils, such as vegetable oils and hexadecane. In this work, we study the effect of extended-surfactant structures (such as effect of PO#, degree of branching) on the interfacial properties with triglyceride oils and their microemulsion phase behaviors. We also discuss the potential use of extended-surfactants in detergency and vegetable oil extraction applications. In detergency applications, extended-surfactants show high triglyceride oil removal efficiency (80%) at very low surfactant concentration (<250 ppm) and low temperature (15-25°C). In oilseed extraction applications, extended-surfactants also show very high canola and peanut oil extraction efficiency at low surfactant concentrations (<0.5 wt%). We have achieved 90-95% extraction efficiency for canola and peanut oil extraction. The surfactant-based extracted vegetable oils are superior to hexane-based extracted vegetable oils.

**Laboratory-based Small Pilot Scale Surfactant Microemulsion Based Oil Seed Extraction.** Sezin Islamoglu Kadioglu<sup>1</sup>, Linh Do<sup>2</sup>, David A. Sabatini<sup>1</sup>, <sup>1</sup>University of Oklahoma Department of Civil Engineering and Environmental Science, Norman, OK, USA, <sup>2</sup>University of Oklahoma Department of Chemical Engineering and Material Science, Norman, OK, USA

The aim of this study is (i) to evaluate the feasibility of extracting oil from peanut and/or canola seed by microemulsion based surfactant extraction method, (ii) optimize, at lab scale, sample preparation and extraction time, (iii) and optimize the system parameters. Two different kinds of anionic extended surfactants proved to be effective in corn oil and canola oil extraction; namely C12,14-(PO)10-(EO)2SO4Na and C10-(PO)18-(EO)2SO4Na were used. The effect of the pre-conditioning process on extraction yield was evaluated. Based on interfacial tension measurements, the surfactant and salt concentrations were optimized. Extraction system mainly consists of two different centrifuges. One for solid/liquid separation; for removing crushed oil seeds from surfactant/oil mixture and another centrifuge for liquid/liquid separation; fractionation of extracted oil from surfactant solution. To reach maximum efficiency operational parameters including feed flow rate, frequency were evaluated. This research serves as a scale-up proof-of-concept of previous bench-scale studies that showed greater than 90% oil seed extraction.

**Adsolubilization and Solubilization using Carboxylate-based Extended Surfactants.** Noulkamol Arpornpong<sup>1</sup>, Jirapat Lewlompaisan<sup>1</sup>, Ampira Charoensaeng<sup>1</sup>, David A. Sabatini<sup>2</sup>, Sutha Khaodhiar<sup>3</sup>, <sup>1</sup>National Center of Excellence for Environmental and Hazardous Waste Management, Chulalongkorn University, Bangkok, Thailand, <sup>2</sup>Schools of Civil Engineering and Environmental Science, University of Oklahoma, Norman, Oklahoma, USA, <sup>3</sup>Department of Environmental Engineering, Chulalongkorn University, Bangkok, Thailand

Adsolubilization of organic solutes by surfactant-modified adsorbents is an important phenomenon for surfactant-based environmental technologies. Surfactant aggregates adsorbed at the solid-liquid interface are capable of solubilizing organic solutes due to partitioning from the aqueous phase into the admicelle. In this research, the adsorption, adsolubilization and solubilization studies of two novel anionic carboxylate-based extended surfactants were measured and compared to an anionic sulfate-based extended surfactant and an anionic conventional surfactant. Adsorption and adsolubilization studies were on alumina oxide surfaces. Three organic solutes with differing degrees of polarity (phenylethanol, styrene, and phenanthrene) were evaluated in adsolubilization and solubilization studies. In consideration of surfactant losses from the solid surface, the desorption capacity was determined to evaluate the stability of the surfactants adsorbed onto the surface. The results indicate that the carboxylate-based extended surfactants has lower desorption capacity as compared to the conventional surfactant. Therefore, the use of extended surfactant adsorbed onto solid surface can reduce the surfactant losses from the surface and improve the operating characteristics of the surfactant-modified adsorbent.

**Application of the HLD-NAC Model to Formulate Detergents Using Extended Surfactants.** S.K. Kiran, E.J. Acosta, University of Toronto, Department of Chemical Engineering and Applied Chemistry, Toronto, Ontario, Canada

The use of surfactant mixtures have garnered considerable attention due to their enhanced synergism which results in

ultralow critical micelle concentration (CMC) and interfacial tension values. Although the phase behaviour and properties of systems composed of various types of surfactant mixtures have successfully been modeled in the past, such aspects have yet to be explored for anionic-cationic surfactant mixtures. The primary goal of this study is to address this gap in the literature using the HLD-NAC model. This model is a semi-empirical equation of state for microemulsion ( $\mu$ E) systems which predicts  $\mu$ E properties according to their thermodynamic formulation parameters. The secondary objective of this study is to apply this model to formulate detergents using a mixture of anionic extended surfactants and benzethonium chloride. This is of particular interest as it is hypothesized that such systems will exhibit superior solubilization performance in comparison to commercially available detergents at lower electrolyte concentrations.

**Effect of Hydrocarbon Tail Branching on the Packing of Extended Surfactants at Oil Water Interfaces.** Charles Hammond<sup>1</sup>, Edgar J. Acosta<sup>2</sup>, <sup>1</sup>Sasol North America Inc., Westlake, LA 70669, USA, <sup>2</sup>Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, ON, Canada

In chemical enhanced oil recovery, reducing the interfacial tension increases the capillary number, increasing the potential for greater oil recovery. This opportunity creates the need to formulate the surfactant packages to specific reservoir conditions (i.e temperature, oil type, salinity, etc.). Anionic surfactants, especially those based on extended surfactants, alcohol propoxy sulfates, are showing to have good oil recovery performance in core evaluation studies. This investigation examines how the alcohol hydrophobe structure effects the optimum salinity. Salinity phase boundary studies were conducted with alkane oils at 20°C and 40°C using several fatty alcohol with carbon chain in the C12-13 range with 4 moles of propoxylate thin film sulfated and neutralized to the sodium salts. Various degrees of branching on the alcohol hydrophobes were examined. The characteristic curvature defined in the Hydrophilic-Lipophilic Deviation (HLD) model is presented. For alcohol propoxylate sulfates, introducing side alkyl chains (branching) in the alcohol hydrophobe has the effect of increasing the characteristic curvature.

#### **S&D 1.1: General Surfactants I**

Chair(s): M. Ventura, Church & Dwight Co Inc., USA; and S. Adamy, Church & Dwight Co Inc., USA

**Effect of Sodium Bicarbonate on Wetting Synergies in Mixed Surfactant Systems.** S.T. Adamy, Church & Dwight Co., Inc., Princeton, NJ, USA

It is well known that mixtures of surfactants exhibit synergism with regards to properties such as critical micelle concentration (cmc), interfacial tension, and contact angle. Characterization of such synergism has often been expressed in terms of an interaction parameter, which in turn is used to calculate surfactant activity coefficients. Though such an approach is in practice straightforward for cmc characterization, calculation of an interaction parameter from contact angles is more challenging. Thus, such an approach is often not easily utilized in an industrial setting, where quick screens of systems are necessary. In this paper, we discuss a method of characterizing non-ideal wetting behavior by comparing deviations of experimental adhesion tension values from those calculated via a weighted average of values for the individual surfactants. The results are discussed in the context of mixtures containing sodium dodecyl sulfate, alkyl amine oxides, and sodium bicarbonate.

**Synergistic Interactions in Mixed Anionic-cationic Surfactant Mixtures: Palm-based Methyl Sulfonate-alkyl Trimethylammonium Bromide Mixtures.** Siew Pui Wong<sup>1,2</sup>, Wen Huei Lim<sup>2</sup>, Sit Foon Cheng<sup>1</sup>, Cheng Hock Chuah<sup>1</sup>, <sup>1</sup>University of Malaya, Kuala Lumpur, Malaysia., <sup>2</sup>Advanced Oleochemical Technology Division (AOTD), Malaysian Palm Oil Board (MPOB), Bandar Baru Bangi, Selangor Darul Ehsan, Malaysia.

