S&D 1: Home Care and Laundry Performance Boosters and New Benefits

Chairs: Michael Williams, Evonik Industries, USA; and Stephen Gross, BASF Corporation, USA

A Rapid Screen to a Dispersion Builder System
Fred Holzhauer*, *Univar USA, USA*

STTP and NTA, long time leaders of the dispersive builder function, have been under regulatory fire for regional and national Phosphate restrictions and CA Prop 65, respectively. CPG giants have developed dispersive polymer laundry systems that compete favorably with those traditional performance benchmarks of the past, especially with laundry. These are high actives systems featuring concentrations higher, dilutions lower, and margins better than many I&I systems. Our I & I colleagues are under as much time and margin pressure as ever, today. A fast, low cost screen to a cost-effective dispersive platform could educate on alternate formulation strategies, and perhaps guide product optimization. Experience shows that laundry swatch tests are faster, more economical, and often repeat better than tiles. Can a laundry swatch test predict best approach surface performance? We're going to give it a go. The presentation will describe the assumptions, formulation layout, reference the ASTM methods employed, highlight challenges, and discuss results, confirmations and conclusions.

Formulating Liquid Detergents with Improved Enzyme Stability
Eric Dodge*[1], and Arjen J. Hoekstra[2], [1]*DuPont Industrial Biosciences, USA;* [2]*DuPont Industrial Biosciences, The Netherlands*

Globally, liquid detergents are becoming the main product format for consumers to do their laundry in automatic washing machines. In North America, liquids have dominated the laundry aisle for many years, and the laundry segment has been complemented more recently by liquid single unit dose products with both formats addressing the consumers' need for convenience. One factor for the growth of liquid detergents has been consistent performance improvements over time. Enzymes contribute to improved performance across consumer relevant soils and enable a more sustainable laundry process by their ability to remove stains at ambient washing temperatures, hereby reducing the need to heat up the wash liquor. Also, enzymes are biodegradable proteins and can be used at low inclusion level as a result of their catalytic action. However, formulating with enzymes in detergents is still a challenging task. Most enzymes lose (catalytic) activity during the shelf life of liquid detergents, especially at elevated storage temperature, due to the destabilizing action of water, surfactants and ingredients such as chelants. Traditionally, formulators have used stabilizing agents such as boric acid, sodium formate and propylene glycol to inhibit protease activity in the liquid detergent, and consequently reduce the activity loss of enzymes during storage. Recently, DuPont has employed its protein engineering capabilities to develop a new generation of enzymes with improved resistance to proteolytic breakdown. This includes a protease that is engineered to remain stable in liquid detergents without the need for additional stabilizers, hereby reducing formulation cost and complexity, and providing a way for detergent brands to deliver robust performance during the shelf life of their liquid detergent.

Cationic Inulin, A Novel Biopolymer for Home and Fabric Care Robert Nolles*, *Cosun Biobased Products, USA*

Introduction Cationic biopolymers are increasingly used in homecare, I&I and personal care formulations. Additionally, thanks to their renewable and biobased character, cationic biopolymers are very suitable for 'greener' formulations, combining performance and sustainability. Cationic inulin is particularly good as (surfactant) deposition enhancer and at hydrophilization of surfaces. Properties As a result of the chemical and physical differences of cationic inulin compared to other cationic biopolymers, it offers improved performance in multiple applications. The reactive inulin backbone allows unique properties like high charge densities and short chain lengths (low Mw), leading to distinguishing benefits like excellent solubility and compatibility as well as low viscosity. These properties enhance the ease of formulation and offer more flexibility. Initial results Application research has shown cationic inulin helps to boost the performance of various home and fabric care formulations. For instance, in ADW detergent the secondary cleaning performance (filming and spotting) increased after the addition of cationic inulin. Furthermore, in laundry detergent improved softness was observed in a panel test after washing tests. Typical dosage levels range from 0.01 to 1.0 wt%. Other areas of interest are hard surface cleaning and hair conditioning. Benefits Benefits that are found:

- High deposition of surfactant at low concentrations.
- Good compatibility with a range of surfactants: no turbidity, particularly with low substituted cationic inulin grades.
- High solubility and low viscosity enable easy formulating (no heating required).
- Excellent performance in various home and fabric care applications: e.g. improved drying in ADW and better softening in fabric care.

Improving Color and Fabric Care in Fabric Softeners David Joiner[1] and Nathan Reese*[2], *[1]Novozymes North America, Inc., USA; [2]Novozymes, USA*

Fabric softener formulators have an ongoing battle between feel, color and care. Cationic surfactants are well utilized to generate a soft fabric feel but have little impact on color loss and fabric care, caused by normal wear and tear. Furthermore, they can reduce the water absorption in towels which is a critical fabric functionality. Recent advancements in enzymatic technology can help maintain the look, feel, color and wettability of fabrics compared to cationic surfactants alone.

Study on the Comfort Created by Fabric Softener Sae Kumagami, Emiko Hashimoto, Eiji Ogura, Yoshiko Ito, and Takahiro Okamoto, *Lion Corporation, Japan*

In addition to smelling fragrant, consumers expect fabric softener to make fabric feel good against the skin. This feeling is known to be an important part of comfortable clothing, along with clothing microclimate and clothing pressure. In this study, we focused on comfortable texture as a value created by fabric softener and studied the relationship between comfortable texture and the physical properties of the fabric. First, we surveyed consumers to identify the factors that make fabrics feel comfortable to consumers. This revealed that in addition to softness, which was already known, smoothness is an important factor. Second, we studied various combinations

of softener ingredients and found that combining a cationic surfactant, the main ingredient in softener, with a specific silicone was effective in making the fabric feel smoother. Third, we evaluated the physical properties of washed fabrics and found an inverse correlation between smooth-feeling fabric and the amount of friction. Finally, we tried on clothing that had been washed with water or two different types of softener and rated the clothing according to various descriptors ("fluffy", "fresh", "seems absorbent", etc.)

New ADW Formulation Opportunities with Improved Polyitaconate Polymers Jim W. Gordon*, *Itaconix, US*

Polyitaconate polymers combine very good chelation properties with anti-scalant properties that are more like high performing polymers. This makes them very suitable for use in ADW where formulators, who have been used to sodium tripolyphosphate, do not have a drop in replacement that meets the required performance and legal requirements across all states. This presentation details the improvements that have been made to the Itaconix ADW polymer range and how it is now possible for formulators to replace sodium citrate, aminopolycarboylates, polymers and phosphonates with one bio based polymer.

High Performing Rinse Aid Surfactant for Plastics
Ashish Taneja*, *BASF Corporation, USA*

Rinse aids are commonly used in auto dishwashing machines as they enable, prevent, and control the formation of spotting and filming on utensils. While considerable work has been reported in industry literature on the effects of rinse aids on glass, stainless steel and ceramic substrates, their effect on plastic substrates has not been widely studied. In this presentation, we will discuss the recent findings in our laboratories on the effects of surfactants on spotting and filming on plastic surfaces when washed and dried under typical institutional cleaning conditions.

Re-thinking Value-tier Formulations— New Technologies to Boost Performance
Ann Lee* and David Joiner, *Novozymes North America, Inc., US*

Stringent value-tier cost targets have forced formulators to continually optimize formulas within tight constraints. Until now, formulators have solely relied on surfactant systems and high pH for cleaning performance. With new innovations in enzymatic technology providing greatly improved stability, high-pH and high-water detergents can be enhanced to further differentiate against the competition and deliver new cleaning benefits to consumers.

S&D 1.1a: New Technologies in Industry

Chairs: Eric (Rick) Theiner, Evonik Industries, USA; and Hongwei Shen, Colgate-Palmolive Co., USA

NINOL® CAA: A Novel Multi-functional Amide for Mass Efficient Formulation
Ron A. Masters, Sarah Kovach, Anatoly Dameshek, Renata Butikas, and Scott Dillavou, *Stepan Company, USA*

NINOL® CAA is a low-HLB natural-oil-based surfactant that brings multi-functional benefits to cleaning products, including foaming, viscosity build, fragrance solubilization, and total actives reduction in anionic-dominant formulas such as foaming car wash, body wash, shampoo, and manual liquid dish/laundry products.

