106th AOCS Annual Meeting and Industry Showcases

Surfactants and Detergents Division Technical Program Abstracts

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The presenter is the first author or otherwise indicated with an asterisk (*).

S&D 1: Surfactants: Industrial Applications

Chairs: P.T. Sharko, Shell Global Solutions Inc., USA; and B.P. Grady, University of Oklahoma, USA

Effect of Acid Modification of Soy Glycinin on its Interfacial and Emulsifying Properties. C. Abirached[1], P. Moyna[1], M. Añón[2], and L. Panizzolo[1], [1]Universidad de la República, Uruguay, [2]Universidad Nacional de La Plata, Argentina.

A modification of soybean glycinin was performed by acidic pH treatment to improve its emulsifying properties. Glycinin was obtained by isoelectric precipitation (11Sn) and then was treated with acid pH (11St). Surface hydrophobicity (H_o) and thermal behavior were determined. Oil-water interfacial tension and rheology were measured. Rate constants of adsorption (k_a) and rearrangement (k_r) of proteins at the interface and dilational (E), elastic (E_d) and viscous modulus (E_v) of protein interfacial film were determined. Particle size distribution (PSD), interfacial protein concentration (G) and creaming stability were analyzed in oil:water 25:75 (v:v) emulsions, being the aqueous phase a 1mg/ml protein solution in sodium phosphate buffer pH 7.0, 0.01M.

The acid treatment caused an irreversible denaturation of 11S and increased H_o, Γ, k_a, E, E_d, and E_v increased significantly ($p \leq 0.05$), resulting in a greater rate of adsorption to the interface and a stronger interfacial film. The PSD exhibited droplets with diameters (d) larger and smaller than 4µm. Smaller droplets moved towards smaller diameters for 11St. 11St showed lower values of creaming destabilization constants, k_s ($d \leq 4$ microns) and k_l ($d \geq 4$ microns). In conclusion, 11S creaming stability was enhanced by improving interfacial properties and reducing the droplet size.

Optimization Methods on Surfactant Mixture to Quickly Improve the Formulation Performance in Chemical EOR. J.L. Salager and A.M. Forgiarini, University of the Andes, Venezuela.

The formulation of surfactant systems to attain a low interfacial tension in EOR often requires a large number of experiments with many different species, often with trial and error techniques, which are only slightly improved from being random by previous experience or intuition. As a consequence many laboratory studies include hundred of phase behavior and interfacial tension experiments with many variables but little predictive planification, since the huge information available in the literature has not resulted in general rules, but only trends with exceptions.

The proper analysis of the optimization concepts, particularly the HLD general relationship between formulation variables, allows to planify a sequence of experiments progressing toward a better performance at each step, so that the total number of experiments to attain a final solution is considerably reduced. It is shown that such optimization method typically requires a combination of three surfactant species with different characteristics linked to the oil/brine/temperature case. The progression toward optimum is described in a ternary diagram in which the EOR performance is mapped versus the composition of a three-surfactant mixture for some examples.

Effect of Intrinsic and Extrinsic Factors on the Stability of the α-gel Phase of a GMS-water System. F.C. Wang and A.G. Marangoni, University of Guelph, Canada.

Glycerol monostearate-water (GMS-water) systems undergo a polymorphic transition from the α-gel phase to the coagel phase. This phase transition results in a destabilization and loss of water in monoglyceride-structured systems, commonly found in personal care and food products. In this study, we examined intrinsic factors (type and concentration of co-emulsifiers) and extrinsic factors (cooling rate and applied shear) on the stability of the α-gel phase. The methods used to study the polymorphic transition were differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Results suggested that the transition from the α-gel phase to the coagel phase caused a change in the gel's physical appearance. More specifically, opaque and pearly white spots developed in the translucent α-gel. The stability of the α-gel phase can be increased by using an a-tending co-emulsifier, such as sodium stearyol lactylate (SSL), and by increasing the concentration of the co-emulsifier. Slow cooling rates without shear will also increase the stability of the α-gel phase. This work will help improve the shelf-life of food and personal care products containing monoglyceride emulsifiers.

Synergistic Effect Between Silica Nano Particles and Non-ionic Surfactants on Oil Recovery from Condensed Corn Distillers Solubles (CCDS). L. Fang, T. Wang, and B.P. Lamsal, Iowa State University, USA.

Most of the oil in condensed corn distillers soluble (CCDS) is in emulsified form and centrifugation alone is not sufficient to recover the oil in high yield. The synergistic effect between non-ionic surfactants (Tween 80 and Span 80) and silica nanoparticles (hydrophilic and hydrophobic) on oil recovery was investigated. Tween 80/ Span 80 blends having Hydrophilic-Lipophilic-balance (HLB) value between 15 (Tween 80) and 4.3 (Span 80) recovered 4 to 11% more total oil than control. Tween 80/silica mixture improved the oil recovery to 80~83% compared with 65~75% for control, whereas, Span 80 alone was not effective. The highest and most stable oil recovery was obtained with the mixture of Tween 80/Span 80 blends at 1:1 w/w ratio and 2.5% w/w hydrophilic silica nanoparticles; oil recovery significantly improved to 83 % of total oil in CCDS. Heating and shaking procedure significantly reduced oil body stability. Silica/surfactant addition can make the centrifugation process more efficient by destabilizing oil-in-water emulsion and washing out tiny oil droplets. The reason the total oil recovery was always below 85% is due to the oil being contained in the unbroken cells or germ pieces in CCDS.

Novel Polymeric Co-builder for Laundry Applications. Y. Zhu, K.T. Selvy, G. Hsu, V. Gibson, and S. Carbone, Lubrizol Advanced Materials, Inc., USA.

Laundry detergent powders contain significant levels of builders, which are used to remove water hardness to improve cleaning efficiency. Presently global production of laundry detergent powder to liquid is 5:1 ratio. Sodium tripolyphosphate has been used to provide builder functionality. Due to regulation and environmental impact, formulators chose polymeric co-builders with inorganic builders, e.g., carbonate and zeolite, to match phosphate performance. However, there is an unmet need for an improved builder system that increases the manufacturing efficiency in addition to matching STPP performance. A novel polymeric co-builder, derived from renewable sources, has been developed. It offers chelation, anti-encrustation, and anti-redeposition properties. Additionally it provides operational benefits, cost saving on energy consumption, and improves product sustainability. This new polymeric builder effectively reduces detergent slurry viscosity, resulting in increased throughput. This unique polymeric builder is suitable for phosphate and zeolite replacement and is also applicable for use in all laundry formulation platforms. Powder laundry performances such as slurry viscosity, flow curve, chelation, anti-redeposition, anti-encrustation, and detergency of this polymer will be presented in detail.

Unique Rheology Modifiers for Home and Personal Care Applications. J. Shulman, A. Keenan, and J. Hayes, Dow Chemical, USA.

There are several distinct types of rheology modifiers which a formulator can utilize to achieve the appropriate flow characteristics. One class of synthetic thickeners, known as HASE (hydrophobically modified alkali swellable emulsions) rheology modifiers, derives some of its unique properties through associations with other components (i.e. surfactants) in a formulation. The selection of a given polymeric thickening agent is strongly dependent upon the type of formulation being modified, the charge of the system, the relative hydrophilicity/hydrophobicity of the composition and the desired flow characteristics. Recent developments in this class of rheology modifiers have targeted the suspension of actives/visual cues in household and personal care matrices. This paper describes the unique behavior of this family of polymer chemistry, highlighting the differences in efficacy related to polymer structure, concentration and alkalinity, in addition to detailing their interaction with various surfactants.

Microbial Biosurfactants: Closing the Gap in the Innovation Chain. S.L.K.W. Roelants[1,2], L. Van Renterghem[1], R. Gheys[1], H. Moens[2], B. Everaert[2], I. VanBogaert[1], B. Vanlerberghe[2], and W. Soetaert[1,2], [1]University of Ghent, Belgium, [2]Bio Base Europe Pilot Plant, Belgium.

Biosurfactants are produced by a variety of microorganisms. Their biodegradability, application potential and the fact that they can be produced from renewable resources gives them an advantage over their chemical counterparts. The major two factors limiting further commercialization of biosurfactants are firstly the limited structural variety and secondly the high production price due to low inherent productivities and/or a lack of process knowledge.

A solution can be offered by an integrated process design (IPD) approach, where the entire

innovation chain is taken into account. Genetic engineering on one side of the spectrum generates engineered strains, which efficiently produce new-to-nature biosurfactants. Key to the IPD approach is the subsequent and thorough investigation of the production processes (fermentation and purification) with feedback coupling to the strain level. The scale up provides the opportunity to assess the scalability of the processes, while at the same time producing enough product to enable specialized application testing. This IPD approach is expected to result in real market penetration of microbially derived surfactants in the near future and will be illustrated with one of the showcases for biosurfactant production; the yeast *Starmerella bombicola.*

Characteristic Curvature of Secondary Alcohol Ethoxylates Using High Throughput Techniques. M.P. Tate, B. Karl, and C.J. Tucker, Dow Chemical Co., USA.

Secondary alcohol ethoxylates find utility in applications from cleaners and agrochemicals to oilfields, and for each of these applications there is a need to rapidly develop microemulsion based formulations. To that end, we have developed a high throughput method to formulate, measure, and analyze phase behavior at varying temperatures of surfactant, oil, salt, and water systems. This approach combines three specific tools: 1) multichannel liquid handler, 2) a custom-built image-capture station that captures images under well-controlled, uniform lighting conditions, and 3) a custom data-analysis algorithm to identify and determine the volumes of each phase.

Using these techniques, we determined and report here the characteristic curvature, as defined by hydrophilic lipophilic difference, of multiple secondary alcohol ethoxylates with varying EO lengths from 5 to 9. The phase behavior is captured under varying monovalent salt concentrations (0.05wt% to 10wt%), temperature (15 -40°C), and oils (C8 – C14). We show that the calculated characteristic curvature varies linearly with changing conditions, e.g., for EO=5, the characteristic curvature varies from 1.5 for a C10 oil to 1.9 for a C14 oil, and is hypothesized to be the result of the non-discrete nature of commercially available secondary alcohol ethoxylates.

Ultra-long Chain Fatty Acid Sugar Alcohol Monoesters: A Novel Class of Surfactant. W. Wei[1,2], B. Peréz[1], F. Feng[2], M. Dong[1], and Z. Guo[1], [1]Aarhus University, Denmark, [2]Zhejiang University, China.

Fatty acid sugar alcohol esters are widely used non-ionic surfactant. By changing both the acyl chain tail (length and number) and the sugar alcohol head group will allow us to systematically tune the physic-chemical properties of the amphiphilic fatty acid derives. Here we present a class of ultra-long chain fatty acid sugar alcohol monoesters based on behenic acid (22:0) with modified sugar alcohol (ethylene glycol, glycerol, erythritol, pentaerythritol, arabitol, xylitol and sorbitol) head groups. The compounds are synthesized in both enzymatic and chemical ways which confirmed by ^{1}H NMR, FTIR and MS. DSC and Temp-Ramp-FTIR indicated that the compounds are highly thermostable and molecular arrangements are governed by hydrophobic interaction among ultra-long alkyl chains. While the various head groups determine the molecular packing patterns, also give the compounds different surface activity like critical micelle concentration, Langmuir monolayer and critical packing parameter. This novel class of surfactants show potential applications in drug delivery.

S&D 1.1: Surfactants in Energy

This session is sponsored in part by Ultimate EOR Services, LLC

Chairs: S. Natali, Halliburton, USA; and U.P. Weerasooriya, University of Texas, USA

Interfacial Tension and Compressibility of Heavy Oil-aqueous Systems at Elevated Temperatures: Effects of Diluents. D. Nguyen, V. Balsamo, and J. Phan, Nalco Champion, An Ecolab Company, USA.