Surface and micellar properties of binary mixtures of sodium laurate methyl  $\hat{I}\pm$ -sulfonate (C<sub>12</sub>MES) and alkyltrimethylammonium bromide (C<sub>n</sub>TAB) of varying chain length (even number of carbon between 12 and 18) were studied by means of surface tension measurement. Results of critical micelle concentration (CMC) and concentration required to reduce the surface tension of the solution by 30 mN m<sup>-1</sup> (C<sub>30</sub>) showed that mixed systems exhibited higher surface activity and greater efficiency in reducing surface tension of solution when compared to individual surfactants. Experimental CMC for the mixed systems also showed strong deviations from the ideal CMC (CMC<sub>ideal</sub>). Interactions

of the mixed system were further explored by evaluating the surface monolayer interaction parameter,  $\hat{\Gamma}^2$  and micelle interaction parameter,  $\hat{\Gamma}^m$  using Rubingh's equation. The negative values obtained suggest the synergistic interactions between the oppositely charged surfactant molecules. Besides that, maximum surface excess,  $(\Gamma)_{\max}$  and minimum area per molecule ( $A_{\min}$ ) values also proved that mixed surfactants have higher surface activity as compared to the single surfactants. Finally, in the mixtures of  $C_{12}$ MES and  $C_n$ TAB, the interactions become stronger when the hydrocarbon chain length is longer.

**An Investigation into Inhibition of Precipitation of Mixed Anionic Surfactant Systems.** A. Maneedaeng<sup>1</sup>, K.J. Haller<sup>2</sup>, B.P. Grady<sup>3</sup>, A.E. Flood<sup>1</sup>, <sup>1</sup>School of Chemical Engineering, Suranaree University of Technology, Nakhon Ratchasima, Thailand, <sup>2</sup>School of Chemistry, Suranaree University of Technology, Nakhon Ratchasima, Thailand, <sup>3</sup>School of Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, Oklahoma, USA

Binary anionic surfactant was used to investigate the synergism in the increase in the induction time for nucleation of anionic surfactants precipitated by divalent ions. The induction time was investigated via an online turbidity device for two binary systems; NaDS/NaOBS and NaDS/NaDeS, with various degrees of supersaturation, in order to monitor the increase in the induction time. The Regular Solution and Pseudophase Separation theories were employed to quantify surfactant concentrations in micellar and monomeric phases. The results show that the NaDS/NaOBS system is ideal while the NaDS/NaDeS is not ideal due to the difference in the size of the molecules. The degree of counterion binding to the micelle was monitored by activity measurement using an ion-specific electrode. The chemical equilibrium of unbound and bound counterions during the micellization can be used to model the fraction of counterion binding to the micelle relatively well. The results show that the inhibition of anionic surfactant precipitation is due partly to the thermodynamic change and also partly due to a change in the energy required to create the surface of the critical nuclei, as shown by mixed systems having a different nucleation time dependence on supersaturation than the related pure system.

**Influence of Hydrophobic Chain Length on the Properties of Phosphate Based Gemini Surfactants.** V.K. Tyagi, Dipti Shukla, Harcourt Butler Technological Institute, Kanpur, Uttar Pradesh, India

Anionic gemini surfactants having two phosphate head groups and two long alkyl groups were prepared in good yield. Performance properties of synthesized surfactants (LG-4, DG-4 and OG-4) viz. foaming, wetting, emulsification and detergency were evaluated. Besides this, anionic content of these surfactants was also determined. The effect of hydrophobic chain on the performance properties of anionic gemini surfactants was investigated. The experimental results depicted that the geminis with long hydrophobic chain (LG-4) showed 61.2 % detergency, 42 sec wetting time and produced 30 ml foam immediately whereas geminis having shorter alkyl chain (OG-4) showed 28.0 % detergency, 38 sec wetting time and produced 26 ml foam immediately. The anionic content of synthesized geminis were found in range of 65.3- 74.8 %.

**Mixed Micelle Formation in the Mixture of a Bile Salt and a Cationic Fluorocarbon Surfactant.** Zhongni Wang, Tonghao Wu, Wu Zhou, College of Chemistry, Chemical engineering and Materials science, Shandong Normal University, Jinan, Shandong, China

Mixed micelles of fluorinated and hydrogenated surfactants that possess opposite charges are rarely investigated. Bile salts show behavior different from traditional surfactants. Here, the micelle formation for the mixture of an anionic bile salt (NaDC) and a cationic fluorocarbon surfactant (FC-4) has been investigated through surface tension measurements in 0.1M NaCl at 30 ° C. Precipitation occurs at the mole fraction of NaDC ( $\alpha$  NaDC) in between 0.38 and 0.80 in the total concentration of 1.0 M. By analyzing the surface tension data using Clint and Rubingh and Rosen theory, it is shown that (1) Mole fraction of the bile salt in the micelle is all less than 0.3 even at a  $\alpha$  NaDC of 0.9. (2) The mixed micelle formation shows a negative deviation to the ideal behavior at  $\alpha$  NaDC above 0.8, while from negative to positive when  $\alpha$  NaDC less than 0.38. (3)  $\beta^M$  is from -3.0 to -6.0, which is much positive than that of the typical anionic-cationic systems. The micro-calorimetric determinations are being processed to estimate thermodynamic parameters in the micelle formation.

**Vegetable Oil Detergency: Removal of Highly Unsaturated Triglycerides Using Optimized Microemulsion System at Low Surfactant Concentration and Bath Temperature.** Chodchnok Attaphong, Tri Phan, David A. Sabatini, The University of Oklahoma, Norman, Oklahoma, USA

Health considerations have led to increased use of highly saturated vegetable oils. However, the highly unsaturated triglycerides are much more challenging to clean during detergency. From previous studies, Winsor Type I microemulsion using extended surfactants achieved good vegetable oil detergency efficiency even at low surfactant concentration (125 ppm). The objective of this study is to minimize the amount of extended surfactant required for highly-unsaturated-triglyceride in vegetable oil detergency with the goal of formulating cost-effective cleaning systems. In addition, surfactant phase behavior was carried out at lower temperature (10°C) to optimize the microemulsion system for low temperature applications. These results will provide useful information for design of surfactant systems for use in personal and industrial applications.

**The Cleaning of Heavy Oils from Solid Particles.** S. Quraishi, E. Acosta, University of Toronto, Toronto, ON, Canada

The cleanup of beaches following oil spills is a complex process dependent on the properties of the contaminant oil along with the properties of the contaminated solid such as polarity, surface area, shape and porosity to name a few. One of the most commonly employed remediation technology is combustion based in which the contaminant is burned off yielding clean solids. However this method produces greenhouse gases and should therefore be avoided. Other methods include hot water washing, which is energy intensive, and bioremediation, which is an extremely slow process. In this work a series of soil washing experiments were conducted on silica sand artificially contaminated with coker fed bitumen using a 1000ppm surfactant solution of sodium dihexyl sulfosuccinate (SDHS) formulated to produce ultralow oil water interfacial tensions. The cleaning process was aided with the addition of toluene required to reduce the viscosity of the heavy oil contaminant. This method resulted in upwards of 97% bitumen liberation and is highly advantageous over the remediation methods previously mentioned as it is a rapid and clean process with low energy requirements.

**Aggregation of a 4-armed Starblock EO-PO Copolymeric Surfactant in Aqueous Solutions.** P. Bahadur, VNSG University, Surat Gujarat India

The results on concentration /temperature/pH/salt/alcohol induced micellization and sphere-to-rod growth in the aqueous solutions of star-block ethylene oxide-propylene oxide (EO-PO) based copolymers from viscosity, scattering, thermal and spectral studies will be presented. Depending on molecular characteristics and concentrations, pH and temperature, the copolymer solutions in water may contain unimers or micelles but the micellar properties are greatly modified in the presence of added salt/alcohol or both. The salt effect follows Hofmeister series while alcohols modulate the properties as per their hydrophobicity. The salt effect has been attributed to an increasing ability of structure making anions to dehydrate the PEO shell whereas the alcohols affect through their partition in the micelle. The combined effect of different salt/alcohol pairs on the copolymer solutions will also be discussed. The solubilization of drugs in the micelles will also be discussed. The results will be compared with those of linear PEO-PPO-PEO triblock copolymers.