New and Unique Biorenewable Hydrophobes for Surfactants Risha Bond*, *REG Life Sciences , USA*

Recent breakthroughs in biotechnology have produced unique medium- and long-chain hydrophobes functionalized with hydroxyl and alkyl methyl groups that are not practically accessible through traditional synthetic and oleochemical processes. In biobased surfactants, for example, these functionalities provide lower Kraft point and tolerance to electrolytes and therefore higher surface activity compared to traditional fatty acid-derived hydrophobes. These biorenewable surfactants have recently attracted a great deal of attention in their intriguing potential for differentiated high performance, as well as replacing traditional sulfates, sulfonates and phosphate-based surfactants. These new functionalized compounds, by themselves and/or as precursor to a number of anionic, cationic, amphoteric, and non-ionic surfactants, offer potential sustainable and performance enhancements for formulating mild, safe, and natural cosmetic and personal care products. The uniqueness and diversity of these new hydrophobes and their derivatives are envisioned to provide exceptional enhancement in performance—including hard- and cold-water performance, detergency, mildness and synergism in mitigating irritancy—in combination with other surfactants.

Rheology Modifiers in Personal Cleansing Applications: Recent Trends Martin S. Vethamuthu*, *Ashland Specialty Ingredients G.P., USA*

The aim of this work is to present recent advances in polymeric multi-functional rheology modifiers used in surfactant-rich cosmetic products. The suspension stability of formulations depends strongly on the value of the yield stress and zero shear viscosity and is surfactant chassis and target pH dependent. The rheological performance parameters also depend on the composition, namely polymer selected, surfactant types; mix ratio, pH and co- additives. Over structuring formulations will result in unacceptable flow properties and contribute to poor tactile or negative foam sensory ratings during use. The talk highlights key functionalities of a newly introduced commercial acrylates copolymer called SurfaThix™ N, a surfactant-functional technology, and presents wide range of formulation examples to demonstrate versatility and benefits [including simplified processing] across different surfactant chassis and pH range.

A Novel Amphoteric Surfactant for Personal and Home Care Marcie Anne Natale and Neil Boaz, *Eastman, USA*

Abstract not available.

Structure-property Relationships of Co-solvents and Co-surfactants in Microemulsion Formation Using High Throughput Techniques Troy Knight, Neeraj Rohillia*[1], Pramod Patil[1], Carol Mohler[1], Christopher Nelson[1], Tom Kalantar[1], Pete Rozowski[1], and Quoc Nguyen[2], *[1]The Dow Chemical Company, USA; [2]The University of Texas at Austin, USA*

Chemical flooding technologies involving surfactant (SP/ASP) are critical to recover additional oil from mature reservoirs close to residual oil saturation. One of the critical risk factors is formation of highly viscous phases during chemical injection/propagation through the reservoir. Functionalized co-surfactants and co-solvents are known to prevent formation of such high viscosity phases. Moreover, a chemical flooding formulation optimized by the addition of co-surfactants/co-solvents reduces phase trapping of the primary surfactant, which increases the economic viability of the process by reducing primary surfactant dosage. The current work focuses on utilizing high throughput screening methods to generate structure-property relationships governing optimal salinity, type III microemulsion occurrence and stability, and tolerance of phase behavior to divalent ions. The ability of various functionalized co-solvents to reduce viscous emulsions was also investigated using high throughput screening. The high throughput resources at Dow uses state-of-the-art image analysis to observe microemulsion phase behavior and fluidity. The structure-property relationships of co-solvents and co-surfactants were utilized to identify favorable low viscosity microemulsion phase behavior without significant impact on ultra-low IFT and oil solubilization ratios. We will also discuss results from co-solvent screening studies that permitted expansion of the salinity range within which type III microemulsion phase behavior occurred. High throughput screening enabled optimal selection of a co-surfactant/ co-solvent package for a specific oil/brine system at a desired temperature.

S&D 1.1b: Manufacturing, Commercialization and Delivery of Raw Materials and Finished Products

Chairs: Troy Graham, LightBox Laboratories, LLC, USA; and Sukhwan Soontravanich, Ecolab, USA

Phase-stable Surfactant-thickened Formulations at High Caustic Levels Daniela Fritter*, *The Clorox Company, USA*

Elongated mixed surfactant micelles are one of the most common ways to thicken cleaning products, due to their versatility and cost-effectiveness. However, problems occur when the product being thickened has a much higher caustic (and/or oxidant) level such as is sometimes used for drain cleaning, where a thick product is desirable for both pouring control and cling to the walls of the pipe to maximize contact with active ingredient(s). Mixed surfactant blends that work well in cleaners with more moderate caustic (and/or oxidant) levels are pushed over a phase boundary when the latter is added in excess, causing the system to flocculate into a surfactant-rich and a surfactant-poor phase. This phase instability can be corrected for by shifting to a very low charge ratio in the mixed surfactant blend, leading to uniform, monophasic formulations at very high caustic (and/or oxidant) level. For example, compositions containing 2.5–10 wt. % of a hydroxide and 4–12 wt. % of a hypochlorite oxidizing agent can be effectively thickened with a mixed surfactant blend with ratios of charged:uncharged surfactant from about 1:10 to 1:50.

Preservation: Finished Goods and Manufacturing Vidya Ananth and Mrudula Srikanth, *Clorox, USA*

Preservation is a key factor in protecting Household and Industrial (H&I) water-based products/ingredients from microbial spoilage. Microbial spoilage could potentially lead to decreased cleaning efficacy, undesirable aesthetics, pose a human health safety risk, or lead to expensive recalls. All of this could lead to negative publicity causing damage to the brand equity or company. Given the above, the need for finished product preservation becomes critical. Further, the available water content in these products and ingredients is >90% which is an ideal environment for supporting microbial growth. Ingredients such as surfactants, emulsions, fragrances, etc. serve as essential nutrients for microbial growth. Unpreserved or under- preserved formulations/ingredients may be at risk for spoilage. Factors that go into developing good formulations include understanding the quality of ingredients, preservation package used, packaging material and closures used, manufacturing location (and controls including sanitation/industrial hygiene), the intrinsic product parameters such as pH and water activity. Typical criteria for a good preservative are: registration with regulatory agencies, broad spectrum activity, product compatibility, shelf life, safety and toxicology, commercial availability and cost. The landscape of the preservative package is changing and challenging at the same time because many companies are moving towards incorporating natural and sustainable preservatives whose spectrum of activity is not very broad. A review of the preservation landscape for H&I products will

be discussed and a few case studies that highlight the selection criteria and various tradeoffs would be included.

Screening and Scaling Liquid-to-Solid Conversions for Efficient Process Development of Solid Products Steve D. Rowley, *Division by Zero Labs, USA*

With the advances in packaging technology over the last decade, manufacturers have a need to offer chemical products in a solid form that provides superior bulk density, particle size and flowability. Likewise, drying technology has expanded and diversified to accommodate consumer needs and processing needs within the industry. The task of selecting the appropriate drying technology for a novel product can be a time consuming and expensive process involving multiple trials and cost analyses, with each technology having different effects on the bottom line. Here, a basic overview of the foremost drying technologies including spray drying and fluidized bed drying will be given. General principles of efficient drying, the advantages and disadvantages of each technology, and key points to consider while screening technologies from R&D to piloting and production will be discussed.

The Effect of Alcohol Ethoxylate Branching on Dry Mix Powder Flow—Chasing the Ghost Mike Wint*, *Amway Corporation, USA*

Abstract not available.

S&D 2: New Technologies for Cold Water Laundry Detergency

Chairs: Rajan Panandiker, Procter and Gamble Company, USA; and Paul T. Sharko, Shell Global Solutions, Inc., USA

The Fundamentals of Low-Temperature Laundry: Property Control of Grease
Bernhard von Vacano[1], Matthias Kellermeier[2], Juergen G. Tropsch[2], and Keith E. Gutowski[1], *[1]BASF Corporation, USA; [2]BASF SE, Germany*

Food grease and fat removal at low temperatures in household and/or commercial laundry is a well-known and difficult challenge for traditional detergents. The basis for this challenge can be attributed to the physical state of the soils at these temperatures. In cold water, they are often solids or have crystalline structures at the surface and in the bulk and therefore are less susceptible to surfactant action and the traditional mechanisms of detergency and emulsification. This presentation will attempt to address several fundamental questions associated with the properties of grease and grease removal: 1) What is the composition/microstructure of "hard" consumer average grease, 2) What happens during the wash—not only before and after, and 3) How do process conditions and additives influence these interactions? This attempt is supported is several ways, including analytical characterization to understand the importance of crystal modification versus amorphous phase attack, the use of QCM-D as a "nano-washing machine" to probe interactions and temperature effects during the wash with nonionic based detergents, and finally cleaning with microemulsions and the correlation with their solubilization capacities.