In Steam Assisted Gravity Drainage (SAGD) operations the produced fluids are complex water-in-oil-in-water emulsions. A diluent is often added to reduce the density and viscosity of the heavy crude oil, but more surfactants are added to the oil coming from the diluent streams. To simulate elevated temperatures of SAGD operations, this paper studied the effect of three different diluents on interfacial tension and compressibility of a Canadian heavy oil and aqueous at 120°C and 120psi and then correlated with emulsion stability. When compared to 20°C, all three diluents at 120°C exhibited higher compressibility, lower "phase change" area ratio (area ratio at which the phase change from high compressibility region to low compressibility region), and lower crumpling ratio (ratio of the compressed surface area to the original area at which the interface starts to collapse). These results suggest that emulsion would be less stable as the temperature is increased as expected. The interfacial tension (IFT) did not change much with increasing temperatures. An increase in "phase change" area ratio suggests a more elastic film as asphaltenes start to cross-link on the interface.

Removal of Particulate Fines from Organic Solvents Using Water as Collector Droplets. S. Malladi and A. Ramchandran, University of Toronto, Canada.

Owing to the need for reduction in the usage of fresh water in Clark process of bitumen extraction, the oil sands industry has focused its attention on the development of an alternative, solvent-based extraction method. A key challenge in this new process is the removal of particulate fines from bitumen-solvent mixture. Current methods for particulate removal such as centrifugation and solvent evaporation are energy intensive and carries potential emission hazards. Our project aims to explore the feasibility of using an aqueous phase for collecting and separating fines from oil phase by obtaining statistical data for particle-drop impingement process. A PDMS-based microfluidic aspiration device has been developed to perform impingement experiments. Simulations were performed to obtain a measure of particle interaction time with the drop surface. We observed that at capillary numbers around 10^{-4}, hydrodynamic drainage was not the rate limiting step for 10µm sized particle capture. The possibility of other hydrodynamic or thermodynamic processes such as contact line motion or hole-nucleation on particle capture will be discussed. We map out the relationship between particle capture efficiency and flow rate, viscosity ratio and radius of collector droplets. These results will provide design guidelines for a mixer for effective particle removal.

The Potential Application of Sulfonate- and Carboxylate-based Surfactants in Steam Foam EOR. T. Nguyen and G. Trahan, Sasol Performance Chemicals, USA.

Since heavy oil is very viscous and essentially immobile at reservoir temperature, traditional recovery technologies of heavy oil often require the application of heat melt these oils in order to mobilize them for recovery. One of the challenges in recovery heavy oils is their high viscosity, as high as several million centipoise at low temperature. Another is the low permeability of sand formation. Therefore, existing conventional steam techniques still produce low oil recovery. Adding the right surfactants that are able to produce good and stable foam at steam condition has shown to improve the oil recovery. Therefore, this research identifies and investigates the thermal stability and foam quality at high temperature of sulfonate- and carboxylate-based surfactants. The effect of salinity, temperature and presence of oil on the foam quality is evaluated. Surfactants that are thermally stable and have stable foam at high temperature are potential candidates for recovery of heavy oil using steam-foam technologies.

Oilfield Chemicals—Solvents and Surfactants for Well Stimulation, Completions, and Production. J.M. Fernandez, Sasol Performance Chemicals, USA.

This research studies the use of surfactants and solvents in well stimulation. Acid emulsions are shown to effectively remove carbonate/sandstone deposits from the wells. Dialkyl ethers are investigated as potential solvents to replace BTEX. The research also focuses on using

solvent/surfactant blends as pour point depressants to interfere with the solidification of parafin at cold temperatures.

Upscaling and Delivery of a Surfactant for an Enhanced Oil Recovery (EOR) Pilot and Lessons Learned. L.A. Pretzer[1], J.R. Barnes[2], and T.E. King[1], [1]Shell Global Solutions (US) Inc., USA, [2]Shell Global Solutions International B.V., The Netherlands.

For commercial roll out of surfactant-based EOR projects it is important to manufacture and supply surfactant products that have consistent quality. Such products will likely use existing manufacturing processes currently used to make surfactants for non-EOR applications, that can also be applied to make the large quantities required for EOR. To support upscaling of surfactant production for EOR, it is important to identify key composition and performance parameters that should be monitored during manufacture. This paper discusses the protocol to upscale and deliver a consistent surfactant product for almost 2 years for an EOR pilot. Three key topics will be highlighted:

- The need for establishing correlations between key performance and composition indicators to support surfactant upscaling and product quality control,
- An example of an upscaling and quality assurance program used to produce a commercial-scale surfactant over an extended period, and
- Technical and non-technical learnings from a surfactant manufacturer perspective. Based on these learnings, recommendations to better manage technical and non-technical risks will be presented.

Small-molecule Organogelators for Hydraulic Fracturing Fluids. G.P. Funkhouser, Halliburton, USA.

Alkylphosphonic acid monoesters were synthesized having alkyl chain lengths from 10 to 18 carbon atoms and ester groups of methyl, ethyl, isopropyl, and *n*-butyl. The esters were complexed with iron(III) in dodecane to form organogels. Storage and loss moduli were measured by oscillatory rheology. Alkyl chain length of the phosphonic acid had little effect on rheological properties, but more sterically-demanding ester groups, particularly isopropyl, decreased the relative contribution of the storage modulus to rheological behavior, as indicated by a larger phase-shift angle in the linear viscoelastic region (Me=6.9°, Et=8.4°, *i*-Pr=74°, *n*-Bu=15°). Metal-phosphonate bonding was studied with EXAFS. A chelate bonding configuration is associated with a weak gel. Phosphonate bridging between metal ions is the predominant configuration in a strong gel. The chelate configuration can be converted to the bridging configuration upon heating. SANS of a gel prepared with the iron(III) complex of monomethyl hexadecylphosphonic acid indicate the structure is a fibrillar network with a fiber radius of 15 Å. Iron(III) complexes of dialkylphosphinic acids also form organogels under similar conditions. The presence of two oxygen atoms available for bonding to metal ions is a common feature to carboxylic acid, phosphoric acid diester, alkylphosphonic acid monoester, and dialkylphosphinic acid organogelators.

Chemical Gradient Surfactant/Polymer Flood Design Using Seawater. E. Trine, P. Suniga, and C. Britton, Ultimate EOR Services LLC, USA.

Offshore oil fields are developing, and enhanced oil recovery technologies are being deployed all over the world. Surfactant/polymer flooding for offshore fields warrants the use of seawater as the injection brine. However, anionic surfactants are sensitive to high salinity and divalent cation concentrations, as in seawater. Developing chemical formulations to meet these challenges will expand the technology in offshore projects.

A chemical formulation was selected for a crude oil using surfactant/oil/water phase behavior experiments. Well-designed chemical floods require surfactant injection at optimum salinity followed by a polymer solution in Winsor Type-I phase. To achieve the gradient design, different strategies were tested including desalinating seawater, adding hydrophilic co-solvents and surfactants, and adjusting the surfactants to better tolerate hardness. Adding a hydrophilic surfactant to the polymer drive proved the most effective strategy at driving the surfactants into the Type-I region in the polymer drive.

The surfactant formulation and chemical gradient was then tested in a coreflood experiment where it left a final oil saturation (S_{orc}) of only 0.04. This result indicated that a surfactant chemical gradient can effectively supplement salinity gradients in creating a robust SP process in hard brine.

Latest Developments in Chemical Enhanced Oil Recovery. U.P. Weerasooriya and G.A. Pope, University of Texas, USA.

Surfactant synergy in chemical EOR offers tremendous benefits to formulation characteristics as well as to performance attributes. These, in turn, can be used advantageously not only in surfactant applications for CEOR, but also in preparing and transporting ultra-highly concentrated surfactant blends as flowable fluids.

This latter function helps to drastically lower transportation costs by minimizing the amount of water needed to keep blends flowable during and after transportation.

S&D 2: New Product Forms and Use Innovations

Chairs: D.S. Stott, Church & Dwight Co. Inc., USA; and T. Graham, Rivertop Renewables, USA

A Novel Naturally Derived Hydrophilization Polymer that Provides Multiple Benefits in Hard Surface Cleaners. J. Kiplinger, F. Lambert, K. Karagianni, and C. Orizet, Solvay USA, Inc., USA.

Household and industrial cleaners like hard-surface cleaners and dish wash & fabric detergents have to provide more and more benefits beyond detergency on a growing variety of surface types. Many desired benefits like easy cleaning, fast drying, shine or anti-scaling can be achieved by changing the surface properties by depositing the right polymer from a cleaning product onto the respective surfaces. This presentation shows the multiple benefits in hard surface cleaners that can be obtained by the addition of a low level of this novel polymer. Performance improvement of the cleaners is seen by application testing on a variety of surfaces. The benefits demonstrated include easier next time cleaning, anti-re-soiling, faster drying, less streaking and spotting and anti-fogging. The polymer is used at low levels, provides several observable benefits, and is safe for all surfaces.

Overcoming Performance Perturbations of Amylases in Heavy Duty Liquid (HDL) Laundry Detergents. K. Harris and E. Dodge, DuPont Industrial Biosciences, USA.

Alpha amylases play an important role in the cleaning performance of liquid laundry detergents (HDLs) by breaking up high molecular weight starch molecules in foods and sauces that cause staining on fabric. Alpha amylases, like other proteins, have very complex structures that can be disrupted by perturbations in their environment (such as dosing in HDL, storage conditions or wash conditions). This can lead to loss of structural integrity and a decrease in wash performance. One challenge faced when formulating liquid laundry detergents with a high performance, low temperature alpha amylase is enzymatic stabilization in a myriad of harsh conditions such as high surfactant levels, different builders and incompatible chemicals in the HDLs. We will show how alpha amylases can have different stability profiles in different detergents and how to address stabilizing them in HDLs.

Achieving Laundry Cleaning Performance in Lower Wash Temperatures. K. Gutowski and A. Taneja*, BASF Corp., USA.

By 2050, the population of Earth is expected to grow to nine billion people. This makes the development of sustainable technologies and solutions which utilize renewable resources and lower quantities of water and energy very critical. It is estimated that during household laundry process, an activity that is performed several times during a week by a typical family, 90% of the total energy spent is used to heat water. While significant energy savings can be realized by washing at lower temperatures, achieving superior performance under these conditions has been highly challenging. Performance is typically measured by attributes such as 1) the ease of dissolution of the detergent formulation into cold water, 2) the degree of particulate removal and oily soil emulsification, and 3) the extent of removal of complex, organic food soils and stains from fabrics. In this presentation, we discuss approaches and chemistries (based on surfactants and polymers) which enable formulators to develop cold water detergents that can provide excellent performance and rapid dissolution at low wash water temperatures.

Cleaning by Hydrophilic-hydrophobic Surface Modification. A. Nagy[1], M. Hisamoto[1], D. Kuppert[2], and J. Peggau[2], [1]Evonik Corp., USA, [2]Evonik Industries AG, Germany.

In a traditional cleaning process, surfactants serve essentially three functions: first, they reduce the surface tension of water to facilitate the wetting of a surface; second, they penetrate into and lift contaminants; and third, they adsorb onto the particles to suspend them in solution. A shortcoming of this process is having residual surfactant remain on the cleansed surface. Eventually the liquid dries, and the cleaned surface is susceptible to re-soiling and having an unattractive appearance. In addition, the drying process is slow due to the strong interactions between the water, surfactants, and surface.