**Gemsurfs; Preparation from Butanetetracarboxylic Acid.** Chau Ngoc Huynh, Tatsuo Oida, Tokuzo Kawase, Kyoto Institute of Technology, Kyoto-shi, Japan

Gemsurf<sup>®</sup>, a diester at 2- and 3- positions of 1,2,3,4-butanetetracarboxylic acid (BTC), is a carboxylic type Gemini surfactant. Commercially, Gemsurf has been prepared from tetrahydrophthalic diester via oxidation of C=C double bond. Here, we wish to report the preparation of a mixture of diesters of BTC which we named Gemsurfs, via an esterification. Also, the surface properties of Gemsurfs were investigated and compared with Gemsurf and its structural isomers.

## AFTERNOON

### **S&D 2: Dynamic Properties of Surfactants**

Chair(s): D. Wood, Dial Corp./Henkel, USA; and B. Lin, Dial Corp./Henkel, USA

**Predicting the Morphology and Viscosity of Ionic Surfactant Microemulsions Using the HLD-NAC Model.** S.K. Kiran, E.J. Acosta, University of Toronto, Department of Chemical Engineering and Applied Chemistry, Toronto, ON, Canada

This work focuses on extending the HLD-NAC model to help predict the shape and viscosity of SDHS-toluene-water microemulsions from readily available formulation parameters. To do so, a new shape-based NAC model was introduced which relates the net and average curvatures to the length and radius of microemulsion droplets possessing a hypothesized cylindrical core with hemispherical end caps. Knowing the shape of these droplets, theoretical scattering profiles and maximum hydrodynamic radii were predicted. Furthermore, considering the predicted volume fraction of the dispersed droplets alongside the shape allows for the accurate prediction of the microemulsion viscosity. It was found that treating the microemulsion phase as a dilute suspension of rigid rods yielded predicted viscosities close to the experimental values near the bicontinuous phase transition limits. The predicted microemulsion morphology and viscosity may be useful in the design of formulations for nanoparticle synthesis, enhanced oil recovery, and various environmental remediation technologies.

**New Applications for Multifunctional Cleaning Ingredients.** J. Shulman, M.I. Busby, Dow Chemical, Midland, Michigan, USA

Specialized polymers can provide unique properties to cleaning formulations. Manipulation of polymer variables such as monomer mix and degree of polymerization, as well as the incorporation of branch points and functionality allows the preparation of polymers with a very wide range of properties. Polymers can then serve a multifunctional role in cleaners. They can be used as anti-redeposition agents, dye transfer inhibitors, soil dispersants, and soil release agents. They are also useful as process aids for the preparation of powder or granular cleaners. By proper design, such polymers can also be made biodegradable. Use of designed polymers for various applications will be discussed.

**Particulate Soil Detergency: Performance and Mechanism of Hydrophilic Soil Removal.** Sureeporn Rojvoranun<sup>1</sup>, Sumaeth Chavadej<sup>1</sup>, John F. Scamehorn<sup>2</sup>, David O. Sabatini<sup>2</sup>, <sup>1</sup>The Petroleum and Petrochemical College, Thailand, <sup>2</sup>The University of Oklahoma, USA

In this research, the effects of surfactant type, surfactant concentration, fabric type and solution pH on the process performance of particulate soil detergency were investigated. Kaolinite was selected as a model of hydrophilic particulate soil and three types of fabrics were used: pure polyester, pure cotton, and blended polyester/cotton. The detergency experiments were carried out in a Terg-O-Tometer by using an anionic surfactant (methyl ester sulfonate, MES) and a nonionic surfactant (alcohol ethoxylate with 9 oxyethylene groups, AE9). In order to gain a better understanding, the adsorption isotherms of the surfactants and the measurements of the zeta potential and the contact angle were carried out. For any given types of surfactant and fabric, detergency performance increased with increasing solution pH and the maximum performance was found at pH 11. Additionally, MES exhibited a better detergency than AE9 and the cotton fabric showed the highest detergency efficiency while the polyester gave the lowest performance.

**Production of New Types of Glycolipid Biosurfactants by Yeasts and their Interfacial Properties.** Dai Kitamoto, Tokuma Fukuoka, Tomotake Morita, Tomohiro Imura, National Institute for Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan

Biosurfactants (BS) produced by a variety of microorganisms show unique properties compared to petroleum-based surfactants. Among BS, glycolipid-types are the most promising, due to high productivity from renewable resources. Mannosylerythritol lipids (MELs), which are glycolipid BS produced from different vegetable oils at a yield of 100 g/L by *Pseudozyma* yeasts, exhibit not only excellent surface activities [1] but also versatile biochemical actions including antitumor activities [2]. Recently, we tried to characterize the self-assembling properties of MELs and their derivatives. Accordingly, MEL-A, the major component of MELs, self-assembles to form sponge (L3) phase at a wide

range of concentrations, while MEL-B forms lammellar ( $L\alpha$ ) phase [2]. MEL-C shows higher hydrophilicity compared to MEL-A and -B, and seems advantageous for the use in water-in-oil systems. We also investigated the ternary phase behaviors of MEL-A and MEL-B, and succeeded in preparation of oil-in-liquid crystal (O/LC) emulsion in the biphasic  $L\alpha + O$  region of the MEL-B/water/n-decane system. MELs have thus great potentials for novel advanced surfactants in various industrial fields.[1] T. Imura et al., *Langmuir*, 23, 1659-1663 (2007).[2] D. Kitamoto et al., *Curr. Opi. Colloid Interf. Sci.*, 14, 315-328 (2009).

### **Partitioning Behavior of an Acid-Cleavable, 1,3-Dioxolane Alkyl Ethoxylate, Surfactant in Single and Binary Surfactant Mixtures for 2- and 3-Phase Microemulsion Systems According to Ethoxylate Head Group Size.** J.A.

Gomez del Rio<sup>1</sup>, D.G. Hayes<sup>1</sup>, V.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

Partition coefficients for a pH-degradable 1,3-dioxolane alkyl ethoxylate, or "cyclic ketal" surfactant, CK-2,13-E5.6,ave, between oil- and water-rich phases of 2- and 3-phase microemulsion systems (Kn) were determined as functions of the ethoxylate group size, n, and temperature in single and binary surfactant mixtures, in order to develop a predictive capability of the combination of parameter values needed for forming 3-phase microemulsion systems. A semi-empirical thermodynamic mathematical model was developed that described the partitioning data well, despite the occurrence of a broad set of operating conditions: non-optimal temperature and the coexistence of 2- and 3-phase microemulsions within data sets. Small-Angle Neutron Scattering demonstrated that the aqueous bottom phases of the 2- and 3-phase microemulsions consisted of oil-in-water microemulsions. Using a straight-line relationship between  $\log K_n$  and n as a criterion for optimal conditions, the model demonstrated that the tail group of CK-2,13-E5.6,ave is more polar than ethoxylated fatty alcohols and alkyl phenyl ethoxylates, yielding higher partition coefficients.

### **Effect of Fatty Imidazolines on Properties of Laundry Detergent Compositions Based on Nonionic Surfactants.**

V.K. Tyagi, Divya Bajpai, Harcourt Butler Technological Institute, Kanpur, Uttar Pradesh, India

The present study emphasizes on the synthesis of cationic imidazolinium surfactants based on easily available and cheap fatty materials. Surface active properties of 1% aqueous solution of imidazolinium surfactants were evaluated in terms of surface tension, interfacial tension, cmc, dispersability and emulsion stability. To evaluate the performance properties, laundry detergent compositions were made using different percentages of synthesized imidazolinium surfactants with nonionic triton x-100 and properties were evaluated in terms of foaming, softening, rewettability and detergency. The presence of cationic imidazolinium surfactants in laundry compositions, increased the detergency, rewettability, foam stability and softening of compositions.