Detergent Compositions Containing a Branched Surfactant for Cleaning Laundry in Cold Water
Phillip K. Vinson and Patrick Stenger, *[1]The Procter & Gamble Co., USA*

Changes in fabric trends, rising energy costs, and ecological concerns are driving a change from the once popular warm and hot water washes to washing fabrics in cold water. The need to achieve satisfactory washing results at lower temperatures places a high demand on detergents. Detergent compositions containing 2-alkyl primary alcohol sulfates and alkoxylated sulfates having specific alkyl chain length distributions and/or specific fractions of certain positional isomers are shown to provide increased greasy soil removal in cold water. The physical properties and cleaning performance associated with these materials is discussed.

Detergent Amylases for Cleaning at Low Temperature
Rajenda Kulothungan Sainathan*, *Novozymes South Asia Pvt Ltd, India*

The focus on low temperature washing is getting increased attention all over the world among end consumers and detergent producers. The main drivers in this movement are sustainability and energy savings—as lower wash temperature reduces both the CO2 emission and energy consumption. In parts of the world, low temperature wash has always been used. This fact together with the increased focus from the traditional higher temperature wash parts of the

world, makes development of low temperature enzymes even more relevant. However, a lower temperature in wash affects the final cleaning result and the stain removal performance is decreased in general. This also applies to starch stains, which amylases can remove. A reduced temperature effects both the amylase and the detergent. If no changes are made to the detergent, the amylase should compensate for the reduction in detergent wash performance if same wash performance should be obtained. Recently, short wash cycles have also been introduced to the market—as a sustainability benefit, and as a direct benefit for the end consumer being able to spend less time washing and a cost saver by saving energy. A shorter wash cycle reduces the stain removal performance as well and requires a faster acting amylase. To support the trends in the market, we are therefore developing amylases suited for low temperature and short cycle conditions.

Delivering Effective Bleaching under Low Wash Temperatures Jane Mathews[1], Jenny Wilkinson[1], and Smita Brijmohan*[2], *[1]Lubrizol Corporation, UK; [2]Lubrizol Corporation, USA*

Attaining satisfactory laundry cleaning and hygiene at low wash temperatures is becoming increasingly important for consumers globally. The requirement for detergent ingredients to deliver multifunctional performance when included at low levels in laundry detergents also remains of key importance as detergent become more compact in product form. The introduction of Mykon Cold wash is one such laundry detergent ingredient which is designed to meet the market needs of low temperature washing, particularly for use in the emerging markets and delivers multiple performance benefits when included in formula. Data will be presented to illustrate how this material based on tetraacetylethylene diamine delivers peracetic acid in wash to give both effective stain removal, whiteness maintenance and hygiene at low wash temperatures.

The Effect of Surfactant and Additives on Cold Water Detergency of Semi-solid Soil Parichat Phaodee and David A. Sabatini, *University of Oklahoma, USA*

This work attempts to improve removal efficiency of semi-solid soil below their melting point using a range of extended surfactants along with the introduction of additives. Current thinking is that cold water detergency of semi-solids soil can be achieved by systems that produce a reduction of interfacial tension (IFT) with the soil above the melting point, an improvement of wettability to the soil surface and decreasing melting point of the soil. In this work, coconut oil (melting point is 27.5°C) was used as a model semi-solid soil. C14-15-8PO-SO4Na was the initial surfactant selected to remove the soil from 65/35 polyester/cotton fabric. Intermediate to long-chain alcohols were used as additives. The percentage of coconut oil removal was higher at washing temperature of 20°C than those of 10°C. Optimum salinity (S*) was obtained from dynamic IFT measurement at 30°C. The coconut oil removal using C14-15-8PO-SO4Na at 8% NaCl was relatively poor, whereas the addition of 1-heptanol or 1-octanol in the surfactant formulation without added NaCl further improved coconut oil removal. Interestingly, an additional introduction of optimum NaCl (S*), based on 30°Cmeasurements, in the surfactant formulation with added intermediate-chain alcohols was able to achieve coconut oil removal as high as 95.4±0.2% at 10°C; shorter and longer chain alcohols did not show

the same level of improvement. The improvement of coconut oil removal at low temperatures can possibly be attributed to lowering IFT above melting point, lowering contact angle, and being larger in size of displaced coconut semi-solid particle in the wash solution.

Laundry Detergency of Solid Non–Particulate Soil or Waxy Solids: Effect of Surfactant Type
David A. Sabatini*[1], Jarussri Chanwattanakit[2], John Scamehorn[1], and Sumaeth Chavadej[2], [1]*University of Oklahoma, USA;* [2]*Chulalongkorn University, Thailand*

In this work, methyl palmitate or palmitic acid methyl ester, having a melting point around 30°C, was used as a model of solid non-particulate soil or waxy soil being removed from either a hydrophilic surface (cotton fabric) or a hydrophobic surface (polyester fabric) by using different surfactants: alcohol ethoxylate (EO9), sodium dodecyl sulfate (SDS), methyl ester sulfonate (MES), methyl ester ethoxylate (MEE), and two extended surfactants (C12, ^{1}4-10PO-2EO-SO4Na and C12, ^{1}4-16PO-2EO-SO4Na). The effects of surfactant type and concentration, salinity, washing temperature, and soiling procedure on detergency performance and oil redeposition will be presented. The results showed that the detergency efficiency at a 0.2 wt% surfactant concentration and 5 wt% NaCl concentration gradually increased with increasing washing temperature whereas the oil redeposition exhibited an opposite trend to the oil removal for both above and below the melting point of methyl palmitate on both studied fabrics. The nonionic surfactant (EO9) showed the highest detergency efficiency (73 to 94 %) at any washing temperature especially on the polyester fabric. The conditions resulting in highest detergency below the melting point correspond to those above the melting point. Charge of particles or fabric is not an important detergency mechanism, but steric factors due to surfactant adsorption affects redeposition and soil removal. So, surfactant adsorption leading to good wetting and dispersion stability due to steric forces are shown to be important mechanistic factors in waxy solid detergency. The bulk of detached soil both above and below the melting point is in unsolubilized forms (particles or droplets).

Microbes in Your Laundry: Does Washing on "Cold" Make a Difference?
Darci L. Ferrer*, *American Cleaning Institute, USA*

Microorganisms are around us, on us, and in us; and therefore are transferred to our clothing and other fabrics. When consumers do their laundry, the notion of clean often is aesthetic. Does it smell nice? Has the soil been removed? The hygienic aspect of "clean" often is not considered. Companies, the U.S. government, and non-governmental organizations are encouraging consumers to wash on lower temperatures due to sustainability benefits, such as reducing greenhouse gas emissions. How does washing on "cold" affect microbial load on washed fabrics? This presentation explores whether there is a difference in microbial reduction from washing on "hot" compared to washing on "cold" based on hold wash water temperatures representative of the United States.

Study on Bacteria Flora to Prevent Fabric Odors

Keisuke Mori*, Nanami Sasaki, Takahiro Hayashi, Hiroyuki Masui, and Takahiro Okamoto, *Lion Corporation, Japan*

Consumers are becoming increasingly sensitive to personal hygiene and demand greater odor care in their everyday lives. Much research has been done on odor in the fabric care field in response to this consumer need, and there are now many laundry detergents with hygiene functions in the market. At the same time, technologies to analyze bacteria have become more sophisticated, making it easier to identify bacteria flora using gene-sequence homology comparison. In this study, we focused on bacteria flora on clothes and the odors caused by these bacteria. From the bacteria flora data, we identified which species of bacteria were found with the highest frequency on actual household clothes. We then studied their growth rates under several conditions as well as the relationship between these growth conditions and odor. We found that certain bacteria have a high growth rate under severe conditions such as low nutrition. Moreover, from solid-phase microextraction (SPME) and gas chromatography/mass spectrometry (GC/MS) analysis, we also found that the amount of odor-causing substance generated by specific bacteria increased when the bacteria grew under severe conditions. Using these results, we then explored more effective antibacterial approaches to preventing odor in household clothes.