Nature, however, provides a unique route for self-cleaning using superhydrophobicity. Certain

plant leaves, such as those from tomato or lotus, are composed of a nano-structured hydrophobic architecture which prevents effective wetting of the surface. As rain accumulates on the leaves it readily beads up at a high contact angle and rolls off. During this event the contaminant particles are picked up and removed without the use of any chemicals. These super-hydrophobic, self-cleaning surfaces can be created artificially. The chemistry, application, and new developments in this area will be presented.

Modification of Rheological Properties of Compacted Liquid Laundry Formulations. V. Prasad and J. Shulman, Dow Chemical Co., USA.

There is a trend in home care markets towards increased compaction of liquid laundry formulations. Some of these formats include superconcentrates and unit dose products, characterized by lower levels of water and higher levels of surfactants in the formulation. In the case of unit dose products, the formulation may be contained within a pouch made with a polymer such as PVOH. For superconcentrates, high active concentrations may lead to increase in the viscosity of the formulations, or in viscosity/gel-like behavior on dilution with water. Use of unit dose products involves dissolution of the PVOH, and release of the contents of the pouch in a large bath of water. The complex interactions between the polymer, water, and the formulation result in phenomena such as undispersed polymer flocs, gel formation, or increased viscosity of the detergent as it exits the pouch.

In this study, we describe alternate solvents and surfactants for formulation in compacted liquid laundry products to mitigate some of these phenomena. The solvents we investigate are primarily glycol ethers, while the surfactants are neutralized alkylbenzene sulfonic acids. Some of the new formulations demonstrate reduced viscosity by themselves or on dilution with water; as well as modified interactions with the PVOH polymer. Finally, the cleaning performances of these new formulations are benchmarked against current formulations.

Enzymatic Liquid Unit Dose Detergents. L.M. Mikkelsen, Novozymes A/S, Denmark.

Inclusion of enzymes in liquid laundry detergents has been essential in driving the performance to greater levels. In US, “classical” pourable liquid laundry detergents dominate the market, but one of the fastest growing segments is the liquid unit doses resulting in increasing market value. The convenient format is enabled by preserving the water soluble film around the liquid detergent until hit by the wash water, and this represent new formulation constraints as obviously water has to be limited within the capsule. Enzyme performance is as needed here as in “classical” liquid laundry detergents, and it’s possible to formulate liquid unit dose detergents with optimal enzyme stability with enzymes from different classes taking advantages of the recent developments in stabilization technologies.

Water Soluble Film Innovations for Single Unit Dose Applications. Y.S. Parulekar, MonoSol, USA.

The introduction and subsequent exceptional growth of soluble unitdose (SUD) delivery systems has led to the desire for new innovation and concepts to fulfil the high expectations that have been established with this format. Developments in water-soluble film (WSF) technology have enabled the substantial contributions of SUD delivery systems to the home care detergent and agrochemical markets. This unique and convenient format has facilitated combinations of otherwise incompatible chemistries to be delivered in the SUD. Unitdose packaging of automatic dishwasher (ADW) detergents was one of the first commercial applications of water-soluble films in the household sector followed later by SUD laundry detergents. Over the past decade, these consumer detergent product categories have grown in the developed world through continuous innovation, including new product development in water-soluble films. Similarly, the penetration and growth of SUD in the developing world will be driven by innovation; however, these markets present a different set of challenges. This presentation highlights new products, including functionalized films, which can enable penetration and growth in both developed and developing markets.

S&D 2.1/SCC: Surfactants: Cosmetic Science

This session is sponsored in part by Colonial Chemical, Inc.

Chairs: M.S. Vethamuthu, Ashland Specialty Ingredients, USA; and D. Abbeduto, Society of Cosmetic Chemists/Colonial Chemical, Inc., USA

Surfactants and Human Skin: Perspectives from 40 Years of Skin Science Research. R.R. Wickett, University of Cincinnati, USA.

This talk will review effects of surfactants on human skin from a perspective acquired during 40 years in personal care research. Recommendations for future research will be discussed.

There has been considerable progress toward mitigating the effects of surfactants on human skin but many challenges remain. Mild cleansing systems can be formulated but we still do not completely understand the factors controlling surfactant skin interactions. It is clear that surfactants can penetrate the SC causing reactions in the viable epidermis. Relative roles of micelles and monomers in surfactant skin penetration have been investigated for many years but in my opinion complete understanding is yet lacking for reasons that will be discussed.

Another mystery is the wide variation in response between individuals treated with the same surfactant system. We may find some individuals dropping from a test due to high scores while others show little or no irritation even at the end. We also see a wide range of preexisting irritation scores in our studies on health care worker. Some of the variation in response may be explained by polymorphisms in genes for inflammatory cytokines but there are still many factors remaining to be elucidated.

Microbial Biofilm Evaluations: Impact and Insights for Industry. B. Glembocki, D. Grinstead, S. Lyon, K. Roach, and C. Spangenberg, Sealed Air Inc., USA.

Microbial biofilm is the dominant form that microbes assume in a real world setting in which they develop a complex matrix of cells, proteins, polysaccharides and DNA. It has been estimated that 99% of microorganisms on Earth live in biofilm. Biofilm formation characteristics can be exhibited within seconds of a single organism attaching to a surface. Biofilm is not necessarily visible to the naked eye. If you have moisture and a surface you will have the potential for biofilm formation. This simple fact points to the need for methodologies to evaluate sanitizers, disinfectants or other microbial control agents in a representative setting beyond what has been done historically.

Biofilm has become a defined and recognized form that microbial communities exist in. Recently there has been significant activity surrounding biofilm standard test method development for hard surface sanitization and disinfection. This has set the stage for regulatory impact from agencies such as the US EPA. Beyond registering products for a product label claim, cleaning practices and formulations need also to be considered.

This presentation discusses recent activities in method development and standardization. Included in this discussion will be insights gained from initial biofilm evaluations against several disinfectant product classes.

The Effectiveness of Natural Oils in Cosmetic, Beauty, and Personal Care Products. G.R. Watkins* and G.A. Smith, Huntsman Performance Products, USA.

There is a general assumption amongst consumers that “natural” products are healthier than similar ones using synthetic ingredients. Often these “natural” ingredients are no different in chemical composition than their synthetic counterparts. In fact, a synthetic substance which mimics a natural one can sometimes provide a purer, more stable ingredient which gives the product a longer usable life.

Natural oils such as “Hemp seed oil is made up of 80% essential fatty acid, the highest amount of any other plant. Hemp seed oil prevents moisture loss on a physiological level. It contains the ideal ratio of Omega 6 to Omega 3 based on our skin needs. Hemp so closely matches our own skins lipids it is able to penetrate inside our cells and lubricate the surface between them, thus bringing the EFA's within our body. For this reason EFA's have been proven to play a preventative role in skin aging and a healthy moisture balance. Not only does Hemp seed oil contribute greatly to the barrier function and appearance it also has other skin benefits such as offering relief to acne, minor abrasions, psoriasis and eczema”.

How can the formulator maintain these "benefits" when developing a product, if at all? This research will explore the effectiveness, real and imagined, when using these natural or essential oils in Cosmetic, Beauty and Personal Products.

Surfactants in Personal Care Applications: Challenges and Recent Trends. M.S. Vethamuthu, Ashland Specialty Ingredients, USA.

Objective: The aim of this work is to present surfactants used in cosmetics and highlight key functions, different microstructures, and any problems associated with their use in personal cleansing products. It is well known that cleansing skin with surfactant-rich compositions can result in irritation & skin barrier damage often leading to dry and compromised skin.

Methods and Results: The foam creation and decay characteristics have been evaluated and compared using an instrumental foam method called the SITA foam tester and compared to an *in-vivo* measurement method. The irritation potential of the surfactant mix have been measured using the Zeta Nano Laser Doppler electrophoresis method. The measured Zeta potential distribution (mv) of formulations and individual surfactant micelles have been correlated directly to flex wash clinical studies published in the literature.

Discussion and Conclusion:
Many earlier studies have shown cleanser induced damage to skin *stratum corneum* as arising due to surfactants binding to exposed protein domains during cleansing and causing swelling and de-naturation. This study also highlights current trends moving to sulfate free and low surfactant based innovative cleansing compositions.

Optimized Microemulsion Systems with Low Surfactant and Salt Concentration for Detergency of Vegetable Oils at Low Bath Temperature. C. Attaphong, J.F. Scamehorn, and D.A. Sabatini*, University of Oklahoma, USA.

Triglycerides from vegetable oils are among the most difficult oils to remove from fabrics, especially at low temperature. Moreover, it is very challenging to get high efficiency of cold detergency with semi-solid fats or waxy soils. Recently, extended surfactants have shown very promising performance for detergency at ambient temperature. Therefore, the microemulsion systems of extended surfactants are of interest for cold temperature detergency of vegetable oils and waxy soils. The objective of this study are to explore the optimized microemulsion systems with low surfactant and salt concentration using extended surfactant for vegetable oil detergency at low temperature, and to investigate different microemulsion formulations of anionic extended surfactants and conventional surfactants to obtain the greatest cold detergency of waxy soils. In addition to studying the effects of surfactant and salt concentration, preliminary results on the impact of hydrophilic/lipophilic linker addition and formulating in the Winsor Type II region on detergency efficiency of waxy soils will be presented. These results will provide useful information for design of surfactant systems for future research.

Formulated Solutions for Hair Repair. S. O'Connor, C. Lepilleur, and M. Ruffing, Lubrizol Advanced Materials, USA.

Hair repair remains one of the most rewarding and challenging claims to satisfy consumer needs in Hair Care. Using a combination of technologies and formulated solutions, products can be created which deliver the delight of hair repair applicable to different hair types having varying degrees of hair damage incurred by exposure to chemicals, environmental conditions and mechanical stresses from regular grooming practices. In addition to an interpretation of hair repair the presentation will provide a sound outline of core fundamentals in hair conditioning, key chemistries to deliver best in class care performance and innovative formulation concepts.

S&D 3: Tools of the Trade: Measurement and Characterization

Chairs: T. Zander, Henkel, USA; and E. Theiner, Air Products & Chemicals Inc., USA

Emulsion and Suspension Characterization: Is There Possibly a Direct, Better, and Faster Way? D. Dinair, LUM Americas, USA.

Time. For most of us a scarce commodity. In today's competitive world, we are all under increasing pressure to improve existing products and introduce new ones in shorter and shorter time frames. This means that the correct and efficient characterization of physico-chemical properties for emulsion and suspension based products is an absolute must. Traditionally, particle sizing, zeta potentials, and rheology have been used to accomplish this. As useful and important as they are, for complex systems they have some important analytical limitations (e.g. need for dilution, lack of accuracy, and incomplete resolution). The STEP technology based approach does not suffer from these limitations and allows for the direct and complete in-situ characterization of emulsions and suspensions. Stability, particle size, and accelerated shelf life prediction results and methods for both dilute and concentrated emulsions and suspensions will be presented.

Instrumental Methods for a Reliable Assessment of Fabric Surface Appearance. T.J. Burns, Novozymes North America, Inc., USA.

Claims of improvements to the appearance of fabrics such as consumer garments are regularly made to designate advantages between commercial laundry detergent formulas. However, attributions of such differences in appearance are typically subjective, and perceptions can vary considerably from one observer to another. Several sensory (human-evaluation) and mechanical (instrumental) methods will be discussed, with assessments as to their relative robustness and reliability in making determinations of both the extent and significance of such benefits to the fabric surface appearance. In our laboratories we have adapted instruments which have traditionally been used for assessment of other sorts of laundry performance criteria in order to provide quantifiable test results that can provide a statistical basis for competitive claims support.

The Use of Small-angle Scattering to Determine Surfactant Micelle Structure. B.P. Grady, University of Oklahoma, USA.