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

Chair(s): G. Dado, Stepan Co., USA; and J. Pytel, Stepan Co., USA

### **Oligomeric Surfactants Derived from the Sulfonation of Fatty Acids.** G. Dado, J. Weitgenant, Stepan Company, Northfield, IL, USA

The need for ingredients with acceptable cost/performance that can also meet the increasing demands for environmental sustainability is an important driver for new surfactant technology development. Oligomeric surfactant compositions, derived from the sulfonation of unsaturated fatty acids, can meet this need while also enabling highly concentrated product formulations. These surfactant compositions are comprised primarily of monomeric, dimeric, and trimeric sulfonated fatty acids, wherein oligomerization occurs via the formation of ester linkages. This lecture will provide an overview of the rich reaction chemistry associated with the synthesis of these oligomeric sulfonates. In addition, several means by which the composition of these surfactant mixtures may be manipulated will be described.

### **Physical and Performance Properties of Sulfonated Oligomeric Surfactants.** D. Murphy, E. Filipovic, L. Alonso, Stepan Company, Northfield, IL, USA

Sulfonated oligomeric surfactants afford a unique combination of physical solution properties. In aqueous solution they are highly soluble, produce low-viscosity systems, and are very low-foaming. The solubility and solution viscosity

properties of sulfonated oligomeric surfactants enable the production of highly concentrated product formulations. When incorporated into liquid laundry detergents, the resulting formulations provide a very good cleaning profile. Various aspects of performance evaluation including methodology, formulation and cleaning results will be discussed.

**Formulation Engineering: Opportunities and Challenges.** Edgar Acosta, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, ON, Canada

The formulation of detergents, pharmaceuticals, food products, cosmetics, and oilfield chemicals has been largely undertaken in industrial settings with limited academic attention. Although the principles of physical chemistry and colloid science are applied, the practice of formulation remains, for the most part, a trial and error endeavour. Sustainability concerns, increased regulatory constraints, and complex functionality (e.g. controlled release) call for an engineering approach to formulation. Formulation Engineering (FE) involves incorporating chemical engineering principles (thermodynamics and transport phenomena) in the formulation of surfactant-based products and processes. The introduction of equation of states for surfactant-oil-water systems (e.g. the HLD-NAC model) and the understanding of fluid mechanics and mass transport in surfactant-based processes have enabled the FE approach. This approach will be illustrated in the development of (a) formulations for enhanced oil recovery, (b) essential oil extraction and (c) soil washing. The challenges and opportunities for this FE approach will be discussed.

**Alpha-tocopherol-Ascorbic Acid: A New Surfactant of Antioxidant Properties.** C.E. Astete<sup>1</sup>, D. Dolliver<sup>3</sup>, L. Khachatryan<sup>2</sup>, C.M. Sabliov<sup>1</sup>, <sup>1</sup>Louisiana State University, Agricultural Center, Baton Rouge, LA, USA, <sup>2</sup>Louisiana State University, Dept. of Chemistry, Baton Rouge, LA, USA, <sup>3</sup>Southeastern Louisiana University, Hammond, LA, USA

The goal of the study was to synthesize a surfactant made of  $\alpha$ -tocopherol and ascorbic acid of antioxidant properties dubbed as EC, and to use this surfactant to make poly(lactic-co-glycolic) acid (PLGA) nanoparticles. Self-assembled EC nanostructures and PLGA-EC nanoparticles were made by nanoprecipitation, and their physical properties (size, size distribution, morphology) were studied at different salt and surfactant concentrations, and polymer:surfactant ratios. EC surfactant was shown to form self-assembled nanostructures in water, measuring 11 to 140 nm. Synthesis of polymeric nanoparticles was accomplished by adding the hydrophobic polymer PLGA, and using EC or Span 80 as surfactants. Polymeric PLGA-EC nanoparticles presented a size of 90 to 126 nm depending on the PLGA:surfactant ratio (40% to 120%). For the same mass ratios, the PLGA-Span 80 formed bigger particles that measured 155 to 216 nm. Polydispersity of polymeric nanoparticles made with EC or Span80 was similar, with values ranging from 0.11 to 0.17. The PLGA-EC nanoparticles and EC surfactant showed antioxidant activity based on DPPH technique and EPR study, which was not characteristic to commercially available Span80. The newly synthesized EC surfactant was therefore found successful in forming uniform, small size polymeric nanoparticles of intrinsic antioxidant properties.

**O-Acylated Hydroxy Carboxylic Acid Anhydrides: Novel Building Blocks for Surfactants and Emulsifiers.** Rachid Ihizane, Hans Josef Altenbach, Manfred P. Schneider, Karsten Lange, Bernd Jakob, Bergische Universität Wuppertal, Wuppertal, Germany

The conversion of fatty acid with natural hydroxycarboxylic acids, especially malic-, tartaric- and citric acid resulted in the easy formation of acylated hydroxycarboxylic anhydrides[1]. We have shown that this class of anhydrides provides convenient entry into a variety of products. They readily react with natural or synthetic nucleophiles like alcohols, carbohydrates, amines and amino acids[2]. A series of compounds were synthesized and characterized, their surface and antibacterial properties have been measured. References: 1. Lange K, Schneider M P, DE 10 2006 014 732 A1 2. Lange K, Altenbach H J, Ihizane R, Jakob B, Schneider M P, WO/2009/100890

**Lecithin-Based Biocompatible Microemulsions Using Sophorolipid and Rhamnolipid Biosurfactants.** T. Nguyen<sup>1,2</sup>, D. Sabatini<sup>1,2</sup>, <sup>1</sup>University of Oklahoma, Norman, OK, USA, <sup>2</sup>Institute for Applied Surfactant Research, Norman, OK, USA

The objectives of this research are first to evaluate the hydrophilicity/hydrophobicity of sophorolipid biosurfactants relative to conventional synthetic surfactants and then to formulate and evaluate microemulsions of



lecithin/rhamnolipid/sophorolipid biosurfactants with a range of oils (varying EACN values and oil types). We found that sophorolipid biosurfactants are more hydrophobic than sodium bis(2-ethyl) dihexyl sulfosuccinate (SBDHS), which is more hydrophobic than sodium dihexyl sulfosuccinate (SDHS) and rhamnolipid biosurfactant. Sophorolipid thus played an important role as the hydrophobic component in lecithin/rhamnolipid/sophorolipid biosurfactant formulation. This biosurfactant formulation was able to produce Winsor Type I, III and II microemulsions and the corresponding ultralow IFT for limonene, decane, isopropyl myristate and hexadecane. The phase behavior of this formulation with isopropyl myristate did not change significantly with changing temperature (10, 25, 40 °C) and electrolyte concentration (0.9 and 4.0% w/v), making it desirable for cosmetic and drug delivery applications. The hexadecane detergency performance of our biocompatible formulation was higher than that of a commercial liquid detergent at the same surfactant active concentrations.

## TUESDAY

### AFTERNOON

#### **S&D 3: Green Ingredients and Labeling**

Chair(s): C. Choy, Seventh Generation Inc., USA; and M. Wolf, Seventh Generation Inc., USA

**Sustainable Approaches to Surfactants and Detergents.** Andrew Douglass<sup>1</sup>, Manial Dahanayake<sup>1</sup>, Pascal Herve<sup>1</sup>, Viot Jean-Francois<sup>2</sup>, <sup>1</sup>Rhodia, Inc, Cranbury, NJ USA, <sup>2</sup>Rhodia Operations, Lyon, France

Sustainability issues are revolutionising the surfactants and detergents industry yet they are difficult to quantify which creates confusion in the marketplace. Rhodia has developed simplified metrics based on Life Cycle Analysis to assess the sustainability of our ingredients and new product development programs. We will present the market trends and drivers in Home, Personal Care and Industrial Markets and show through examples how the developed metrics can be used to give a clearer picture of which ingredients and formulations are sustainable.