S&D 3a: Surfactants in Agricultural Applications

Chairs: Michael Tate, Dow Chemical Company, USA; Ryan Totten, Stepan Company, USA; and Dennis Abbeduto, Colonial Chemical Inc., USA

Compatibility Agents for Complex Tank Mix Systems Jacob P. Bell*, Julia A. Sheehan, and Kelly Buchek, *Stepan Company, USA*

In today's agricultural landscape, herbicides and liquid fertilizers are commonly tank mixed to reduce time and money spent on spraying fields. This presents an interesting challenge in the form of chemical and physical incompatibility of the components. Herbicides are typically complex organic compounds formulated as emulsifiable concentrates, wettable powders, solution concentrates as well as others. Liquid fertilizers are high electrolyte systems that vary by pH, salt concentration and analysis which can negatively impact an herbicide spray solution in the form of gels, separation, or flocculation. Compatibility agents are used to correct for incompatibility in mixed systems of fertilizers and herbicides. They can have a number of different chemistries that can act over a broad range solution combinations or for specific combinations. This presentation will examine several compatibility agent chemistries as they pertain to herbicides on the market. It will also present current work to study the performance of phosphate esters as compatibility agents based on chemical structure.

Fundamentals of Multi-Surfactant/Solvent/Water Phase Behavior in Agricultural Applications Using High Throughput Techniques Michael Tate, Laura Havens, Matthew Benedict, Thomas Boomgaard, Jeff Michalowski, Matt Entorf, Romain Britton, and Bethany Karl, *The Dow Chemical Company, USA*

Emulsifiable concentrates (EC) are amongst the most common forms of agricultural active delivery for oil soluble actives, as they combine the benefits of easy transport & storage with ease of use in the field. However, as more complex actives become available and the use of multi-active (new & existing) formulations increase, the need for more complex formulations is increasing. Given the long, regulatory-driven development timeline of active containing formulations in the agricultural market, there is a need to develop innovative EC formulations rapidly. To that end, we have developed a high throughput method to formulate, measure, and analyze the phase behavior of multi-surfactant & solvent formulations, as concentrates containing only surfactant and solvent, and 100X dilutions into water hardnesses of 20, 342, and 1500 ppm. This approach combines a multichannel liquid handler, an imaging station, and a custom image analysis algorithm to accurately identify the phase behavior. Using these techniques, we report the development of a large number of functional phase diagrams for these systems, which are based solely on a new image analysis algorithm that classifies, with 85% accuracy, the observed phase behavior of the dilutions 24 hours after mixing. Classification categories include: clear single phase, uniform emulsion, actively settling, fully sedimented, or observed microemulsion phase. Finally, we report the development of structure/property relationships between the components based upon these results.

Adjuvant Use for Crop Protection Products
Douglas J. Linscott, Madan M. Somasi, Hongyoung Jeon, and Suresh B. Annangudi Palani, *DowAgroSciences, LLC, USA*

Objective Presentation will discuss adjuvant uses in agricultural product formulations with focus on optimizing the expression of an active ingredient's biological activity. Methods Used Discuss approaches and methods employed to characterize spray mixtures to derive solutions that can affect plant coverage and active ingredient uptake. Results Delivery needs vary for different active ingredients depending on their specific chemistries and their physical/chemical properties. Conclusions Surfactants, oils, and other functional material adjuvants are essential additives to optimize the performance of crop protection product formulations.

Structured Surfactants as Rheology Modifiers for Electrolyte Systems Kelly Buchek, Elodie Shaw, and Ryan Totten*, *Stepan Company, USA*

It is well-known that surfactants self-assemble into different phases such as lamellar phase, hexagonal phase or multi-lamellar vesicles. This phenomenon is mainly driven by the surfactant concentration and its chemistry. Our technology consists of the formation of multi-lamellar vesicles by the self-assembly of two carefully chosen surfactants of high and low hydrophilic-lipophilic balance, combined at an optimized ratio in the presence of water. This technology can be used to provide an elastic suspensive media to water-based suspension concentrate (SC) formulations and can also be harnessed to modify the rheology of electrolyte solutions. We believe that it could show superior properties in Agricultural formulations compared to typical thickeners such as Xanthan gum, which fails to incorporate in the presence of concentrated electrolytes. In this presentation, we report on the application of this technology towards thickening liquid nitrogen fertilizer and Glyphosate salts. These high electrolyte thickened systems can support particle suspension, allowing the combination of suspension concentrates and soluble liquid (SL) formulations without the inclusion of xanthan gum or additional compatibility aids in the formulation concentrate. Thickened liquid fertilizers and Glyphosate salts also give the appearance to consumers of a more concentrated product, therefore giving the impression of increased efficacy.

S&D 3b: General Surfactants

Chairs: Robert Coots, Colonial Chemical, USA; and Erika Szekeres, Method, USA

Virtual Detergency Experimentation
Rodrigo J. Olmedo* and Nicolas A. Olmedo, *CONSUMERTEC, Ecuador*

Despite considerable efforts in the last decades more than 75% of laundry R&D are not producing marketable products using conventional physical detergency approaches. There is a high expectancy that new digital strategies change innovation efficiency toward a reduction of product development cost and get products to market faster with high revenue returns. The paper presents a new experimental approach about going digital by asking how to model and simulate spectral radiance from surfaces capable to reach consumer´s eye retina. Based on current understanding of radiative transfer models, fluorescence spectroscopy models and colour appearance model, new virtual lab experiments include virtual test fabrics, virtual machine or hand washing process as well as virtual drying stages, virtual observers under virtual scenarios to get virtual cleanliness, whiteness and color-care perceptions and finally virtual consumer response maps that include perceptual discrimination thresholds. Validation approaches include novel non-contact spectrofluorimetric techniques to collect spectral radiance under actual relevant natural environments as well as magnitude estimation sensory methods. The study moves the digital field forward presenting a collection of algorithms to change for ever the 100+ years old physical detergency approach to research and develop laundry products.

Characteristic Curvature of Ether Carboxylate Surfactants and Contribution of Functional Groups Thu Nguyen and Carla Morgan, *Sasol Performance Chemicals, USA*

The characteristic curvature (Cc) of a surfactant has been demonstrated to be a useful tool in selecting surfactants for chemical EOR formulations. Our previous studies determined the Cc values and the contribution of the functional groups to the Cc values for a series of alkyl propoxy (PO) ethoxy (EO) sulfates and alcohol ethoxylates. However, there has been limited information on the Cc values of alkyl PO-EO carboxylates reported in literatures. The carboxylate surfactants have recently been identified to be used in chemical EOR formulations at high temperature, high salinity conditions due to their thermal stability at high temperature and their high salinity tolerance. The goal of this study, therefore, is to determine the Cc values for a series of carboxylate surfactants and the contribution of the functional groups to the Cc values. Microemulsions of the surfactants with five alkane oils of known equivalent alkane carbon number (EACN) are formulated to determine the optimum salinity and temperature of each surfactant/oil system. The hydrophilic lipophilic deviation (HLD) concept for anionic surfactants is utilized to calculate the Cc values of the surfactants from the optimum salinity and temperature. The contribution of the functional groups (alcohol structure and numbers of PO and EO units) are also evaluated. The finding of this research will serve as a useful guide for selecting existing surfactant molecules or designing new surfactant molecules by

modifying the hyrophilicity/hydrophobicity of the surfactant structures that are desirable for not only chemical EOR formulations but also potentially for other applications.