In this talk, the fundamentals of x-ray and neutron scattering will be presented and the information that the two techniques can give will be compared. Specific examples of different surfactant scattering patterns will be given, and in particular the ability to determine the structure and number of surfactant molecules in a micelle will be discussed.

Characterization of Sodium Lauryl Sulfate Foams. R. Sanedrin, KRUSS, USA.

Foams, which are composed of a dispersion of gas bubbles bounded by liquid lamellas, have a wide range of applications in various fields, including food industries, enhanced oil recovery, chemical, pharmaceutical, firefighting, construction, and textiles. They are metastable, wherein their stabilities and disintegration varies widely from a few seconds to several days, owing to various physical processes such as bubble coalescence, Ostwald ripening, bubble bursting, and liquid drainage. Herein, we show the ability of the KRUSS instrument, DFA100, to evaluate foams generated from either air sparging or stirring a solution of sodium lauryl sulfate (SDS). Various concentrations of SDS solutions were either sparged with air or stirred and the foamability and stability of the generated foams were evaluated. In addition, the liquid content, liquid drainage, and the structure of the generated foams were also measured. Here we show the versatility of the DFA100 instrument in fully characterizing and evaluating liquid foams.

S&D 3.1: Additives for High Efficacy

Chairs: A.C. Lee, Novozymes North America Inc., USA; and S. Raders, Church & Dwight Co. Inc., USA

Analysis of Structural Viscosity of Fabric Softeners Imparted by Polymers. D. Sasaki, R. Hashimoto, Y. Kohno, E. Ogura, T. Miyahara, and T. Okamoto, Lion Corp., Japan.

The value of fragrance in fabric care products is increasing. Accordingly, in order to last scent on fabrics even when the consumers are taking off clothes, the number of products that have encapsulated fragrance is increasing. To add further value, we believe that fabric care products will expand in scope to contain various functional particles. However, most of fabric care products are liquids, and it is very difficult to produce stable dispersions of functional particles. To produce stable dispersions of the particles, we attempted to impart structural viscosity to the softener by adding various polymers. As a result, we found that the spiral polymer imparts structural viscosity to the liquid softener of emulsion formed from the cationic surfactant. In this study, we report the mechanism of structural viscosity, how the polymer structure changes and its effect on the trap state of free water, and the flocculation of vesicles formed from the cationic surfactant in the dispersed solution.

Narrow Range Ethoxylates versus Standard Alcohol Ethoxylates in the I&I Industry. H. Byrne, G.A. Smith, and P. Weaver, Huntsman Performance Products, USA.

For I&I surfactants, customers desire nonylphenol ethoxylate replacement products designed to provide high-efficiency cleaning for tasks at an industrial level. Formulators are challenged to find new surfactants which provide end users with such cleaning while also keeping costs reasonable. In recent years, alcohol ethoxylates (AEs) have proven to be useful in the I&I market segment, but, while AEs have given good results, they still have performance related drawbacks which could be improved on. One approach to advance AE technology is to use a special catalyst which produces an AE with a narrower oligomer distribution. The surfactants yielded in the process are known as narrow-range ethoxylates (NREs). Laboratory testing showed that the NRE surfactants produce lower surface tensions and lower interfacial tensions than the AEs, indicating that the NREs should remove soils better. Based on these findings, a study was carried out to look for synergistic effects when NREs with varied alkyl chain lengths and varied degrees of ethoxylation are used together. Different NREs were incorporated into formulations directed at assorted laundry and hard-surface cleaning applications. The data obtained to date do indeed show a synergistic effect when NREs of significantly different compositions are combined.

Ester Quats for Low Active, High Viscosity Dispersions. D. Murphy, C. Gariepy, C. Matache, D. Dardugno, and L. Zaporowski, Stepan Co., USA.

A new class of triethanolamine ester quat will be described which affords excellent viscosity building when incorporated as the softening active in low concentrations in aqueous dispersions. In many parts of the world, such product forms dominate and the high viscosity connotes quality and richness. This technology will afford the possibility of reducing or eliminating thickeners currently employed. Various other aspects including softening, storage stability, formulatability, physical properties and regulatory will also be discussed.

Bio-based Polyamide Gellants for Novel Product Forms and Functionality. B.S. Jaynes, Croda, Inc., USA.

A series of bio-based polyamide gellants has been developed that allows product formulators to create novel gelled or thickened materials in both oil based and aqueous systems. The patented polyamide materials are prepared from dimer fatty acids, derived from tall oil fatty acid. The dimer acids are then condensed with diamines and diols with varying levels of polarity to generate polyamides with properties ranging from oil soluble to water soluble. One family of polyamides is prepared with non-reactive end groups, leading to reversible gellants and thickeners. These solid polymers are dissolved by heating in the presence of a solvent of comparable polarity. Upon cooling, the strong hydrogen bonds of the polyamides re-form, generating thickened materials ranging from viscous liquids to clear gels, depending on the concentration of polymer. In the second family of materials, reactive end-groups on the polyamides are cross-linked at room temperature, leading to irreversible stiff gels. These stable materials are well-suited for gelling oil based fragrances or other oil soluble actives. Examples will be presented showing how

each family of polyamides can be used to generate unique, visually appealing product forms exhibiting novel rheology control, fragrance delivery, odor absorption, and other value-added functionality.

Formulations and Guidelines Using Lactic Acid as Biocidal Active for Detergent Applications. P. Stuut[1], E. Lansdaal[1], and R. Wietting[2], [1]Corbion, The Netherlands, [2]Corbion, USA.

Within the home care area there is a clear and continuous trend towards more safe and sustainable ingredients and detergent formulations. Consumers expect safer products and more environmentally friendly products.

Lactic acid is currently used in a wide variety of home care applications because of its functional benefits in cleaning, descaling and anti-microbial properties.

This paper will demonstrate the guidelines for creating optimal antimicrobial effects for both low and high surfactant concentration formulations. It will cover some market compatible examples of detergent formulations using lactic acid as antimicrobial active, both as an active as well as an in-can preservative. Besides the formulation examples, also directions how to create formulas with effectiveness at short contact times will be discussed and explained. Further on the registration update under EPA and BPR for lactic acid and biocide formulations containing lactic acid will be tackled.

Hydrophilic Encapsulation of Multi-walled Carbon Nanotubes. S. Hanumansetty, E. O'Rear, and D. Resasco, University of Oklahoma, USA.

Admicellar polymerization (AP), a surface analogue of emulsion polymerization was used to obtain a thin layer of hydrophilic polymer coating on multi-walled carbon nanotubes (MWCNTs). The hydrophilic nature can facilitate integration of carbon nanotubes into a variety of composite materials. To develop hydrophilic polymer by AP, acrylate monomers were copolymerized using sodium dodecyl sulfate as a surfactant. Development of a system for AP involves measurement of surfactant adsorption and adsolubilization or partitioning of monomer into adsorbed structures (reverse hemimicelles). A modified two-site adsolubilization model was used to calculate the size of surfactant aggregates over the surface of MWCNTs and a binary adsolubilization model was employed to predict number of monomers adsolubilized from single component experiments. Adsolubilized monomers were polymerized to form a polymer nanocomposite, which was then hydrolyzed to obtain a hydrophilic nanocomposite. SEM, Energy Dispersive Spectroscopy (EDS), Thermo Gravimetric Analysis (TGA) and FT-IR confirmed the formation of polymer on multi-walled carbon nanotubes (MWCNTs). Modified MWCNTs readily dispersed in aqueous media and were stable after 3 days.

A New Protease Inhibitor Alternative to Stabilize Protease in Liquid Detergents. V.M. Casella, Novozymes North America, Inc., USA.

Liquid laundry detergents dominate the North America laundry market. Inclusion of enzymes in liquid detergents is an important performance and claim enabler. A known formulation challenge is the stabilization of enzymes in these products.

The use and benefits of a new protease inhibitor system to stabilize protease in liquid detergents is introduced. Currently, many liquid detergents that contain protease use boric acid or borate based protease inhibitor systems to effectively stabilize proteases (inhibit proteolysis) during storage.

Because of greater regulatory scrutiny in regards to boric acid and increased retailer focus on sustainable chemistry an alternative to boric acid/borate based protease stabilization in liquid detergents is desirable.

The enzyme stability and performance properties of liquid detergents containing protease (and other enzymes) stabilized using a new (boron free) protease inhibitor is compared to current protease stabilization approaches (including boric acid).

Furthermore formulation flexibility (multi-enzyme solutions) of this new protease inhibitor system is introduced.

Tailoring Wet Wipe Cleaning Solutions for Consumer Applications—A Systematic Approach. B. Parrish and B. Hill, The Clorox Company, USA.

There is a growing trend in house-hold cleaning toward more convenient product forms such as wet wipes which consolidate cleaning formula and applicator into one. Wet wipes deliver efficacy with control and convenience to remove surface soils, body soils, and germs on a broad range of surfaces. Wet wipes are a system that is highly dependent on the interactions between the nonwoven substrate and the cleaning formula. These interactions can dramatically affect actives delivery, cleaning performance, product stability, and consumer perceived aesthetics including visual appearance, fragrance, hand feel, and residue. The development

of wet wipes requires a systematic approach to determine the correct selection of materials. These materials include nonwoven fiber type and how the fibers are processed, ingredients in the cleaning formula (any antimicrobial actives, surfactants and solvents), assembly of all materials and the final packaging form. An approach to select materials and assemble them based on their chemical and physical properties and interaction will be presented.

The Stabilization of Reactive Benefit Agents in Liquid and Solid Consumer Cleaning Product Formulations. R. Hay and D. Pears, Revolymer (UK) Ltd., UK.

The consumer market trend to liquid unit dose detergents shows no sign of reversing; preferred by consumers for convenience and offering easy use 'mess free' cleaning.

There are limitations, however, on the range of active benefit agents which may be included in such liquid products which has an impact on product performance. In particular oxygen bleaches, widely used in detergent products, cannot be formulated into aqueous based liquid detergents. The bleach, commonly based on a persalt, reacts with the liquid constituents and is deactivated. Because of this issue, the performance of liquid laundry and dishwashing products falls below that of solid, bleach containing, products and therefore consumers will often add a separate bleach boosting product in order to satisfactorily clean their clothes.

We will describe our approach to the development of new oxygen bleach systems which are stable in liquid laundry and dishwash formulations which enable a new level of performance from liquid products.

We will discuss the key aspects of product shelf life and in-use bleach dissolution and stain performance.

We will describe the technology and application for the protection and release of sodium percarbonate (SPC) and phthalimido peroxy hexanoic acid (PAP) in liquid and solid ADW and laundry products.

S&D 4/BIO 4: Biobased Surfactants/Detergents

Chairs: G.A. Smith, Huntsman Performance Products, USA; R.M. Maier, University of Arizona, USA; D.K.Y. Solaiman, USDA, ARS, ERRC, USA; and D.G. Hayes, University of Tennessee, USA;

Surfactants Based on Algae Oil. G.A. Smith and H. Byrne, Huntsman Performance Products, USA.

Modern day surfactants are based on natural, petrochemical or a combination of natural and petrochemical feedstocks. With the recent emphasis on sustainability, surfactants based on natural feedstocks are of considerable interest. Typically, natural surfactants are based coconut or palm oil. Both of these materials are also used as a food source. An alternative feedstock which is not used for food is algae. There are thousands of different algae species which can grow in fresh or salt water.

Work was performed to optimize the growth conditions for chlorella vulgaris algae in photobioreactors (PBR). Light frequencies and fertilizer concentrations were varied to achieve the optimum growth conditions. In order to maximize the lipid yield, the algae were stressed and the lipids extracted. The oil was used to make a variety of different nonionic surfactants. Surface properties and detergency measurements were performed.