**Green Solvents and Ionic Liquids: Formulating for the Sustainable Future.** S. S. Seelig<sup>1</sup>, A. O'Lenick<sup>2</sup>, <sup>1</sup>Waterless Cleaning LLC, Arlington Heights, IL, USA, <sup>2</sup>Waterless Cleaning LLC, Dacula, GA, USA

Green solvents for cleaning applications offer numerous benefits over water and other solvents. These include increased water, energy and chemical efficiencies, low/non-VOCs, non-hazardous, non-toxic, biodegradable, sustainable, and recyclable/reclaimable. Ionic Liquids (ILs) have also been labeled as green solvents but they tend to be very expensive (up to \$300/gm). Green solvents with ionic liquid co-solvents may be the best choice for various consumer, institutional, commercial, and industrial cleaning applications. Definitions for ILs will be discussed as well as examples of potential cleaning applications. Current applications for ILs include extending the life of lithium batteries, solvents for pharmaceutical manufacturing, lubricants, electrochemical reactions, nanotechnology, and much more. We will focus on cleaning applications for non-aqueous ILs as co-solvents with other green solvents.

**Enzymes - Essential, Bio-based Ingredients for High-performance Environmentally-friendly Detergent Formulations.** T. Neal<sup>1</sup>, A. Merete Nielsen<sup>2</sup>, A. Malladi<sup>2</sup>, S. Friis-Jensen<sup>2</sup>, <sup>1</sup>Novozymes, North America, Franklinton, NC USA, <sup>2</sup>Novozymes A/S, Bagsvaerd, Denmark

As consumer demand for superior performance environmentally friendly cleaning products is on the rise, so is the pressure on detergent manufacturers to find the elusive balance between clean and green. Enzymes have been used for decades in detergent formulations as performance boosters - but now through wash trials and Life Cycle Assessments (LCA) conducted in North American conditions, it can be proven that enzymes can substitute traditional detergent ingredients like surfactants and builders while maintaining or even improving performance, and increasing the sustainability profile of the detergent formulations. The LCA findings will show that the environmental impact of doing laundry can be reduced by replacing traditional detergent chemistry with enzymes.

**Rethinking Detergent Formulations – Maintain Your Performance and Manage Your Costs with Enzymes.** N.E.

Prieto<sup>1</sup>, P. Skagerlind<sup>2</sup>, M. Ribeiro Ferreira<sup>3</sup>, J.M. Koehler<sup>3</sup>, C. Cavanholi<sup>3</sup>, <sup>1</sup>Novozymes NA, Franklinton, NC, USA, <sup>2</sup>Novozymes A/S, Bagsvaerd, Denmark, <sup>3</sup>Novozymes LA, Araucaria, PR, Brazil

Current market demands are forcing formulators to find alternate solutions to control cost and reduced impact on the environment. In addition, consumers demanding a more sustainable product will preferentially select it if it offers a similar or lower cost and performance, making it more challenging for the formulators to develop an acceptable product. Enzymes are a sustainable alternative that can provide detergent formulators with an effective solution to current cost, performance and environmental pressures. This paper will demonstrate how to replace laundry detergent ingredients with enzymes while improving the sustainability, reducing the environmental impact, and maintain performance at equal or lower cost.

**Economics, Exposure and Technology Division Office of Pollution Prevention and Toxics.** M. Vrabel, Design for the Environment Branch, Economics, Exposure and Technology Division Office of Pollution Prevention and Toxics, Washington, DC, USA

The Design for the Environment Safer Product Labeling Program allows use of the DfE logo on products that perform well and protect health and the environment. Consumers that want the safest possible products for their families should look for the logo on the product label. The Design for the Environment logo means products have been through a rigorous EPA review to show that they work well and contain the safest possible chemicals. 1,700 leadership products from almost 200 manufacturers now bear the DfE logo, up from fewer than 900 a year ago. DfE-labeled products reduce use and release of chemicals of concern by almost 500 million pounds per year. Most products bearing the logo are cleaners and detergents for consumer and industrial use. The DfE logo can also be found on low-hazard alternatives to lead tire weights, ice-melt products that use less salt, and field paint that is safer for athletes. EPA has set a 2010 goal to make the logo a more recognized and powerful tool for driving use of safer chemicals.

**Use of Life Cycle Assessment in Identifying and Creating Green Products and Processes.** J. Yorzyk, Five Winds International, Boulder, CO, USA

Life Cycle Assessment (LCA) is a rigorous, quantitative method for determining the environmental impacts of products and services and developing defensible product claims. It can be used to model the environmental impacts of entire product systems from "cradle to grave" as well as "gate to gate" within a specific supply chain position (and all variations therein). While LCA has been in practice for over twenty years, it has only recently received significant attention in North America - driven by a growing market desire for more complete and reliable information on products and services. Using examples from recent projects, this presentation will provide an overview of LCA and insight on how leading companies are using this critical tool in ideation, research and development, and eco-labeling. It will also discuss the limitations and challenges of LCA, and some simplified tools that are being used to streamline the development of greener products and processes.

**Looking Back to Look Ahead: The Soap and Detergent Industry's Continuous Commitment to Being Green and Sustainable.** Kathleen Stanton, SDA, USA

This presentation will first reflect on the history of the soap and detergent industry to illustrate its commitment to human health and environmental safety, and then reveal steps the industry is taking to ensure that commitment to safety is maintained into the future. From being one of the first industries to use waste materials as raw materials (i.e. animal fats) to voluntary ingredient replacement in the 1960's to continued research on the human and environmental health and safety of ingredients, the industry has a long-standing history of being 'green'. While the current focus of green recognition and certification programs is predominately on the hazard profile of ingredients, new and enhanced tools and future approaches will be featured.

**Green Seal and its Life Cycle-Based Ecolabel.** S. Cooperstein, Green Seal, USA

Green Seal is a non-profit organization in North America that has over 30 environmental leadership standards available for certification to help consumers and purchasers identify environmentally preferable products and services. Green

Seal has the leading environmental standard and certification program for cleaning products in the US. This is because Green Seal takes a life cycle approach with its program that has proven to effectively identify products that perform and have significantly lower environmental impact. This life cycle approach will be discussed as it relates to cleaning and detergent products to highlight key considerations for companies to consider when developing environmentally preferable ingredients and products. In addition, this life cycle approach will be discussed broadly as it relates to a company and all of its operations.

**CleanGredients: A Tool for Alternatives Assessment to Support Chemical Product Formulation.** Topher Buck, GreenBlue, Charlottesville, VA, USA

Most formulated product manufacturers purchase--rather than make--the chemical ingredients of their products, often without the technical information needed to support alternatives assessment. Consequently, in the face of growing demand for "greener" products from California to Maine, formulators need tools to help them identify, compare and select chemicals that meet performance requirements while possessing low inherent hazard. CleanGredients<sup>®</sup>, a project of the nonprofit GreenBlue, is a multi-attribute information platform that supports chemical alternatives assessment. GreenBlue has developed CleanGredients in collaboration with the U.S. EPA DfE Program and hundreds of stakeholders from NGOs, industry and government. CleanGredients provides physical-chemical data and independently verified data on human and environmental health attributes of listed chemicals, facilitating the consideration of human and environmental health, along with typical product attributes like cost and performance, during product formulation. As such, CleanGredients supports product recognition under a range of ecolabel programs, including DfE. CleanGredients users realize cost and efficiency savings through access to a green marketplace of chemical information, and raw materials suppliers gain greater access to markets for their greener chemical alternatives. Opportunities for growth include expansion to formulated product categories such as personal care products and inks, coatings and adhesives.