Thickener for Cationic Disinfectant-based Formulations Grace N. Mahfouz, Smita Brijmohan, Mark Paczkowski, and Chris Belock, *Lubrizol Corporation, USA*

Commercial disinfectant cleaners primarily contain quaternary ammonium surfactants such as benzalkonium chloride and didecyl dimethylammonium chloride. Thickening such formulations for excellent spray and cling properties and a rich appearance upon pouring is challenging. The currently available anionic rheology modifiers are not suitable for this application due to the lack of compatibility with these difficult-to-thicken cationic surfactants. Conventional associative polymers are unable to build viscosity due to their inability to associate with the small micelles of cationic surfactants. Nonionic thickeners such as cellulosics can thicken these formulations but provide a poor spray pattern. With the goal to help deliver maximum antibacterial performance through improved contact time and rich appearance, we have developed a novel hydrophobically modified polyurethane polymer. The unique polymer architecture has been designed to allow for broad formulation compatibility, efficient thickening and stability while maintaining product clarity. The polymer also provides synergistic thickening with certain nonionic surfactants. In this presentation, we will go over the various types of formulations containing cationic disinfectants. We will discuss the effects of polymer dosage, HLB, as well as nonionic surfactant level and type in these formulations. The efficacy of hard surface cleaning formulations for biocidal activity by EN1276 will be highlighted. The testing undertaken to explain the mechanism for improved thickening efficiency with the polymer such as dynamic light scattering and surface tension measurements will also be discussed.

Surface Activity of Plant Oil-based Monomers in Emulsion Copolymerization Kyle Kingsley*[1], Vasylyna Kirianchuk[2], Oleh Shevchuk[1], and Andriy Voronov[1], [1]*North Dakota State University, USA;* [2]*Lviv Polytechnic National University, Ukraine*

In an effort to increase the bio-based content of conventional latexes, acryl amide-functional plant oil-based monomers (POBM's) from olive and soybean oils were copolymerized with conventional petroleum-based vinyl comonomers. The potential surface activity of these monomers, whose structures are similar to surfactants, was studied by measuring micelle aggregation number, particle size and number, and surface tension of surfactant solutions with increasing concentrations of POBM. Using steady-state fluorescence quenching, it was observed that increasing concentrations of POBM at constant surfactant concentration resulted in a reduction of micelle aggregation number. Dynamic light scattering measurements revealed increasing particle size with increasing POBM concentration, whereas the surface tension of these systems decreased with increasing POBM. These results support the hypothesis that POBM's do interact with the surfactant, ultimately impacting factors such as micelle formation and nucleation mechanism within the emulsion copolymerization reaction.

S&D 3.1: Surfactants and Additives in Enhanced Oil Recovery and Oilfield Applications

Chairs: Upali Weerasooriya, University of Texas at Austin, USA / Harcros Chemicals & Ultimate EOR Services, USA; and Jeffrey Harwell, University of Oklahoma, USA

A Novel Microfluidic Platform to Measure Dynamic Interfacial Tensions at Short Time Scales Sachin Goel*[1], Samson Ng[2], Edgar Acosta[3], and Arun Ramchandran[3], [1]*Dept. of Chemical Engineering and Applied Chemistry, University of Toronto, Canada;* [2]*Syncrude Canada Limited, Canada;* [3]*University of Toronto, Canada*

Emulsion-based materials are of tremendous importance in our day-to-day lives and in the industry. In applications such as foods, detergents, and cosmetics, a critical design criterion is a stability of the emulsion over the product shelf life. In other applications, such as oil extraction, emulsions need to be destabilized for ease of separation. The accurate and rapid determination of the interfacial tension is vital for characterizing the formation and stability behavior of emulsions. Unfortunately, the conventional tensiometers such as pendant drop, Du Noüy ring cannot measure the interfacial tension at short time scales (<50sec).

In this study, we introduce a novel microfluidic platform to measure the dynamic interfacial tension at short time scales ranging from a few milliseconds to a few tens of seconds. We have implemented this microfluidic device to characterize interfacial properties of water droplets in a model oil system containing asphaltenes and/or naphthenic acids (the surfactants indigenous to bitumen). These surfactants are known to significantly impact the interfacial tension and stabilize water-in-bitumen emulsions. However, the dynamic interfacial behavior of this system has remained largely unexplored due to its complexity. Our study reveals that the interfacial tension is the result of a complex interplay between asphaltene self-association kinetics and asphaltene-naphthenic acid association kinetics. When asphaltenes and naphthenic acids both are present in the oil phase, the interfacial tension is higher than the cases when only either asphaltenes or naphthenic acids are present, which is counterintuitive. This and other characteristics of this study will be elucidated in the presentation.

Quantiative Crude Oil Demulsification Analysis Using Multiple Light Scattering Matt Vanden Eynden*[1], Christelle Tisserand[2], Yoann Lefeuvre[2], Pascal Bru[2], and Gerard Meunier[2], [1]*Formulaction, Inc., USA;* [2]*Formulaction, France*

Enhanced oil recovery (EOR) is a critical process for maximizing the yield of crude oil obtained from the oil fields. In the case of demulsification procedures, various demulsifiers are used to separate any aqueous matter from the crude oil and the separation kinetics are usually measured with the naked eye with the help of rulers or burettes. Each demulsifier displays different kinetics and needs to be accurately chosen as the oil from different wells can vary greatly in its composition to allow for optimum performance of the procedure and to provide the maximum amount of oil recovery. In this study, we show how five different demulsifiers can be used to observe different phase separation kinetics of a crude oil mixture with the aid of Multiple Light Scattering (MLS). Specifically, a mobile reading head with an incident light source is used to measure the

transmission percentage of the suspension inside of a glass cell with data taken every 20 µm. This technique allows us to accurately and with high resolution observe and quantify phase separation kinetics such as water quality, interface quality, separation speed and volume of water produced all in a one-hour test. This quick test allows for quantitative analysis of each unique oil well and provides the operators a precise amount and type of chemical to use to optimize operation performance.

Novel Surfactants for Chemical Enhanced Oil Recovery Himanshu Sharma[1], Krishna Panthi*[1], Pinaki Ghosh[1], Upali P. Weerasooriya[2], and Kishore K. Mohanty[1], *[1]The University of Texas at Austin, USA; [2]University of Texas, Harcros Chemicals & Ultimate EOR Services, USA*

Objective: Encouraging results of surfactants flooding (after primary and secondary flooding) have been observed both in the lab and the field. However, the cost of surfactants and their availability is still a cause for concern. In our study, we investigate novel surfactants that do not have “hard” hydrophobes. In particular, we investigated their phase behavior with oil, adsorption on rocks and effectiveness in improving oil recovery. Methods used: The surfactants were synthesized by using methanol as the starting material and various degrees of propoxylation (PO) and ethoxylation (EO), followed by sulfation or carboxylation. The surfactants were characterized for their critical micelle concentrations (CMC) and aqueous stability as a function of temperature. Surfactant phase behavior experiments were performed with crude oils to develop ultralow interfacial tension (IFT) formulations. Single phase and oil recovery corefloods were conducted in outcrop cores. Results: Pendant drop measurements using new surfactants showed a reduction in surface tension and lower CMC values compared to C20–24 internal olefin sulfonate (IOS). Some of these surfactants were found to be aqueous stable up to 100°C. Surfactant phase behavior experiments showed ultralow IFT formulations with different crude oils. Coreflooding experiments showed good oil recovery and low surfactant retentions. Conclusion: These surfactant molecules are versatile and cheaper to manufacture compared to conventional surfactants. These surfactants are hydrophilic at 25°C for easy injection and balanced (in terms of hydrophobic vs. hydrophilic) at the higher reservoir temperature to generate low IFT.

Comprehensive Evaluation of Scleroglucan Biopolymer for EOR under Harsh Reservoir Conditions Mohannad Kadhum, Tryg Jensen, Briana Kozlowicz, Eric S. Sumner, Jeffrey Malsam, and Ramakrishna Ravikiran, *Cargill, USA*

Scleroglucan Biopolymer has tremendous potential to be deployed worldwide in enhanced oil recovery applications. Under harsh reservoir conditions (high temperature/high salinity), Scleroglucan demonstrates outstanding performance benefits compared to synthetic polymer alternatives. In this work, the performance of EOR grade Scleroglucan was investigated in regards to various tests such as injectivity, shear stability, thermal stability, and chemical compatibility. Injectivity was tested in sandstone and limestone cores of varying permeability. Coreflood tests showed high injectivity rates with residual resistance factor close to unity and significant incremental oil recovery. Shear stability behavior of Scleroglucan and polyacrylamide were tested by recycling a

solution through a centrifugal pump and valves. This resulted in less than 5% drop in viscosity after 100 passes for Scleroglucan whereas polyacrylamide lost more than 50% of its viscosity due to shear degradation following 10 passes through the same pump. The viscosity of a Scleroglucan solution was stable to aerobic exposure of 200ppm hydrogen sulfide for 1 week. Anaerobic thermal stability studies of Scleroglucan solution show less than 25% drop in viscosity after 6 months at 115 oC. No change in viscosity was observed at 95 oC after one year. Similarly, anaerobic stability with commercial biocides was tested up to 95 oC and showed no change in viscosity. This work provides insight into the potential of using Scleroglucan for increasing oil recovery in many harsh reservoirs that may not have been candidates for EOR.