Comparison of Performance for Sugar Esters Prepared by a Green Enzymatic Process and a Commercially Available Product. R. Ye[1], D.G. Hayes*[1], R.M. Burton[2], A. Liu[3], and Y. Wang[3], [1]University of Tennessee, USA, [2]MARC-IV Consulting, Inc., USA, [3]Tianjin University of Science and Technology, China.

Sugar esters, important biobased surfactants and emulsifiers for foods, cosmetics, pharmaceuticals, and other applications, are traditionally prepared in high-termperature processes, in the presence of organic solvents, and using a stoichiometric excess of reactant. We have successfully prepared sugar esters using green manufacturing: immobilized enzymes, the absence of solvents, and stoichiometric substrate feeds. Therefore, the green manufacturing approach will potentially yield a product meeting user specifications without the need of downstream purification, and the absence of wastes. In this study, the chemical composition, surface and antimicrobial activity of the enzymatically prepared sugar esters were measured, and compared to a commercially available sugar ester product. Typically, the authors' bioreactor system yields a technical grade product, ~85-90% pure, at the 10-30 gram scale. To achieve a higher purity. the technical grade product underwent further esterification, in a very low water activity environment, achieved by operating the reaction in well-sealed dessicators in the presence of dessicant. The study will compare chemical composition and molecular structure, surface and interfacial tension, emulsification, and antimicrobial activity.

A New and Cost-effective Biosynthetic Process for Hydroxylated PUFA's by the Yeast *Starmerella bombicola*: Opportunities for Bio-medical Research. I.N.A. Van Bogaert[1], G. Zhang[2], B. Hammock[2], and W. Soetaert[1], [1]Ghent University, Belgium, [2]Bruce Hammock Lab, USA.

Poly-unsaturated fatty acids (PUFAs) are essential in human nutrition as they take part in various key signaling pathways. In general, not the PUFAs themselves trigger these effects, but their oxidized or hydroxylated derivatives. Yet, such compounds are rare and if commercially available extremely expensive, in this way hampering *in vivo* experiments. We developed a whole-cell protocol for the generation of ω and ω-1 hydroxylated PUFAs based on the yeast *Starmerella bombicola*.

This yeast is known for its ability to produce sophorolipids, a biosurfactant of commercial interest applied in environmentally friendly cleaning formulations. Biosynthesis involves the action of the cytochrome P450 monooxygenase CYP52M1 hydroxylating C16-18 fatty acids at the terminal or subterminal position. Interestingly, unsaturated fatty acids with 20 and even 22 carbon atoms get hydroxylated as well.

Consequently, the sophorolipid biosynthetic route was used to hydroxylate various PUFAs. The hydroxylated molecules are incorporated into the sophorolipids and secreted in the culture medium, allowing efficient recovery. They can be released from the sophorolipid molecules by acidic hydrolysis. Yield was substantially increased utilizing a modified yeast strain (0.01 vs 20 % after purification).

Production of Biosurfactants Using *Bacillus subtilis* on Pretreated Biomass Hydrolysates in 5-L Bioreactor. R. Sharma, W.J. Colonna, and B.P. Lamsal, Iowa State University, USA.

Surfactin is a *Bacillus subtilis* biosurfactant which has excellent surface active properties but has limited aqueous solubility.Recombinant strain of surfactin producing *B.Subtilis*(E4088), produces a water soluble variant of surfactin called FA-glu due to a less hydrophobic amino acid structure than surfactin. In a study for 50-mL shake flask fermentation for both strains,soy hulls,alfalfa and switchgrass were chosen as the best carbon sources compared to glucose for highest growth and product concentration for FA-glu and surfactin producing *Bacillus subtilis* strains. These 3 biomasses were pretreated with a combination of liquid ammonia and ultrasonication among six fibrous biomasses to generate hydrolyzates,utilized as carbon source in growth media for both *Bacillus* strains in 50-mL shake flask experiments.It was observed that glucose content and relative availability of hexose and pentose sugars in the hydrolysates played an important role in determining highest growth and product titer. We have designed 5-L fermentations of growth media based on these selected biomass hydrolysates as carbon source to study bacterial growth,economic efficiency and product quality of the surfactin and FA-Glu which would provide a comparative analysis of scale up,process kinetics and reactor performance.

Challenges to Realizing the Commercial Potential for Biosurfactants. R.M. Maier, University of Arizona, USA.

Since their initial discovery and introduction to the marketplace in the 1960's, biosurfactants have experienced a steady rise in interest and potential applications as "green" alternatives to traditional petroleum-based specialty surfactants. This is due to a combination of their environmentally friendly characteristics, including low toxicity and ready biodegradability, as well as their excellent surfactant attributes. This presentation will discuss some of the challenges associated with realizing the market potential for biosurfactants. There are still relatively few biosurfactant structures that have been well characterized in terms of their structure, surfactant properties, biosynthesis, regulation, or encoded genetic information. This process is tedious and difficult and further complicated by the fact that it is a combined microbiology and chemistry problem that few laboratories are well-equipped to carry out. An even larger challenge is how to cost-effectively purify these materials for use as specialty chemicals. Biosurfactants are often produced as congener mixes which can lead to batch to batch variability in production that may not be acceptable in a specialty chemical. Finally, discovery of new biosurfactants is limited because currently available molecular screening techniques are of little use and manual culture-based searches are expensive in terms of time and labor.

Tailoring Rhamnolipid Biosurfactant Properties Through Production by Chemical Synthesis. J.E. Pemberton, R. Palos-Pacheco, C.S. Coss, and R. Polt, University of Arizona, USA.

Rhamnolipids are an important class of biosurfactants being explored as greener alternatives to petroleum-based surfactants. These surfactants are generally comprised of a ß-hydroxyalkanoyl alkanoate tail glycosylated by one or two rhamnose units, with the most abundant containing a ß-hydroxydecanoyl deacanoate tail (Rha-C10-C10 or Rha-Rha-C10-C10). To date, attainable rhamnolipid properties have been limited to those of the biosynthesized materials. We use a high-efficiency, cost-effective approach to chemical synthesis that allows production of novel rhamnolipids whose properties can be tailored through control of molecular structure. Here, characterization of a series of monorhamnolipids whose combination of tail lengths is selected to vary the molecular shape from cylindrical to conical is described; Rha-C14-C14, Rha-C14-C12, Rha-C14-C10, Rha-C14-C8, and Rha-C14-C6 have been prepared and studied. In contrast to the expected monotonic change in surfactant properties (e.g. CMC, minimum surface tension, micelle aggregation number) with shape, minima (or maxima) in these metrics are observed across this series of molecules indicating a complex interplay of multiple variables that dictate surfactant properties. These results demonstrate the power of molecular design and chemical synthesis for harnessing the potential of rhamnolipid surfactants.

Scaling Up Rhamnolipid Production: Comparison of Flask, Bench, Pilot, and Demo Scale Fermentations. D. Derr, N. Lohitharn, R. Mirani, and P. Tedrick, Logos Technologies, USA.

Rhamnolipids (RL's) are a promising class of biosurfactants that have achieved only limited commercial success to date. At pH's above their pKa, RL's are anionic surfactants made up of rhamnose

sugar units and medium chain length 3-hydroxy fatty acids. A terminal carboxylic acid provides the anionic functionality. RL's can be produced in a fermentation process using bacteria that excrete the product. This allows straightforward product isolation after fermentation is complete. Two reasons commonly given for RL's lack of commercial success are (1) high cost of production and (2) difficulty in scaling up production processes from the flask scale to commercially relevant scales. In this talk we will briefly discuss a simple, inexpensive method to produce rhamnolipids and then show results from that process at several scales. First we will discuss transitioning from flask scale into small, 1 L working volume, fermenters. This is the barrier that is often hardest to cross in fermentation processes, and we do show a decrease in production metrics. However, as fermentation volume increases, to 2 L, and then 15 L working volume, metrics improve again, and are commercially viable. Expansion to 300 L scale will also be discussed.

Use of Bioenhancers to Improve Growth and Product Quality of Biosurfactants. R. Sharma and B.P. Lamsal, Iowa State University, USA.

Biosurfactants produced through bacterial fermentation have been grown on a variety of sugars and carbohydrate sources. The titers for products formed, however are limited due to inefficient utilization of sugars and nutrients in the media. In this study we aim to study the effect of two bio-enhancers, a) Baclyte© and b) norepinephrine for heightened growth for two well-known biosurfactants: surfactin and rhamnolipids. Baclyte©, a proprietary growth enhancer for gram positive *Bacillus subtilis*, has shown to significantly increase growth with glucose as the main source of carbon in the media. Norepinephrine has also shown to increase the growth of rhamnolipid producing *Pseudomonas aeruginosa* through increased quorum sensing among populations of the bacterium in a glucose rich environment. We have designed bioscreen scale optimization studies for different combinations of sugar and these two bioenhancers for each bacterial strain to test for highest bacterial growth and product formation.The study includes combinations of glucose, sugars mimicking cellulose compositions in biomasses, biomass hydrolyzates at different concentrations (0-5% w/v) in combination with varying concentrations of the two enhancers (0-3% w/v). Initial results for baclyte in combination with glucose for *Bacillus subtilis* have shown accelerated growth and sustained peak absorbance values.

Sophorolipids—The Next Leading Class of Surfactants. D. Kuppert[1], A. Nagy[2], and G. Tian*[2], [1]Evonik Industries AG, Germany, [2]Evonik Corp., USA.

The limited availability of petrochemical feedstock for surfactants demands a change to sustainable raw materials. Mother Nature provides a plethora of renewable and vegetable-based raw materials like carbohydrates or vegetable oils, which are excellent starting materials for biosurfactants. Sophorolipids, a group of biosurfactants with an unique and sophisticated structural composition, are capable of replacing petrochemically based surfactants. There is a need to produce high quality sophorolipids at reasonable costs.

We have been working on an effective fermentation process including down-stream processing to make sophorolipids available on an industrial scale. In this process, sophorolipids are made by a biological process using yeast with a high carbon uptake. They have an excellent toxicological and eco toxicological profile and are completely biodegradable. Moreover, sophorolipids are very gentle to human skin. All three aspects are excellent prerequisites for their usage in typical household care cleaning applications, such as hand dish wash liquids, hard surface cleaners or degreasers. It has been demonstrated that the switch from chemically made surfactants to sophorolipids in such formulation is possible without the loss of performance. Even superior application properties can be achieved with sophorolipids.

Biosurfactants as a Tool for Metal Removal from Waste Effluents. D.E. Hogan, J.E. Pemberton, and R.M. Maier, University of Arizona, USA.

Mining and industrial effluents contain valuable elements at very low concentrations. We are investigating the potential for use of the biosurfactant rhamnolipid produced by *P. aeruginosa* for the recovery of these metals. To determine the conditional stability constants for natural and synthetic monorhamnolipid with a variety of elements, a resin-based ion exchange method paired with inductively coupled plasma optical emission spectrometry was used. Of the metals tested, rare earth elements have the greatest stability constants with natural rhamnolipid. The conditional stability constant sequence for 25 metals tested (from strongest, log K = 9.77, to weakest,

0.96) is Eu^{3+} > Nd^{3+} > Tb^{3+} > La^{3+} > Al^{3+} > Cu^{2+} > Pb^{2+} > Y^{3+} > Pr^{3+} > Dy^{3+} > Lu^{3+} > Cd^{2+} > In^{3+} > Zn^{2+} > Fe^{3+} > Hg^{2+} > Ca^{2+} > Sr^{2+} > Co^{2+} > Ni^{2+} > Cs^{+} > Ba^{2+} > Mn^{2+} > Mg^{2+} > K^{+}. Data showed rhamnolipid selectively removes metals with high log K values over those with low values. Four synthetic rhamnolipid diastereomers were studied for effect of molecular orientation on metal interactions. Different arrangements at rhamnolipid's two stereocenters affected the log K values for Pb and Cd relative to natural rhamnolipid.