### **S&D 3.1: Industrial Applications**

Chair(s): M. Dahanayake, Rhodia Inc., USA; and T.C. Jao, Afton Chemical Corp., USA

**MEE: The Genuine Green Surfactant.** Hiroaki Shindo, Ryo Hyodo, Takahiro Okamoto, Yukihiro Kaneko, Hiromitsu Takaoka, Lion Corporation, Edogawaku, Tokyo, Japan

In this report, we would like to introduce following three features of Methyl Ester Ethoxylate(MEE)compared with general nonionic surfactant AE(Alcohol Ethoxylate).1)MEE has a higher detergency for fatty acid which causes oily smell remained on clothes even after washing.2) MEE is a lower foaming surfactant and its adsorbed amounts on clothes is smaller than AE. Laundry detergent with MEE has an advantage in foamability to be easily rinsed away with only one rinse cycle. So, we can reduce the consumption of rinsing water.3) MEE has a small region of liquid crystal in its phase diagram, whereas AE has wide regions of liquid crystal phase and lamellar phase with high viscosity. We found that MEE was really genuine and green surfactant suitable for super concentrated liquid laundry detergent with high detergency for oily malodor, good rinse property.

**Emulsifiable Green Solvents: Delivering Sustainable Performance.** A. Sehgal<sup>1</sup>, B. Roux<sup>2</sup>, D. Fluck<sup>1</sup>, S. Trivedi<sup>1</sup>, M. Dahanayake<sup>1</sup>, C. Aymes<sup>1</sup>, <sup>1</sup>Rhodia Inc., Center for Research & Technology, Bristol, PA, USA, <sup>2</sup>Rhodia Laboratoire du Futur, Pessac Bordeaux, France

The convergence of ?sustainability? and ?performance? of Green technologies is critical for their successful adoption in the industrial landscape. We have developed a new class of eco-friendly, biodegradable, high-performance solvents (e.g. Rhodiasolv<sup>®</sup> IRIS ? dimethyl methylglutarate) to replace traditional hazardous solvents. Optimized synthetic routes to these alkyl dibasic ester solvents allow access to a broad range of solvencies in Hansen Parameter space. However, application of such low vapor pressure/VOC green solvents may also require a mechanism for delivery and removal of solvent from the substrate. We exploit the synergy of surfactants and solvents to provide novel infinitely dilutable microemulsions of IRIS. Our formulation discovery cycle will be discussed: from exploring properties (solvency), to developing delivery platforms by high-throughput mapping of phase behavior. The influence of surfactant architecture (ionic/nonionic-linear/branched) on colloidal structure, phase behavior, and thermal stability will

be presented. This platform has been further extended to auto-emulsifiable solvent blends that allow spontaneous emulsification of the organic phase into water. These self-emulsifying systems were characterized by spontaneous formation of Winsor III micro-emulsion phases at the oil-water interface without imparting any mechanical energy. Such emulsifiable green solvent platforms help translate inherent properties of solvents to effective delivery in performance and cost.

**Improved Stability of Anionic Surfactants for CEOR Applications.** Upali Weerasooriya, Gary Pope, The University of Texas, Austin, Texas, USA

A process has been developed for enhancing the chemical stabilities of anionic sulfate surfactants at high temperatures under different alkaline environments. An alkalinity window has been identified to maximize the thermal stability of ether sulfates. Consequently, the choice for anionic EOR surfactants has improved greatly.

**Microemulsion Fuels: Phase Behaviors and Combustion Properties.** Linh D. Do<sup>1</sup>, Vinay Singh<sup>2</sup>, Sub. R. Gollahalli<sup>2</sup>, David A. Sabatini<sup>3</sup>, <sup>1</sup>Chemical Engineering, University of Oklahoma, Norman, OK, USA, <sup>2</sup>Mechanical Engineering, University of Oklahoma, Norman, OK, USA, <sup>3</sup>Civil Engineering and Environmental Science, University of Oklahoma, Norman, OK, USA

Vegetable oils (VG) have been considered as a renewable energy for diesel. Due to high viscosity, use of VG causes engine durability problems. Microemulsification is a method to reduce vegetable oil viscosities which requires no chemical reactions. In this work, we study reverse micellar microemulsion (ME) phase behavior at different temperatures with different vegetable oils or their blends with No. 2 diesel fuel (DF). We also studied the combustion emission of the temperature stable ME fuels. We have been able to produce a stable ME with viscosity comparable to that of DF. We are also able to form temperature insensitive ME fuel using sugar-based /methyl-ester-ethoxylated/extended-surfactant systems. Canola ME fuels proved to be the most stable with temperature, whereas coconut ME fuels have the highest lower heating value (LHV) which is comparable to DF. Regarding the emissions index, CO emission of ME fuel is much less than that of biodiesel and DF and NO<sub>x</sub> emissions is somewhat similar to that of DF. The NO<sub>x</sub> emission is reduced as the water content increases in the fuel. Radiation study shows that ME fuels emit much less particulate matters and burn more complete than DF and biodiesel. Thus, through our research we have shown that microemulsification is a very promising technology for producing biofuel without chemical reactions and the fuel properties can be easily adjusted by changing formulation variables.

**Surfactants Derived From High Molecular Weight Mono-Unsaturated Alcohols and Acids.** Paul D. Berger<sup>1</sup>, Christie H. Lee<sup>1</sup>, David C. Taylor<sup>2</sup>, <sup>1</sup>Oil Chem Technologies, Sugar Land, TX, USA, <sup>2</sup>National Research Council of Canada Plant Biotechnology Institute, Saskatoon, Saskatchewan, Canada

Genetic modification of Ethiopian Mustard has resulted in an increase in the amount of nervonic acid (C<sub>24</sub>:1 $\Delta$ 15) from 2% to 45%. Current research is also progressing to develop a high C<sub>26</sub> mono-unsaturated strain. This has provided a source of high carbon chain length fatty acids and alcohol for the manufacture of several unique surfactants. Previously nervonic acid derivatives have found use in pharmaceutical applications for the treatment of various neurodegenerative diseases. Current research has enabled large quantities of the acid to become available for industrial applications. The synthesis and properties of several anionic and amphoteric surfactants will be discussed. Derivatives of mono-unsaturated fatty alcohols from various agricultural sources offer an environmental friendly alternative to internal olefin derivatives. Their application to various industrial processes including enhanced oil recovery as green, renewable alternatives to high molecular weight petrochemicals will be discussed.

**Impact of Asphaltenes and Naphthenic Amphiphiles on the Phase Behaviour of Solvent-Bitumen-Water Systems.** S.K. Kiran<sup>1</sup>, E.J. Acosta<sup>1</sup>, S. Ng<sup>2</sup>, <sup>1</sup>University of Toronto, Department of Chemical Engineering and Applied Chemistry, Toronto, Ontario, Canada, <sup>2</sup>Syn crude Canada Ltd., Edmonton Research Centre, Edmonton, Alberta, Canada

The formation of stabilized emulsions during oil sand processing limits bitumen recovery. Previous studies have demonstrated that such phase behaviour is impacted by the presence of natural surfactant-like materials within the

crude oil phase, referred to as asphaltenes and naphthenic amphiphiles, which reduce the oil-water interfacial tension. Although considerable efforts have been made in understanding the role of such materials on emulsion stability independent of one another, there is a lack of literature characterizing their synergistic effect on oil-water phase separation. This work aims to address this gap by analyzing the impact of process variables such as solvent-bitumen-water ratios, solvent aromaticity, temperature, and pH on the competitive adsorption of natural crude oil amphiphiles at oil-water interfaces. The resulting emulsion stability will be assessed via coalescence studies. Surface pressure isotherms and ToF-SIMS spectra will be collected to provide an in-depth analysis of the oil-water interfacial characteristics.

### **Selection of the Right Hydrophobe Size for the Surfactant Molecule for Chemical Enhanced Oil Recovery (CEOR).** Upali P. Weerasooriya, Gary A. Pope, The University of Texas, Austin, TX, USA

Selection of the right hydrophobe size of the surfactant for a given crude oil helps develop an optimum formulation for CEOR. Large hydrophobe alkylbenzene sulfonates and Internal Olefin Sulfonates are very surface active. However, they have inherent solubility problems as the hydrophobe size is increased. This can be overcome by using large hydrophobe alcohol ether sulfates.