Surfactants as Steam Foam Additives for Thermal EOR Processes Thu Nguyen[1], Ajay Raj[1], and Jorge M. Fernandez[2], *[1]Sasol Performance Chemicals, USA; [2]Sasol North America, USA*

Steam override and channeling due to high steam mobility during steam injection for heavy oil recovery can result in high operating costs and low oil recovery. The high steam mobility issue can be overcome with a sufficient increase in the apparent steam viscosity by surfactant stabilized foams. The objective of this research is to identify surfactants that are thermally stable and generate stable foam at typical conditions of steam injection for thermal steam EOR processes. The thermal stability test is performed in a Parr reactor and the concentration of the surfactant before and after aging is determined by a High Performance Liquid Chromatography method. The bulk foam test is carried out in a high temperature high pressure visual cell. Selected promising foam surfactants are also evaluated in a sand-packed column based on the measured pressure drop as an indicator of foam propagation and strength during steam injection. All the tests are performed at steam condition up to 250°C and 800 psi. The results show that the studied surfactants are stable at up to 250°C for at least 2 weeks. The structure-property relationship shows that the foaming efficiency and effectiveness depends on the temperature and the hydrophobicity of the surfactants. These surfactants at 0.5 wt% concentration are able to generate stable foam in the sand-packed column with steam at 75% quality at up to 250°C. The results demonstrate that this type of surfactant significantly reduces steam mobility, which is needed to overcome steam gravity override and channeling issues.

Amido-Amine Based Surfactants: Synthesis, Characterization, and Physico-Chemical Investigation for Enhanced Oil Recovery in Carbonate Reservoirs Syed S. Hussain and Muhammad Sha Kamal, *King Fahd University of Petroleum and Minerals, Saudi Arabia*

Surfactant stability is the major concern during surfactant flooding as the temperature of carbonate reservoirs is around 100 oC and the salinity ranges from 120,000 ppm to 220,000 ppm. These high temperature and high salinity conditions can cause surfactant decomposition. Therefore, the design and development of surfactant which is stable under harsh reservoir conditions is the great challenge. In order to address the stability issues, range of conventional zwitterionic and gemini cationic surfactants were synthesized and characterized by 1H and 13C NMR, FTIR as well as elemental analysis. Thermogravimetric analysis and aging techniques

were used to identify the short-time and long-time heat stabilities respectively. Spinning drop method was utilized to study the interfacial tension and the surface tension was assessed with the help of pendant drop method at 20 oC. Discovery hybrid rheometer (DHR-3) was used for rheological investigations. The synthesized surfactants showed excellent short-time and long-time heat stabilities. The critical micelle concentration and the corresponding surface tension values of the synthesized surfactants found to be comparable with the commercial surfactants. The rheological studies revealed that the concentration and storage modulus were decreased by increasing the concentration of surfactants at low frequency and shear rate due to charge screening and interaction between surfactant and polymer. The synthesized surfactants displayed excellent tolerance to temperature and salinity and showed great potential in high temperature high salinity carbonate reservoirs.

Oil Compatible Cylindrical Micelles at a Very Wide Range of Temperatures and Salinities
Krishna Panthi[1], Himanshu Sharma[1], Upali P. Weerasooriya[3], and Kishore K. Mohanty[1], *[1]University of Texas at Austin, USA; [3]University of Texas, Harcros Chemicals & Ultimate EOR Services, USA*

Objective/Hypothesis Cylindrical (or wormlike) micelles of surfactants have attracted a considerable interest in various fields including gas and oil. It is because they give viscoelastic property which help to sweep oil during EOR process. As surfactant molecules are small and micelles can break and reform, they can easily be injected into tight rocks. The objective of this work is to evaluate the surfactants for their viscosifying capacity in all salinity brine and all temperatures up to 125 oC and compatibility of micelles in oils.

Methods Used A new class of non-ionic surfactants has been synthesized. The water viscosifying property of these surfactants under different salinity and temperature conditions were studied. The compatibility of these micelles in presence of different types and amount of oils (crude oils and alkanes) was studied.

Results These surfactants form viscous solution in presence of different amount of salt from room temperature up to 125 oC. The viscosity of the solution is more than 100 cP even at a temperature of 65 oC. Only little number of cylindrical micelles may have changed to spherical in presence of oil, thus holding the viscosity significantly in presence of oils.

Conclusions Surfactants which form viscous solution in presence of salt from room temperature up to 125 oC were synthesized. Unusual to cylindrical micelles of other surfactants, the cylindrical micelles of these surfactants do not change much in presence of some amount of oil.

The Ultra-low IFT Behavior and Mechanism of a Novel Combined Cationic/Anionic-nonionic Gemini Surfactants System for Chemical Flooding
Haishun Feng[1], Jirui Hou[1], Liming Zhang[1], Zhe Li[1], Wanli Kang[3], and Hairong Wu[1], *[1]China University of Petroleum (Beijing), China; [2]China University of Petroleum (East China), China*

Gemini surfactants have been the focus of intensive attention by virtue of their unique combination of physical and chemical properties and gradually being used for enhanced oil recovery (EOR). In this work, a novel Gemini surfactant GAES-9 was prepared with ethyl-enediamine, fatty alcohol polyoxyethylene ether

and 2-bromoethanesulfonic acid sodium salt. A combined cationic/anionic-nonionic Gemini surfactant system consisting of CTAB and GAES-9 was used for EOR. The surface performance of the combined system was more superior to the relevant single surfactant. The critical micelle concentration (CMC) data was used to calculate the molecular interaction parameters according to the regular solution theory. The combined CTAB/GAES-9 surfactant system could cause remarkable effect on the interfacial tension (IFT) between water and crude oil, and the influential intensity depended on the mole fraction and concentration of CTAB/GAES-9. It could reduce the IFT to an ultra-low level at a very low concentration of 200 mg/L. The system could still maintain ultra-low interfacial tension at salinity of 10×104 mg/L. The mechanism of the synergistic effect of CTAB/GAES-9 to obtain ultra-low interfacial tension was systematically investigated. A large number of anions and cations were adsorbed on the oil-water interface due to electrostatic attraction. At the same time, the space structure of the elongated, flexible EO chains in the Gemini surfactant entangled at the oil-water interface shields some CTAB cations and therefore more cations were adsorbed. To summarize, the combined surfactants exhibit remarkable ability and are good candidates for chemical flooding to EOR in harsh reservoirs.

Use of Carbonaceous Nanoparticles as Surfactant Carrier in Crude Oil Recovery: Part I. Laboratory Study Changlong Chen*, Ben Shiau, and Jeffrey Harwell, *University of Oklahoma, USA*

Carbonaceous nanoparticles multi-walled carbon nanotubes (MWNTs) and carbon blacks (CBs) exhibit promising properties for potential applications in crude oil and natural gas production. The combination of large specific surface area and the strong affinity toward surfactants of nanoparticles mark their candidacy for delivering surfactant deep inside the reservoir to overcome excessive surfactant adsorption losses onto rock matrix. This study is aimed to assess the feasibility of surfactant carriers in tertiary oil recovery. As a proof of concept, phase behavior of a ternary surfactant microemulsion system confirmed that the chosen nanoparticles (100 mg/L) successfully delivered surfactants and spontaneously released them to the O/W interface. The observed phenomenon is in accordance with calculation of the Gibbs free energy associated with oil/water/surfactant system. Surfactants carried by nanoparticles achieved equilibrium ultralow interfacial tension between excess oil and aqueous phase similar to the values of surfactant-only formulations (0.007–0.009 mN/m). In one-dimensional sand pack tests, injection of MWNT-surfactant blend achieved faster and higher tertiary recovery than surfactant-only formulation, with cumulative tertiary oil recovery of 42.7% versus 38.1%. It has been noticed that once surfactant been released, destabilization of nanoparticle dispersion occurred and thus increased their retention in porous medium. In cases of tight formation, further improvements may be addressed by applying functionalized carbonaceous nanoparticles to assure their transport in porous media after release of surfactant. Use of nanoparticles as carriers for surfactant in harsh reservoir conditions has great potential in ultimately increase of oil recovery by injecting significant less surfactant concentration and offering cost saving benefit.