S&D 4.1: General Surfactants and Detergents

Chairs: G. Dado, Stepan Co., USA; and R. Zehr, Church & Dwight Co. Inc., USA

Reference Framework to Measure the Characteristic Curvature (Cc) Of Alkyl Ethoxylate Nonionic Surfactants. S. Zarate Muñoz, F. Texeira, K. Myint, J. Minchom, and E.J. Acosta, University of Toronto, Canada.

This work introduces a reference framework for measuring the characteristic curvature (Cc) of commercial alkyl ethoxylate nonionic surfactants using phase inversion scans with mixtures of test and reference surfactants Dehydol O5® (C9E4.5), Novel® 810FD-5 (C9E5), and Novel® TDA-6 (C13E6), that undergo rapid phase inversions with a variety of oils with equivalent alkane carbon numbers (*EACN*) from 3-16, and water at different electrolyte concentrations and temperatures. The Cc of the reference surfactants was determined from the optimum salinities *(S*)* obtained from an emulsion stability method, and from solubilization parameter curves. The calibrated Cc of the reference surfactants was used afterwards to measure the Cc of various commercial alkyl ethoxylate surfactants. This reference framework provided reproducible values with an average standard deviation from ±0.1 Cc units to 25% of the mean Cc value. It was determined that using the nominal structure of a commercial sample to calculate its Cc may lead to inaccurate predictions of nonionic microemulsion phase behavior likely due to the polydispersity of polyoxyethylene surfactant chains; consequently, the Cc of commercial nonionic surfactants needs to be measured. The reference framework introduced in this work provides rapid and simple measurements to accurately determine the Cc of nonionic surfactants.

Synthesis of Sugar-fatty Acid Ester Surfactants and Their Emulsion Properties. K. Ren and B.P. Lamsal, Iowa State University, USA.

Sugar-fatty acids esters are surfactants that can reduce surface tension between hydrophobic phase and hydrophilic phase and could have applications in food, detergent and pharmacy industries. Synthesis of glucose palmitate and lactose palmitate with immobilized lipase from *Candida antarctica* was optimized. Palmitic acid (PA) and glucose at four ratios (3:1, 2:1, 1:1 and 1:3) underwent esterification reaction by the lipase in the solvent mix dimethyl sulfoxide (DMSO, 20% v/v) and 2-methyl-2-butanol (2M2B, 80% v/v) at 55°C. The ratio of 3:1 achieved the highest PA conversion of 92.55%. The esterification of PA was verified by nuclear magnetic resonance test at the C6 position of glucose. The lowest conversion were from the ratio of 1:1 and 1:3, with similar value of 55%. Lactose was esterified with PA in acetone and ethanol rather than the DMSO-2M2B system. Lactose was also esterified with hexonic acid in 2M2B, with lower conversion. The esters can be purified with water and methanol that dissolve sugar and fatty acid residue, respectively. These esters will be applied to oil-in-water emulsion to study the emulsion stability, activity and droplet size distribution.

Alkyl Propoxylate Ethoxylate Sulfate Extended Surfactants: The Effect of Functional Groups on Characteristic Curvature. T. Nguyen and G. Trahan, Sasol Performance Chemicals, USA.

This research focuses on characterizing alkyl propoxylate ethoxylate (PO-EO) sulfate extended surfactants. The characteristic curvatures of these surfactants are determined based on the hydrophilic/lipophilic deviation (HLD) concept. Alkyl PO-EO sulfates are made up of different alcohol structures with different numbers of PO and EO units in there molecules. The effect of each function group (alcohol structure and numbers of PO and EO units) on the characteristic curvature value is going to be evaluated. The finding of these effects will be useful in designing surfactant molecules that are desirable in chemical EOR formulations at different temperature and salinity conditions.

Properties and Applications of High Mole Ethoxylates. T. Weemes, Sasol Performance Chemicals, USA.

This project is focusing on characterizing the properties of high mole alcohol ethoxylate surfactants (up to 150 moles of EO). Based on their properties, high mole alcohol ethoxylates are potential candidates for institutional and industrial cleaning formulations and oilfield applications.

The Hydrophilic Lipophilic Difference (HLD) and the Cloud Point Phenomena. S. Zarate Muñoz and E.J. Acosta, University of Toronto, Canada.

The Hydrophilic-Lipophilic Difference (HLD) has been used to predict the phase inversion point of surfactant-oil-water (SOW) systems. Moreover, the characteristic curvature (Cc) in the HLD quantifies the hydrophilic-lipophilic character of a surfactant.

Alternatively, the cloud point (CP) shows the phase inversion point of surfactant-water (SW) systems, indicating the hydrophobicity of nonionic surfactants. The purpose of this work is to determine if there is a relationship between the HLD and the CP phenomena, and to examine if the HLD can be used to predict the CP. The HLD framework was able to predict the cloud points of pure surfactants with EO units =10 using an apparent equivalent alkane carbon number (EACN) to represent the hydrophobicity of the micelle core and the effect of salt on the CP; however, it failed to predict the CP of commercial nonionic surfactants. It was hypothesized that the presence of more hydrophobic components in polydisperse commercial nonionic surfactants dominates the CP. A separation method was implemented to remove these components in the commercial samples and recover the CP of the main surfactant present in the system. The CP of the treated surfactants was close to that expected of the pure surfactant with the same Cc.

Amic Acids as Leave-behind Surface Treatments: Substantive Materials Compatible with a Wide Range of Formulations Enhance Soil Release. A. Hudson, J. Glover*, R. Klare, and J. Steffens, Surface Chemists of Florida, USA.

Surfaces modified with polymeric or monomeric amic acids that comprise one or more tertiary amine functional groups are shown to be hydrophilic, resulting in enhanced oily soil repellency. Using contact angle and bespoke soil release test methods, we demonstrate that the proposed amic acid candidates are effective at promoting oily soil release and are also substantive, water soluble, stable over a wide pH range, and compatible with ionic and nonionic surfactants. Additionally, corrosion inhibition effects are demonstrated. These characteristics make them attractive as additives for cleaning formulations. Due to their favorable economics and ease of production, these chemistries should prove useful in a number of formulations for both consumer and I&I formulations.

Are Bicontinuous Microemulsions Uniform in Their Structure and Composition? D.G. Hayes[1], R. Ye[1], S.V. Pingali[2], and V. Urban[2], [1]University of Tennessee, USA, [2]Oak Ridge National Laboratory, USA.

Winsor-III systems, consisting of bicontinuous microemulsions (BmEs) in equilibrium with water and oil "excess" phases, have many useful applications: enhanced oil recovery, drug delivery, and hosting of chemical reactions, separations, and nanoparticle synthesis. It is generally believed that the subphases of Winsor microemulsion systems are uniform in structure. Surprisingly, when we analyzed the BmE phase of a Winsor-III system formed by Water/Aerosol-OT/CK-2,13 9 cyclic ketal alkyl ethoxylate)/Heptane using small-angle neutron scattering (SANS), we found major changes in SANS-derived parameters in the vertical direction. As one travels in the BmE phase in the upward direction, we found the quasi-periodic repeat distance and correlation length increased, and the surface area of surfactant per volume decreased, suggesting changes in nanostructure and composition. These results may shed light on the formation process for Winsor-III system, leading to improved performance.

Properties and Applications of Low Molecular Weight Ethoxylates. T. Weemes, Sasol Performance Chemicals, USA.

This research focuses on characterizing the physical and chemical properties of low molecular weight alcohol ethoxylate surfactants. Based on their properties, the application of these surfactants in hard surface cleaning and agrochemical formulations is evaluated.

Properties of Novel Bio-inspired Glycolipid Surfactants: Tailoring Function by Disaccharide Headgroup and Alkyl Tail Length. L.L. Kegel, L. Szabo, R. Polt, and J.E. Pemberton, University of Arizona, United States.

Glycolipid surfactants, comprised of sugar headgroups and lipid tails, offer high biodegradability and low toxicity while maintaining excellent surfactant performance. Their potential as greener alternatives to commonly used surfactants requires systematic study of the structure-function relationship of various glycolipid surfactants. This type of study has been precluded previously by costly and difficult synthesis; however, recent advancements in facile synthesis of highly pure glycolipid surfactants enable the analysis of a diverse set of glycolipids. This paper investigates the solution phase properties of two suites of glycolipid surfactants, O-n-alkylmelibiosides and O-n-alkylcellobiosides, which are composed of melibiose or cellobiose headgroups and varying straight-chain alkyl tails of 8-12 carbons. Surface tensiometry shows CMC values of 0.1-40mM and molecular areas of 48-70 $Å^2$/molecule. Dynamic light scattering documents multiple aggregate populations with a predominant micelle population of R_h ~2nm with an

aggregation number of 50-100 by fluorescence spectroscopy. The comparatively larger headgroup size of melibiose and greater hydrophobicity and tail length of longer alkyl chains greatly affect the principal surfactant properties.

Physico-chemical Understanding of the Synthesis of Partial Glycerol and Diglycerol Esters of Undecylenic Acid. R. Valentin, G. Nyame Mendendy Boussambe, and Z. Mouloungui, Université de Toulouse, France.

If some partial esters properties and synthesis methods were demonstrated since 1960s by several research groups, few studies were carried up on partial esters of undecylenic acid.

Here, physico-chemical methods were crossed to understand how the physico-chemical contribution of the partial glycerol esters of undecylenic acid (PDEU) and partial diglycerol esters of undecylenic (PDGEU) acid influence their reactivity during the physico-chemically complex reaction of esterification.

Reconstitutions of reaction media were studied by calorimetry (DSC) coupled with polarized light microscopy. This highlights how the reactants and partial esters are able to freeze the produced water by hydrogel forming during the esterification reaction. On the other hand, surface tension analysis and cryo-TEM microscopy demonstrated that PGEU and PDGEU were able to decrease the surface tension of the air/water interface by self-organizing in “hydrogel like” nano-objects. Over a critical aggregation concentration, depending on the polar head, glycerol or diglycerol, PGEUs are self-assembled in 200nm vesicles whereas PDGEUs formed 100-200nm plate and ovoid aggregates. PUEGs and PUEDGs can be called solvo-surfactants. They can act as emulsifier or gelling agent depending on the temperature and composition of the reaction medium.

S&D 5: Surfactant Manufacture, Processing, and Sustainability

Chairs: M. Williams, Air Products & Chemicals Inc., USA; and J.E. Pemberton, University of Arizona, USA

"Wash and Go" Approach: Chemical Modification of Biopolymers for Green Surfactants. C. Stevens, E. Delbeke, S. Mincke, and K. Van Geem, Ghent University, Belgium.

With the limited reserves of fossil fuels, the development of chemicals and materials from renewable resources stays an important topic for the future. However, the sustainability of the production methods for renewable based materials is a key aspect and needs to follow the "benign by design"-principle. Therefore, it is advantageous to exploit the enzymatic power of plants to provide quite complicated architectures that can be turned into green surfactants by a minimal chemical modification.

Inulin, a fructose-based biopolymer isolated from chicory root, can be modified by a one-step approach to a renewable emulsion stabilizer. The developed molecules are actually on the market for applications in the cosmetic sector.