## **WEDNESDAY**

### **MORNING**

#### **S&D 4: General Cleaning ? New Surfaces**

Chair(s): M. Dery, Akzo Nobel Surface Chemistry LLC, USA; and E. Endler, Shell Global Solutions, USA

**Development of Novel Bleach Catalyst and its Application for Detergents.** Tomonari Suekuni, Yukiko Iwasa, Yohsuke Kohno, Toshiaki Majima, Takayasu Kubozono, Nobuyuki Yamamoto, Lion Corporation, Edogawaku, Tokyo, Japan

Recently, consumers have come to pay much attention to hygiene. Similar trends are also seen in the laundry product's field, so they have come to expect the functions to wash out various kinds of dirt. In order to enhance detergency of laundry detergents, bleaching agents such as hydrogen peroxide or conventional organic bleach activators are utilized. But their effect is not necessarily sufficient to obtain consumer satisfaction. Therefore, in order to achieve higher detergency, we developed novel bleach catalyst available for laundry detergents. Our catalyst can activate hydrogen peroxide and decompose several stains. It is interesting to note that our catalyst is effective not only for bleaching colored food stains but also for decomposing other organic dirt or disinfecting bacteria, which cannot be decomposed by conventional bleaching systems. Meanwhile, we confirmed that our catalyst doesn't cause any problems such as fabric damage or discoloring. In this presentation, we will show some interesting features of our catalyst and availability for laundry detergents.

**Hydrophobic Particulate Soil Removal in Laundry Detergency.** W. Pengjun<sup>1</sup>, S. Chavadej<sup>1</sup>, N. Rojvoranun<sup>1</sup>, J.F. Scamehorn<sup>2</sup>, <sup>1</sup>Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand, <sup>2</sup>Institute for Applied Surfactant Research, University of Oklahoma, Norman, Oklahoma, USA

The mechanism of particulate soil detergency is not well understood. Removal of carbon black, a model hydrophobic soil, from cotton and polyester fabric is studied here. High pH yields better soil removal due to a higher negative electrical potential on soil and fabric despite lower surfactant adsorption. While electrostatic effects are important, surfactants are crucial to good detergency, even when they dampen electrical effects, due to interfacial tension reduction and antiredeposition effects. Anionic surfactants are more effective than nonionic surfactants because surfactant adsorption and negative electrical potential of soil and substrate are higher. Polyester is easier to clean than cotton, possibly because the fibers are smoother and less entanglement of soil particles occurs as shown by SEM images.

**A New Developed Bleach Activator Cogranule with Improved Stain Removal and Hygiene Wash Properties.**

Melanie Sajitz, Gerd Reinhardt, Clariant Produkte (Deutschland) GmbH, Frankfurt am Main, Hessen, Germany

Improved bleach systems in laundry applications are required due to the increasing energy costs and changing nutrition habits. Recently we developed a granulated bleach system which enables the removal of hydrophilic and hydrophobic stains at low washing temperatures. Next to TAED (tetraacetyl ethylenediamine) there is a surface active bleach activator DOBA (4-Decanoyloxybenzoic acid) enclosed. The bleach system TAED (standard activator in Europe) and persalt (perborate or percarbonate) removes hydrophilic stains efficiently at 40 – 60°C, is gentle to dyes and fabrics and is toxicological and ecological safe. In the wash liquor the reaction of TAED and persalt leads to the formation of peracetic acid as the active species. DOBA is known as low temperature active bleach system which works mainly on hydrophobic stains. In combination with persalt DOBA forms perdecanoic acid as active species, which reacts excellent on textile surfaces and on oily or dingy soils. DOBA is even more gentle to colours and fabrics. The combination of TAED and DOBA shows synergistic effects in regard to the bleach performance and improved hygiene properties. With all these benefits we developed an improved bleach system for laundry detergents and also for activated bleach booster, which is a new and growing market for the US.

**New Silicone-Based Granulated Products for Home-Care Applications.** Kathelyne Everaere, Jacqueline L'Hostis, Dow Corning, Sebeffe, Belgium

Evolving requirements in the laundry detergent market for powdered antifoams have led to specialized granulation technology across home care applications. This presentation reviews a range of developments and performance criteria. In laundry applications, foam must be controlled throughout the wash and rinse cycles. Process control and the selection of silicone active, carrier, and binder are crucial to product performance. In automatic dishwashing (ADW) applications, a new high performance granule controls foam from high-foaming anionic or nonionic surfactants. Selected benefits include powerful cleaning efficiency at lower temperature cycles, the potential for reduced high cost components, and less energy consumption. Beyond antifoams, a 3-in-1 eco-softener granule for the denim industry improves softness, acts as antibackstaining agent, and aids fading of the denim. Compatibility with enzymes allows the combination of treatment steps and reduced water consumption.

**Liquid Innovation in Automatic Dishwashing.** Thomas Eiting, Christian Nitsch, Johannes Zipfel, Henkel AG & Co. KGaA, Duesseldorf, Germany

For laundry detergents the trend from solid to liquid products is observed since years. So has in North America the ratio solid to liquid, which was nearly 1:1 in 1998, now changed to over 80% liquid products. Despite that, in the field of automatic dishwashing detergents this trend is up to now not observable. In Europe over 80% of the market is controlled by tablets, the rest are powder and liquid detergents, where liquid products reach only about 5% market share. Main reason for this trend is the missing innovation in the field of liquid dishwashing detergents; the existing liquid formulations are no multifunctional products, not fulfilling the wish for convenience of the consumer. In this work we will summarize the development and functions of liquid multifunctional products and how they contribute to sustainable cleaning.

**Development of Allergy-friendly Home Care Products.** M. Dreja<sup>1</sup>, K.C. Bergmann<sup>2</sup>, T. Zuberbier<sup>2</sup>, <sup>1</sup>Henkel AG & Co. KGaA, Duesseldorf, Germany, <sup>2</sup>Charité Universitätsmedizin, Berlin, Germany

Allergy is a disorder of the immune system, and allergic reactions occur to normally harmless environmental substances known as allergens. Common allergic reactions include e.g. eczema, hives, hay fever, asthma and food allergies. In developed countries, the number of consumers suffering from allergies is already on a level close to 30 % and steadily increasing. Thus, allergies are of relevance also to the field of laundry and home care. One common misbelief is that contact to ingredients in laundry detergents and cleaners often leads to allergies. In most cases, the consumer cannot well distinguish between an allergic reaction and other, more general irritations. Nevertheless, finding an understandable approach to guide the consumer in his choice of a suitable, allergy-friendly product can be a great support for a better and healthier life. We have conducted for the first time clinical studies with different types of hard surface cleaner formulations. Adult test persons without and with rhinitis and asthma bronchiale with nasal and bronchial hyperactivity were exposed to a defined test setup in which cleaners were aerosolized. The reactions of the

nose, eyes, lung function and skin were controlled during the experiment. In parallel, we were able to show that the use of such cleaners significantly reduces the exposition to particulate airborne allergens in a household environment.

#### **New Technologies in Surface Care.** J. Wates, Akzo Nobel Surface Chemistry, Brewster, NY, USA

Interesting properties were observed when surface modifying materials were incorporated into cleaning formulations. The properties of the surface modifier were transferred to the substrate resulting in new attributes. In one case the surface modifier was colloidal silica, which is a very hydrophilic material. Ceramic tiles treated with formulations containing colloidal silica showed benefits in terms of stain resistance making the surface easier to clean the next time around, while glass cleaned with these formulations exhibited anti-fogging properties. In this presentation we will briefly review how surface modification can lead to easy-clean behavior and discuss in more detail the benefits of hydrophilic modification with colloidal silica.

#### **Clear View into a Green Future - Starch-based Polymer for Hard Surface Cleaning.** S. Gross<sup>1</sup>, T. Albers<sup>2</sup>, C. Schunicht<sup>2</sup>, J. Huh<sup>3</sup>, <sup>1</sup>Cognis Corporation, Ambler, PA, USA, <sup>2</sup>Cognis GmbH, Duesseldorf, Germany, <sup>3</sup>Cognis Korea, Ltd., Seoul, South Korea

In this presentation, a new biodegradable starch-based surface modification polymer for application in hard surface cleaners is introduced. Its numerous advantages, such as convenience for cleaning, suitability for Ecolabels, low ecotoxicity, as well as its aerobic and anaerobic biodegradability are discussed. The "Green Convenience" claims of this new polymer are as follows: Easy to clean again, uniform wetting, spotless drying, streak-free, high gloss, ecofriendly, and natural-based polymer.