BIO 4.1/S&D 4: Biosurfactants and Additives

Chairs: Daniel K.Y. Solaiman, USDA, ARS, ERRC, USA; and George A. Smith, Sasol North America, USA

Next Generation Castor Oil Ethoxylates Ollie James*, Dustin Landry, Liam McMillan, and George Smith, *Sasol North America, USA*

Castor oil ethoxylates have been material of commerce for many years. Castor oil is obtained by pressing the seeds of the castor oil plant. The oil is rich in ricinoleic acid, an unsaturated fatty aicd containing a hydroxyl group in the 12 position. Castor oil ethoxylates are typically made by reacting castor oil with ethylene oxide using a base catalyst. The product consists of a complex mixture of ethoxylated fatty acids, ethoxylated partial glycerides and PEG. Castor oil ethoxylated are used as emulsifiers and adjuvants for agrochemical formulations. Surface activity and applications performance depend on the degree of ethoxylation and the species distribution. Recently, new ethoxylation catalysts have been developed which give greater control over reaction kinetics and species distribution. Narrow range catalysts allow for insertion of EO into the ester group but typically are not very effective at ethoxylating secondary alcohols. DMC catalysts are effecting at ethoxylation secondary alcohols but give very little ester insertion. The species distribution of castor oil ethoxylates prepared by different catalysts was determined using a combination of LCMS and HPLC. Surface and interfacial tension was determined by Wilhelmy plate and pendant drop measurements. The performance of castor oil ethoxylates in different applications was related to species distribution and surface activity.

Glycolipid Biosurfactants: Characteristic Curvature and Applications in Microemulsions and Emulsions. Zheng Xue, Dennis Parrish, Eric Theiner, Khalil Yacoub, Andras Nagy, and Terrence Everson, *Evonik Corporation, USA*

Microbial biosurfactants produced by fermentation exhibit favorable properties such as low toxicity, skin mildness, and biodegradability. In particular, glycolipid biosurfactants such as sophorolipids and rhamnolipids have attracted significant commercial interest, owing to the desirable physiochemical properties of these biosurfactants and advantageous economics of large-scale production. In this study, the characteristic curvatures of sophorolipids and rhamnolipids were measured using microemulsion phase behavior study. Then, based on hydrophilic-lipophilic difference (HLD) calculations, a series of surfactant formulation systems comprising biosurfactants were designed. By tuning the HLD, the compositions of the surfactant formulations were optimized for two applications: 1) microemulsions containing terpenes for hard surface cleaning, and 2) efficient emulsification of oily soils for fabric cleaning. The effects of sophorolipids and rhamnolipids on the interfacial rheological properties, interfacial tension reduction, and emulsification in these two applications were investigated. Formulation procedures and comparative results will be discussed.

Glucamide Surfactants: Structural and Interfacial Aspects Brajesh Jha*, *Colgate Palmolive, US*

Surfactants and co-surfactants are widely used in Personal Care and Home Care formulations to provide benefits such as improved foaming, viscosity, and mildness. Innovation continues in the area of surfactant chemistry to meet a growing demand for surfactants which are more versatile and have a greater safety and sustainability profile, and at the same time do not compromise on delivering performance when formulated into consumer products. Glucamides, although not new, are interesting surfactants, since they are based on sugar chemistry. Built from glucose and natural oils, these surfactants usually have a high Renewable Carbon Index (RCI) providing an advantage over the more conventional nonionic surfactants. This presentation will highlight the basic physicochemical phenomena occurring at the air-liquid or liquid-liquid interface in relation to structure-function of a selected group of glucamide surfactants. The select group consists of R-acyl-N-methyl glucamine at 25°C in distilled water, where R = C8/C10, C12/C14 or coco. Particular emphasis will be on the fundamental properties of these surfactants, such as CMC and their ability to reduce interfacial tension and improve foaming properties compared to other similarly structured surfactants. Glucamides' renewable and performance profile makes them an important class of surfactants to study for the fundamental understanding in the formulation development.

NMR Investigation of the Effect of pH on Micelle Formation by an Amino Acid-based Surfactant. Kevin F. Morris[1], Gabriel Rothbauer[1], Elisabeth Rutter[1], Chelsea Reuter-Seng[1], Simon Vera[2], Eugene Billiot[2], Yayin Fang[3], and Fereshteh Billiot[2], *[1]Carthage College, USA; [2]Texas A&M Corpus Christi, USA; [3]Howard University, USA*

Micelle formation by the anionic amino acid-based surfactant undecyl L-phenylalaninate (und-Phe) was investigated in solutions containing either Na+, L-arginine, L-lysine, or L-ornithine counterions. Amino acid-based surfactants like und-Phe are biodegradable, biocompatible, and have a low toxicity. For these reasons, they are used in pharmaceutical and food applications and as selectors in chiral chromatography. NMR spectroscopy was used to measure the surfactant's critical micelle concentration as a function of pH in solutions containing each of the above counterions. NMR diffusion experiments were used to monitor changes in micelle radii with pH and to investigate the fraction of surfactant molecules and counterions bound to the micelles. Finally, two-dimensional NMR experiments were used to study the mechanism of L-arginine and L-lysine binding to und-Phe. In each mixture, the surfactant's critical micelle concentration was smallest at low pH and increased as solutions became more basic. NMR diffusion experiments showed that L-arginine, L-lysine, and L-ornithine bound most strongly to the micelles below pH 9 when the counterions were cationic. Above pH 9 the counterions became zwitterionic and dissociated from the micelle surface. Micelle radii measurements

suggested that L-arginine attached to the micelles perpendicular to the micelle surface through its guanidinium functional group with the remainder of the molecule extending into solution. L-lysine and L-ornithine in contrast, were found to bind parallel to the micelle surface with their two amine functional groups interacting with different surfactant monomers. This binding model was found to be consistent with results from two-dimensional NMR experiments.

Effects of Rhamnolipid on Phagotrophic Algae as Sensitive Ecologically Important Model Organism. Krutika Invally, Suo Xiao, and Lu-Kwang Ju*, *University of Akron, USA*

Surfactants can affect biological activities and pose threats to the aquatic ecosystem. Rhamnolipid biosurfactant has promising agricultural, industrial and biomedical applications. It is important to assess the risk posed by rhamnolipid prior to its wide-spread uses. We have evaluated the effects of rhamnolipid on a phagotrophic alga. The model organism used is a versatile mixotroph capable of photosynthetic, osmotrophic and phagotrophic metabolisms. Phagotrophic flagellates consume small microorganisms like bacteria and blue-green algae. They are ecologically important in transferring organic matter between the microbial and the classic food webs. Without a protective cell wall, they are likely more sensitive to surfactants among aquatic microorganisms. Common synthetic surfactants sodium dodecyl sulfate and Tween 80 were used for comparison. Critical concentrations and/or kinetic profiles for motility loss, cell lysis and membrane permeability were determined. Effects of its more unique phagotrophic metabolism on surfactant sensitivity were also observed.