Sophorolipids are produced by the yeast Starmerella bombicola from renewable resources through fermentation. Despite their tensioactive properties, application of the sophorolipids in the detergent sector is limited because they are not competitive with synthetic surfactants in terms of production cost. Therefore, it is desirable to look for other application areas which are economically more feasible and where chemical modification can be applied to extend the limited set of microbial derivatives. Interesting properties have been obtained from these modified sophorolipid derivatives.

Phase Behavior Study of Sugar-based Surfactants *α*-Glucoside, *β*-glucoside, *α*-maltoside and *β*-maltoside, and Their Applications in Enhanced Oil Recovery (EOR). Y. Wu and F. Fournier, Kemira, USA.

Surfactants have been used in chemical enhanced oil recovery (EOR) such as micellar flood, foam flood and ASP flood for many years. Most of them are ethoxylated sulfates/sulfonates and alcohols with various hydrophobic chains and not readily biodegradable. Therefore, biodegradable surfactants play a key role to achieve long-term sustainability for oil/gas industries, particularly for chemical EOR technologies. Alkyl polyglucosides (APG) are exclusively made on the basis of renewable and vegetable raw materials. APGs are particularly suited for new formulation concepts with excellent ecological and interfacial properties. They display synergistic effects with conventional surfactants in reducing interfacial tension (IFT) at oil/water interface.

Nowadays, environmental concerns are getting more and more attention from oil/gas industry and community. APG can be directly synthesized from glucose and fatty alcohol at commercial scale. This paper presents our study of the phase behavior of several commercial sugar-based surfactants and their applications in chemical EOR. To correlate molecular structure and phase behavior, some purified samples such as *α*-glucoside, *β*-glucoside, *α*-maltoside and *β*-maltoside were also used.

Renewable Chemicals on the Horizon for Surfactant and Personal Care Applications. P. Foley, P2 Science, Inc., USA.

In recent years technological breakthroughs and innovations have broadened the scope of renewable starting materials available to surfactant manufacturers and formulators. Through the use of new chemistries - both traditional and biotechnological - oleochemicals and terpenes are finding new uses in surfactant and personal care applications. Highlighted will be an overview of these trends, as well as an introduction to the work being done by P2 Science in collaboration with industry partners.

Choline-based Surfactants. W. Kunz, University of Regensburg, Germany.

Current charged surfactants usually have chain-lengths of C12-C14. One of the reasons is that longer chain surfactants are insoluble in water, at least at ambient temperature. In Europe and Asia most of the surfactants are derived from plant oils. However, European plant oils, such as sunflower oils, contain essentially long-chain fatty acids (mostly C18) and therefore are not suitable for surfactant production.

However, the solubility of long-chain carboxylates in water at low temperatures can be significantly enhanced when replacing the usual counter-ions (Na^+, K^+) by others that hinder crystallisation. Based on our expertise on specific ion effects we found that especially choline is a very good candidate. It is a natural cation, even admitted in food additives. It significantly lowers the Krafft temperature both of alkylcarboxylates and alkylsulphates. Further to the now possible design of

new long-chain detergents, several other applications can be envisaged. For example, we found that choline soaps combined with another food additive can be dissolved in water even at neutral and slightly acidic pH.

Short-chain choline soaps may also find some application, they are liquid at room temperature. For example, natural bioesters, such as suberin (from cork) can be dissolved in them.

Finally, I will mention that we formulated a completely green concentrated microemulsion that is fully water dilutable without any phase transfer or demixing during dilution.

S&D 5.1/EAT 5.1: Emulsions and Foams

Chairs: E.J. Acosta, University of Toronto, Canada; and T. Tokle, Kalsec Inc., USA

Enhancing the Bioavailability of Lipophilic Nutraceuticals in Fruits and Vegetables: Excipient Food Design. D.J. McClements[1,2], [1]University of Massachusetts Amherst, USA, [2]King Abdulaziz University, Saudi Arabia.

The oral bioavailability of many lipophilic nutraceuticals in fresh and processed fruits and vegetables is limited due to various physiochemical and physiological mechanisms: poor release from food matrices; low solubility in gastrointestinal fluids; metabolism or chemical transformation within the gastrointestinal tract; low epithelium cell permeability. The bioavailability of these nutraceuticals can be improved by controlling their release, solubilization, transport, metabolism, and absorption within the gastrointestinal tract. This presentation discusses the impact of food composition and structure on oral bioavailability, and how this knowledge can be used to design *excipient foods* for improving the oral bioavailability of lipophilic nutraceuticals. The composition and structure of excipient foods is specifically designed to promote the bioavailability of co-ingested nutraceuticals.

Beverage Emulsions. Y. Fang, PepsiCo Research and Development, USA.

Beverage emulsions are typically oil in water emulsions and the oil phase consists largely of essential oil. The emulsions provide two important characteristic to the final product, first is flavor and secondly, it gives the beverage a cloudy appearance. It is possible to separate the flavor emulsion and the cloud emulsion, the latter can be made of an oil that is mostly neutral in flavor contribution such as vegetable oils or medium chain triglycerides. This paper highlights some of the unique challenges in beverage emulsions, and the role of the different components in the oil phase.

Emulsions Stabilized by Edible Colloidal Particles. C.C. Berton-Carabin and K. Schroën, Wageningen University, The Netherlands.

The ability of colloidal solid particles to physically stabilize emulsions has been known since the pioneering work of Ramsden and Pickering in the 1900's, but substantial interest in this area has been rising only recently. Regarding food applications, studies on food-grade Pickering emulsions are still scarce, yet definitely represent a growing research field.

The present work gives an overview of the latest trends in food-grade particles for emulsion stabilization, including our own results. In particular, different kinds of edible particles that have been successfully applied for this purpose (e.g., starch granules, chitin nanocrystals, solid lipid nanoparticles) are presented. Special attention is given to manufacturing strategies for the particles, including chemical modifications to induce dual wettability by oil and water, which is required for effective stabilization. The potential advantages of using particles rather than conventional food emulsifiers in terms of emulsion performance are discussed.

Finally, the challenges that have to be faced for the development of food-grade Pickering emulsions are addressed, including the acceptability of nanoparticles in foods, the prediction of the particle stabilizing efficiency, and the possible changes undergone by particles post-adsorption.

HLD-NAC Guided Formulation of Self Micro Emulsifying Delivery System (SMEDS). M. Nouraei* and E.J. Acosta, University of Toronto, Canada.

Self micro emulsifying delivery systems (SMEDS) are among promising lipid- based delivery systems that enhance the solubility and the bioavailability of lipophilic active ingredients. Conventional SMEDS are composed of oil, surfactant(s) and co-surfactant/co-solvents. Linker-based lecithin SMEDS are a novel approach in formulating biocompatible SMEDS. The objectives of this work were to calculate the characteristic curvature (Cc) of the SMEDS surfactant/linkers by employing the HLD-NAC equation of state and examine the use of HLD to predict the phase behavior of the SMEDS with changes in surfactant linker ratio. The phase behavior of several combinations of ethyl caprate (a food grade fatty acid ester) as oil, lecithin as the main surfactant, glycerol mono-oletae as lipophilic linker and polyglycerol-6-caprylate as hydrophilic linker was investigated, guided by ternary phase diagram.

For the first time, the HLD approach was applied to characterize the properties of the linker -based SMEDS using formulation scanning technique. The results showed the presence of a wide area of single phase fully dilutable system when exposed to

simulated intestinal fluid (FeSSIF). With an increase in lipophilic linker to surfactant ratio, as predicted by HLD, the 2-phase region decreases. However, this was accompanied by an increase in the area covered by the liquid crystal region.

Transport of Self-emulsifying Systems Through Unsaturated Porous Media. A. Stammitti and E.J. Acosta*, University of Toronto, Canada.

Emulsified oil transport through porous media is important for many applications, particularly for enhanced oil recovery. Previous work focused on developing surfactant formulations that display ultralow interfacial tension (IFT) to facilitate the emulsification/mobilization of oil from reservoirs. However, little attention has been paid to wettability changes or drop-solid interactions. In this work, two sets of formulations were prepared using toluene and Heptol (heptane-toluene) as oil phases, and SDHS surfactant with varying NaCl concentrations as aqueous phase. These systems were characterized by IFT, emulsion stability and solid-liquid-liquid contact angle (CA) on glass. Results show that as the formulation approach the phase inversion point, the surface tends to be equally wet by the aqueous and the oil phase. Combined flooding–imbibition experiments were performed on initially empty dry-packed sand columns, and the total oil recovered after 24hour imbibition was measured. For both oils, minimum recovery was observed at conditions that produce maximum emulsion stability. Conversely, maximum recovery was obtained with formulations that produce minimum emulsion stability. These observations will be discussed in light of the potential drop-solid interactions that are neglected in the transport of emulsions through porous media.

Methods to Predict Emulsion Formation and Stability: A Map to the Land of Emulsions. E.J. Acosta, University of Toronto, Canada.

The objective of this presentation is to review the spectrum of approaches used to understand the formation and estability of emulsions, and the guidelines to select the applicable model to a specific set of conditions.

On the aspect of the formation of emulsions, the concept of shear vs. inertia-controlled emulsification will be discussed, and the characteristic numbers that can be used to define these processes. A new concept of film emulsification will be briefly described. Emulsion stability will first be discussed in terms of processes of creaming/sedimentation, and coalescence. We will discuss the different resistance terms that apply in different cases, and the role that polymers, particles and surfactants can play in emulsion stabilization. Potential misconceptions around the role of Ostwald Ripening mechanisms, particularly for nanoemulsion stability predictions will be discussed.

S&D-P: Surfactants and Detergents Poster Session

Chair: M. Wint, Amway Corp., USA

1. **Cleaning Methods for Enhance the Removal of Starchy Soils in the Food Industry.** E. Jurado-Alameda, J.M. Vicaria, O. Herrera-Márquez, and A. Del Valle Chacón, University of Granada, Spain.

Removing dried starch encrusted in industrial facilities is especially difficult during CIP cleaning processes. We present a method for evaluate the detersive performance of cleaning formulations, using starch as a soiling agent. Furthermore, we introduce a cleaning method for improve the detergency of dried starchy soils in metallic surfaces by using a direct current.

The Bath-Substrate-Flow (BSF) device simulates a CIP system. Washing tests are carried out studying the detersive performance of cleaning solutions and modifying operation parameters such as temperature, time and flow rate. Moreover, the proposed experimental device for the cleaning of dried starch is based on the connection of the dirty metallic surface to the negative pole of a direct current source, being the surface in contact with an alkaline solution. Different experimental conditions (temperature, time and pH of the washing solution) were tested.

Detergency results in BSF device are high for wet starch, reaching 76%. Nevertheless, when using dried starch the detergency is only 32% in identical conditions. Cleaning of dried starch has been optimized applying direct current. Optimal washing conditions (68% of detergency) were found at 20°C with an applied voltage of 5V during 20min. Washing performance increases up to 28% with the addition of 1g/L of surfactants (APG and LAS).

2. **Biodegradation and Toxicity of Synthetic and Natural Monorhamnolipids.** F. Tian, D.E. Hogan, J.E. Pemberton, and R.M. Maier, University of Arizona, USA.

Rhamnolipids produced naturally by *P. aeruginosa* are only as the R,R diastereomers. We are exploring synthetic pathways for rhamnolipids that have improved yield over biosynthesis. One difference is that synthetic rhamnolipids are a mixture of the 4 possible diastereomers: R,R; R,S; S,R; and S,S. Therefore, it is important to understand both the biodegradability and toxicity of the diastereomers. In EPA Biodegradability test, CO_2 evolution is measured using a starting substrate concentration of 400 mg/L and an aerated sewage sludge inoculum. Results show that the natural and synthetic rhamnolipid were biodegraded in the order: TB (75.9%), TT and BT (60%), and BB (52.2%). These results could be compared to 100% biodegradation for the natural rhamnolipid and 86% biodegradation for the synthetic diastereomer mix. The Microtox© assay was used to determine toxicity. The effective concentration 50 of the four individual diastereomers, a racemic mix of diastereomers, and the natural rhamnolipid ranged from 33-144 um. The order of toxicity is BB 33 um > BT 38 um > racemic Mix 39 um > natural 44 um > TT 54 um > TB 144 um. TB was the least toxic of the treatments. In summary, the synthetic diastereomers were less biodegradable but met the EPA ready biodegradability criteria with the exception of the BB diastereomer. Toxicity correlated closely with the biodegradation results.