#### **New Classes of Polymer that Exhibit Next Time Cleaning Benefit in Hard Surface Cleaning Applications.** D. Rocque<sup>1</sup>, G. Nunes<sup>1</sup>, S. Mahoski<sup>1</sup>, M. Loeffler<sup>2</sup>, <sup>1</sup>Clariant Corporation, Charlotte, NC, USA, <sup>2</sup>Clariant Produkte GmbH, Frankfurt, Hessen, Germany

Liquid washing, cleaning, and disinfecting compositions are used to remove soil from hard surfaces. However, due to adhesion forces between hard surfaces and adhered soil the removal of the soil often is incomplete or requires excessive treatment such as rubbing or scrubbing of the hard surface. Acrylic based polymers are known to impart some degree of surface modification benefits such as easy cleaning and water sheeting. These polymers often prove to be incompatible with anionic surfactants, to be unstable at low pH or to have a performance that greatly depends on the nature of the treated hard surface. New classes of modified sulfonic acid polymers provide semi-permanent surface modification and show significantly improved stability and efficacy. These polymers, in combination with detergent formulations, can be used to hydrophilize hard surfaces, to reduce adhesion forces between hard surfaces and subsequently occurring soil and thus improve soil release/removal. Performance data (e.g. cleaning efficacy) and physical properties (e.g. contact angle) provided by modified sulfonic acid polymers on hard surfaces are discussed.

#### **Novel Surfactant Applications in Household Cleaning.** P.T. Sharko, Shell Global Solutions, Houston, TX, USA

In the not too distant past, recommending a surfactant blend for hard surface cleaning was fairly straightforward. Most of the products in the market were diluted prior to use and used with vigorous scrubbing. Cleaning performance was the main requirement. Performance could be demonstrated in a simulated scrubbing test in which a heavy oily soil was scrubbed from linoleum tiles by mechanically driven weighted sponges. Today's consumer can choose from a wide range of product forms. Dilutable cleaners have been joined by a multitude of spray-on liquids, foams, and wipes. Many of these promise specialized benefits such as disinfection, or particular efficacy against certain types of soil. This trend has made the optimization of surfactant systems more complex and requires the application of a variety of test methodologies to support technical recommendations. In this talk I will present a snapshot of our current evaluation techniques and recommendations for surfactant systems for hard surface cleaning.

#### **The Wonderful World of Solvents.** M.I. Busby, M.L. Tulchinsky, S.A. Elliott, The Dow Chemical Company, Midland, MI, USA

Water is the greenest solvent of all, but because of its properties, it is not always useful by itself for cleaning. One of the goals of cleaning formulation development is to use small amounts of organic solvents to enable water to be the primary solvent in cleaners. Existing oxygenated solvents cover a broad range of properties, and skillful formulation with them allows the preparation of effective cleaners with improved environmental properties, especially through the incorporation of new, more environmentally friendly surfactants, chelants, and biocides. At the same time, several new types of solvents, which are inherently low VOC and low toxicity, are being developed from biorenewable raw materials. The coupling characteristics of these solvents have been studied. One class of new solvents has shown excellent ability to couple d-limonene into water-based cleaning formulations, while another class of very low VOC solvents has demonstrated the ability to couple long chain hydrocarbons as a mimic for greasy soils while maintaining acceptable filming and streaking performance.

#### **BIO 4 / S&D 4.1: Biobased Surfactants and Ingredients**

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

**Chemical Modification of Sophorolipids for Improved Water Solubility.** J.A. Zerkowski, D.K.Y. Solaiman, ERRC, USDA, ARS, Wyndmoor, PA USA

Sophorolipids (SL) are biosurfactants produced from fats or oils by yeasts. They can be produced in good yields (approx. 100 g/L) and have attracted attention for commercial materials, but they have the drawback of being poorly soluble in water (roughly 50 ? 100 mg/L). This talk will present our recent work on attempting to prepare sophorolipid derivatives with improved water solubility. Our first approach is to append charged units to the carbohydrate headgroups. The goal is to preserve the macrolactone version of the sophorolipid, since this structure appears to be the better surfactant. The groups we are attaching via esterification are simple amino acids, which permit positive, negative, or zwitterionic groups to be introduced. Preliminary results indicate that in some cases, solubility of the sophorolipids is much improved, while surfactancy, at least as measured by minimum surface tension, is little affected. A second route to increasing water solubility that we are investigating is to apply olefin metathesis chemistry to SL. This route involves use of the open chain form: the fatty acid side chain is shortened from its native C18 length. New functional groups can simultaneously be included in the hydrophobic chain.

**The Use of Biosurfactants in Detergents.** Dirk Develter, Ecover Belgium N.V., Industrieweg 3, 2390 Malle, Belgium

Glycolipids can be produced by bioconversion of native and renewable feedstocks such as rapeseed oil. Sophorolipids and rhamnolipids for example are currently finding their way to the detergent market. These attractive surfactants combine green chemistry and a lower carbon footprint without the undesirable side products or environmental downsides found in many market reference surfactants. Sophorolipids are reported to be fully aerobically and anaerobically biodegradable and to have a low acute toxicity. They furthermore do not affect *Daphnia* reproduction, resulting in a chronic toxicity of an order of magnitude lower than reference surfactants with a no observed effect concentration (NOEC) of an order of magnitude higher than reference surfactants. Their minimum surface tension was found to be 32.1-34.2 mN.m<sup>-1</sup> depending on the method used. Sophorolipids are shown to be useful in hard surface cleaning and automatic dishwashing rinse aid formulations. This is attributed in part to their low foaming profile combined with their surface activity properties, which are of potential interest in additional applications. They thus combine an outstanding environmental profile with excellent performance, which resulted in their use in commercial household products.

**Alkyl Polyglyceride Surfactants.** G.A. Smith, H. Zhao, Huntsman Corporation, The Woodlands, TX USA

There is a growing demand for green surfactants based on sustainable raw materials. In an effort to generate surfactants from sustainable raw materials, we have concentrated on the use of polyglycerin due to the availability of cheap glycerin and its favorable environmental profile. Products derived from polyglycerin produced by conventional base catalyzed polymerization don't produce water soluble materials due to the low degree of polymerization and the presence of cyclic compounds. To increase the degree of polymerization and reduce the amount of cyclic species, we have developed a novel synthesis scheme based on glycerin carbonate. Polyglycerin produced by the present invention



can be reacted with aliphatic epoxies to produce water soluble surfactants. Water soluble alkyl polyglycerides have been prepared in good yields using sustainable raw materials. The green score for these materials is around 92% based on biobased carbon. A series of products with different alkyl chain distributions were prepared and the surface properties determined. In general, alkyl polyglycerides surfactants have good surface properties including low equilibrium surface and interfacial tension, low dynamic surface tension, short wetting times and a low to moderate foam profile. In detergent applications, APG surfactants show good cleaning performance in textile cleaning and hard surface applications.

**Control of Water Activity of Solvent-Free Lipase-Catalyzed Synthesis of Saccharide-Fatty Acid Ester Biobased Surfactants.** R. Ye, D.G. Hayes, University of Tennessee, Knoxville, TN, USA

Saccharide-fatty acid esters, biodegradable, environmentally-friendly, and biobased nonionic biobased surfactants that are utilized in foods, pharmaceuticals and cosmetics, have been synthesized using lipases and 10-200 micron-sized suspensions of saccharide in solvent-free medium. The reaction by-product water plays several significant roles. High concentrations of it promote hydrolysis, leading to the limitation of final conversion. However, excessively low liquid-phase water concentration promotes the diffusional loss of water from lipase, reducing the enzyme activity. Therefore, it is of vital importance to identify the optimal liquid-phase water concentration during the time course of lipase-catalyzed esterification. The highest conversion yield (90%) was achieved by employing a means of water removal when the conversion reached