3. **Enhancement of Heavy Oil Biodegradation by Double-chain Cleavable Surfactants Bearing Sucrose.** D. Ono[1], Y. Nishida[2], T. Numata[2], M. Minamitani[2], S. Kawano[1], H. Sato[1], M. Shizuma[1], and A. Masuyama[2], [1]Osaka Municipal Technical Research Institute, Japan, [2]Osaka Institute of Technology, Japan.

The marine pollution with the oil spill becomes the big environmental problem. It is thought that the oil spill treatment agent may cause second pollution. Therefore, the development of the oil spill treatment agent with good biodegradability has become desired. We have reported that the preparation and properties of a series of acid- and alkali-cleavable surfactants and clarified that the biodegradability of these surfactants was almost the same as or higher than that of the corresponding conventional surfactants. On the other hand, it is known that gemini surfactants have much higher solubility in water, smaller cmc and lower surface tension at cmc than the corresponding surfactants having one lipophilic part and one hydrophilic group in the molecule. In this work, double-chain cleavable surfactants bearing a sucrose were prepared from diethyl tartrate without any expensive reagents or special equipment. We clarified that they have good surface-active properties in artificial seawater. The biodegradabilities of these cleavable surfactants

after 28 days are more than 60 % according to the guidelines based upon the OECD 301C with activated sludge. They were able to improve biodegradability of the heavy oil with a commercial product equally.

4. **SEM Survey on the Effects of Some Nonionic Surfactants on Epicuticular Structure of *Lemna minor* L.** G. Yilmaz and H. Akbas, Trakya University, Turkey.

Surfactants are widely used in household cleaning detergents, personal care products, textiles, paints, polymers, pesticide formulations, pharmaceuticals, mining, oil recovery and pulp and paper industries. This study describes the effects of nonionic compounds on a common and widespread aquatic vascular plant, *Lemna minor*.

The mechanism of phytotoxicity of surfactants is poorly understood on penetrating plant tissues. Because of that in this study nonionic surfactants Brij 35, Brij 76, Triton-X-100 and Triton-X-405 were added 1% and 0.5% concentrations with 5 ml to the 25 ml tap water in each Petri dishes in laboratory conditions. *Lemna minor* plants were treated with these surfactants for 72 hours.

As a result phytotoxic effects of Triton–X-100 and Triton–X-405 were seen on epicuticular surface more than the effects of Brij 35 and Brij 76. Phytotoxic effects were determined by scanning electron microscope on the epicuticular structure of leaves of *Lemna minor* L. It was determined that high doses of Triton-X-100 and Triton-X-405 made cuticular shrinks on cuticula as given in SEM micrographs.

The result is important, because it shows us some nonionic surfactants make water and soil pollution and make phytotoxic effects on epicuticular structure of plants.

5. **Fluorescent Whitening Agents in Laundry.** K. Gutowski and A. Taneja*, BASF Corp., USA.

Optical brighteners also known as Fluorescence whitening agents (FWA) have been used in the laundry industry for a long time now and it is very well known that they improve the brightness/whiteness of washed white fabrics over a wide range of temperatures. However it is not very well known the various conditions that influence the performance on these FWAs. With the industry moving towards cold water detergency, the importance of incorporating FWA in detergents is even more relevant and we want to use this opportunity to dive a little deeper into this topic and discuss various factors that impact the performance of FWAs.

6. **Novel Color Washfastness—Polyacrylamidopropyl Trimonium Chloride Polymers for Color in Care Laundry Detergents.** T. Crutcher, R. Rigoletto, and P. Shah, Ashland Specialty Ingredients, Inc., USA.

The number of color care detergents appearing in retail outlets is on the rise. Color washfastness, color care, color protection, and color preservation all are terms used to describe garment color care in the laundry detergent industry. Fabric color care is a strong sector in the micro-marketing and segmentation of laundry detergents vying for the attention of the discerning consumer. Promotional approaches aim to formulate products with broad premium color preservation claims. Color care technologies functionally include dye transfer inhibitors, anti-encrustation agents, color fixative deposition polymers, enzymes, UV protectors, in-situ dying chemistries, and even mild oxidative bleaches. Color washfastness detergents are unique because they emphasize color care and adjuvant cleaning. Today's technical challenge is to optimally preserve garment color over repeated laundry cycles while maintaining efficient cleaning. There persists an unmet need for new and improved technology. The proposed research will disclose the color care benefit of Polyacrylamidopropyl trimonium Chloride (PolyAPTAC) and its structural analogs. Polyacrylamidopropyl trimonium Chloride and its derivatives have been found to minimize color loss upon laundering over multiple cycles. This was quantified both instrumentally such as colorimetry as well as sensorially through panel studies. The research further discusses additional advantages provided by the technology, e.g. dye transfer inhibition, soil dispersion, and improved cleaning. A proposed mechanism of action is described to elucidate this technology. This novel technology with its consumer perceivable benefit will fulfill the development needs of tomorrow's advanced detergent systems.

7. **Activity of Mannanase Detergent Enzyme in Relation to Mixed Micelle Formation of Linear Alkyl Benzene Sulfonate with Linear Ethoxylated Alcohol.** J.D. Seyfert[1,2], F. Pala[1], and J. Evans[2], [1]Battelle, USA, [2]University of Massachusetts, USA.

It is known that anionic surfactants such as linear alkyl benzene sulfonate (LAS) can inhibit enzyme activity in detergent formulations. In the

presence of a non-ionic surfactant, such as an alcohol ethoxylate (AEO) the reduced enzyme activity caused by the LAS is negated. This study evaluates the hypothesis that "free" LAS, i.e. LAS not associated in a micelle, causes the decreased enzyme activity while the incorporation of LAS into mixed micelles LAS:AEO reduces the concentration of free-LAS in solution and its correspondent adverse effect to mannanase activity. The effect of the formation of LAS:AEO mixed micelles on the enzymatic activity of mannanase and the concentration of free-LAS in solutions were studied with a combination of tensiometric, potentiometric and enzymatic assays analyses to provide experimental evidence of the link between mixed surfactant micelle formation, reduced free-LAS concentration and mannanase activity. Results show that the formation of mixed micelles does cause a decrease of free- LAS which allows for normal mannanase activity in the formulated mixture. This study propose a simple equilibrium base model to calculate the concentration of free-LAS activity in a mixed surfactant LAS:AEO solution and predict the extent of an adverse effect of free-LAS to mannanase activity.

8. **The Evolution of Builder and Polymer Systems in Dishwashing Detergents Commercialized in North America and Europe.** F. Pala, J.D. Seyfert, and C. Usher, Battelle, USA.

The builder and polymer systems of home care products commercialized both in North America and in Europe have been the subject of significant innovation in recent years in response to market demands and regulatory requirements. The need for reformulation of automatic dishwashing detergent (ADW), following the U.S. phosphate ban in 2010, posed a new challenge to formulators in search of effective and economic builder alternatives. Similar challenges will be faced by European formulators with the enforcement of phosphate- free ADW formulations commercialized in European Union countries as of January 1, 2017. In addition to phosphate-free regulations, the use of biodegradable anti-redisposition polymers is increasing in eco-friendly formulations as a response to consumer awareness of environmental issues. This paper investigates the compositional evolution of builder systems and the use of anti-redisposition polymers in phosphate-free ADW products commercialized in North America and European Union countries.

9. **Synergistic Effects of Precipitated Silicon Dioxide and Zeolite 4A, for Increased Surfactant Loading.** S. Mohammed and S. Rao, Evonik Corp., USA.

By utilizing various particle chemistries and properties, systems that absorb and contain large quantities of liquid ingredients can be made. Depending on the design of the carrier system, various release profiles are possible. This technology can be incorporated into a variety of products and industries, making it possible to increase active loading and efficacy.

Liquid actives have to be closely controlled within formulations. If the limits of existing systems are exceeded, formulation issues such as caking and poor flow are possible. The lead chemical and physical properties that factor into absorption and flow behaviors were explored.

Blends of silicon dioxide and Zeolite 4A were evaluated as a concept for higher active detergent systems. By increasing the ratio of silica in the blends, a much higher loading can be realized. In addition, powder rheology analysis techniques were employed to confirm and evaluate flow properties. In addition to higher loading levels, there is a positive effect on powder flow parameters.

10. **Synthesis and Surface Activity of β-branched Phosphodiesterquat Gemini Surfactants.** S.V. Patil and A.P. Pratap, Institute of Chemical Technology, India.

Novel *ß*-branched phosphodiesterquat gemini surfactants, *N*,*N*-dimethyl-*N*-alkyl-2-[[hydroxy(alkoxy)phosphinyl]oxy]-alkylammonium referred to as $C_x(-)C_yC_z(+)$, x = 8, 12 and 14, and y = 2 and 3, z = 12, 14 and 16, were synthesized. These surfactants are composed of two non-identical hydrophilic polar heads in which one of the hydrophilic groups is a phosphodiester anion (negative charge) and the other is an ammonium cation (positive charge). These zwitterionic gemini surfactants consists of two hydrocarbon chains, where one is *ß*- branched, differing in length and with an alkyl spacer. The present work describes the approach for synthesis and study of surface active properties of *ß*-branched phosphodiesterquat gemini surfactants for establishing areas of their industrial applications. It was found that these gemini surfactants had better surface tension lowering properties than their conventional counterparts as evident by Wilhelmy plate technique. The efficiency, critical micelle concentration (CMC) in pure water was evaluated as

a function of surfactant concentration by means of surface tension measurement, electrical conductivity (measuring both specific and molar conductivity) and dye micellization. All synthesized surfactants were characterized by IR, ^{1}H NMR, and Mass spectral studies.

11. **Reducing Harshness on Skin of Cleanser Formulations Through Addition of Bio-based and Biodegradable Sodium Polyitaconate.** Y. Durant, I. Morosov, and A. Augustyniak, Itaconix Corp., USA.

Consumer perceptions of product quality and richness in cleansers often depend on the viscosity of the product and the volume of foam generated during use. The higher levels of surfactants added to generate this perception increase the harshness of a formulation by causing tightness, dryness, irritation and even barrier damage to skin. The common use of sodium chloride as a salt to increase viscosity contributes further to skin dryness and formula harshness. Cationic polymers are possible to add for skin conditioning benefits to counteract undesirable effects of surfactants and sodium chloride. Their high cost, formulation incompatibilities and synthetic production can limit their use, especially in the growing market for products with natural ingredients.

Biodegradable and bio-based sodium polyitaconate addresses all of the above issues through its unique multi-functionality.

A cleanser formulation with 3% sodium polyitaconate was prepared and evaluated. This bio-based polymer allowed to reduce surfactant level by 20% at the same time improving the foam volume by 60% as determined by Cylinder Shake Foam Evaluation method.

A sensory panel showed conditioning properties of sodium polyitaconate comparable to those of polyquaternium-10.

Reduction of sodium chloride content by 60% allowed to obtain desired viscosity as measured by Brookfield Viscometer.

Cleanser formulation prepared with 3% sodium polyitaconate addressed harshness of the product on skin while retaining costumer acceptability.