Application of Sophorolipids to Control Food Pathogens Daniel K.Y. Solaiman*, Richard D. Ashby, Xuetong Fan, and Modesto Olanya, *USDA, ARS, ERRC, USA*

Sophorolipids (SLs) are glycolipid-class biosurfactants produced by Starmerella bombicola and certain other yeast species. Previous studies had shown that SLs possessed varying degrees of antiviral and antimicrobial activity against viruses, bacteria, and fungi. In this paper, we present the results of our studies in which the antimicrobial activity of SLs was specifically tested against foodborne human pathogens (i.e., Escherichia coli O157:H7, Listeria monocytogenes, and Salmonella enterica). SL varieties isolated from fermentation broths of S. bombicola grown on palmitic (C16), stearic (C18), and oleic (C18:1) acid as the lipid substrate were screened in the study. Whereas there was no significant difference observed among the SL varieties (i.e., SL-C16, SL-C18, SL-C18:1) against the test bacteria, the Gram-positive L. monocytogenes was however found to be more susceptible to the biosurfactants in comparison to the Gram-negative E. coli O157:H7 and S. enterica. We further examined the effects of temperature and storage time on the efficacy of SL-C16 against the test bacteria, and found that higher temperature (25°C vs. 5°C) and longer storage time (24 h vs. 30 min) were more effective to decrease the pathogen population. Washing of artificially contaminated spinach leaves (i.e., E. coli O157:H7 inoculation) with SL solutions (1% w/v) did not significantly reduce the bacterial population in comparison to washing with water. However, the combined application of SL-C16 and a food sanitizer to treat pathogen-inoculated grape tomatoes led to significant reductions of the bacterial population.

The Stability of Nanoemulsions and Emulsions Containing Cinnamaldehyde and Biosurfactants, and their Antimicrobial Performance against Escherichia. coli O157:H7 and Listeria Monocytogenes Kangzi Ren* and Buddhi Lamsal, *Iowa State University, USA*

Two novel biosurfactants—surfactin and fatty acyl glutamic acid (FA-glu)—were compared with commercial emulsifiers—lecithin, and a mixture of Tween 80 and lauric arginate (TLA) for formation and stability of nanoemulsions and emulsions containing cinnamaldehyde (CM). The nanoemulsions'/emulsions' antimicrobial performance against two common foodborne pathogens E. coli O157:H7 and Listeria monocytogenes was also evaluated. The objectives of this study were to investigate how the processing parameters affect the emulsions' stability and how the emulsion droplet size affected the antibacterial efficacy. Two emulsifier concentration levels (0.5% w/w and 1% w/w) and two homogenizing pressures (9000 PSI and 18000PSI) were studied for their effect on droplet stability during storage for 46 days at 4, 25, and 37°C. Surfactin, FA-glu and TLA mixture formed nanoemulsions at both concentrations, but lecithin did not. Emulsion droplet sizes did not change significantly during 38 days at all temperatures for surfactin- and TLA mixture-stabilized nanoemulsions. However, FA-glu and lecithin stabilized emulsions coalesced after 13th day when stored at 37°C, FA-glu stabilized emulsion also formed viscous structure during elongated storage days at 4°C. The incorporation of CM in nanoemulsions or emulsion did not lower the minimum inhibitory concentration (MIC) in bacterial broths. However, at the concentrations lower than MIC, nanoemulsions and emulsions containing CM formulated with FA-glu, lecithin, and TLA, showed enhanced effects in inhibiting bacterial growths compared to CM alone, with smaller droplets inhibiting more.

Unique Characteristics of Sophorolipid, Yeast Glycolipid Biosurfactants, and its Application as Eco-friendly Bio-detergents. Yoshihiko Hirata, Glen Lelyn Quan, Michiaki Araki, and Mizuyuki Ryu, *Saraya, Japan*

Biosurfactants (BSs) are natural amphiphiles which are abundantly produced from a variety of renewable resources by microorganisms. They have been receiving great attention because of their unique properties including higher biodegradability, low toxicity, and versatile biological functions, compared to petroleum-based surfactants. So far, the use of BSs has been limited to a few specialized applications because they have been economically uncompetitive. We started the research on sophorolipid (SL), which is a kind of promising glycolipid BS, for practical use as bio-detergents since 1998. We found that SL is a biodegradable low-foaming surfactant with excellent washing ability and commercialized the only automatic-dishwashing detergent containing SL as surfactant in 2001. At present, our SL brand, SOFORO, is originally being fermented using RSPO (Roundtable on Sustainable Palm Oil)-certified "segregated" palm oil. In this study, we will report about the unique "rinsability" of sophorolipid, which is the activity to reduce the amount of surfactants adsorbing on skin surface, and introduce its recent product application, our new detergent brand "Happy Elephant".

Applisurf: Functionality Driven Design and Synthesis of New-to-Nature Glycolipid Biosurfactants. Sophie L.K.W. Roelants[1], Sofie Demaeseneire[2], and Wim Soetaert[3], *[1]Bio Base Europe Pilot Plant, Belgium; [2]Ghent University, Belgium; [3]Centre for Industrial Biotechnology and Biocatalysis (InBio.be), Ghent University, Belgium*

Industrial biotechnology holds the opportunity to use and redirect nature's many inventive capabilities to produce a variety of biological amphiphiles with a variety of (new) potential applications like the fermentative glycolipid portfolio recently developed at InBio.be and BBEPP. However, such technologies are mostly driven by market push and finding the best application for each specific new and thus uncharacterized compound is similar to looking for the needle in the haystack, often resulting in a halt of the innovation. This unfortunate situation could be alleviated by applying an integrated bioprocess design where application development in the form of functional screening is developed in parallel with microbial strain development, driven by synthetic biology. In the AppliSurf project, a molecular glycolipid portfolio generated through a combination of fermentation and green chemistry will be subjected to HTP functional characterisation for surfactant and biological properties. The generated data will be used to build models defining and predicting structure-function relationships. The latter will allow to specifically design and generate promising candidates for dedicated application experiments by industrial end users. Together, this approach is expected to speed up innovation and market uptake of new, innovative and performance biosurfactants.

S&D 5: Surfactant Synthesis and Fundamental Properties

Chairs: Ron A. Masters, Stepan Company, USA; and Michael Miguez, Shell Global Solutions, Inc., USA

Alkyldimethyl Amine Oxides—Determination of pKa and Elucidation of Micelle Structure with FT-IR Spectroscopy David Scheuing*, *Clorox, USA*

The composition of amine oxide micelles and hence the headgroup environment may be controlled through the pH of the solution. With appropriate application of the Gibbs-Duhem equation to the micellar pseudophase, the activities of the surfactant species may be determined via a titration method. Treatment of amine oxide micelles as a binary mixture of nonionic and cationic surfactants leads to the important conclusions that there is no need to introduce the concept of "apparent pKa" for these micelles, and that the origin of non-ideality effects is primarily interactions between charged and uncharged headgroups. Fourier Transform infrared spectroscopy can be applied to elucidate the structural changes in the micelles induced by changes in pH. Interactions between neighboring headgroups at the pKa, i.e. in 1:1 nonionic-cationic "mixed micelles" are clearly detected and interpreted.

2-phenyl or Not 2-phenyl: The Secret Life of Linear Alkylbenzene Sulfonate George A. Smith*, *Sasol North America, USA*

Linear alkylbenzene sulfonate (LABS) is one of the largest production volume anionic surfactants globally. LABS is widely used in household detergents and in different industrial applications. LABS is prepared by air/SO3 sulfonation of linear alkylbenzene (LAB). Commercially, there are several different production methods used to prepare LAB which give different 2-phenyl isomer levels. The level of 2-phenyl isomer and the nature of the counterion used to neutralize the sulfonic acid have a pronounced effect on the properties of LAS. Historically, high 2-phenyl LABS has been used in liquid products because it has somewhat better solubility. Low 2-phenyl LABS is used in crutcher slurries to prepare powder detergents, block cleaners and structured liquids to suspend insoluble particulates. Because of the critical packing factor, high 2-phenyl LABS prefers to form small spherical micelles in aqueous solution. Low 2-phenyl LABS prefers to form large, multi-walled lamellar droplets. The phase behavior and surface properties of low and high 2-phenyl LABS will be discussed in relation to performance in different applications.

Solving a Hard Problem: Oleofuran Surfactants for Hundredfold Improved Hard Water Stability Christoph Krumm*[1], Kristeen Joseph[2], Dae Sung Park[2], and Paul J. Dauenhauer[2], [1]*Sironix Renewables, USA;* [2]*University of Minnesota, USA*

Emerging surfactant technologies have focused primarily on production of existing structures from bio-renewable sources. Despite enabling easier 'drop-in' replacement in formulations, these materials struggle to compete on cost with petrochemical technologies. Recent approaches to design new surfactant structures have focused on enhanced or additional function of new surfactant structures to gain a cost advantage [1]. Here, we present a new class of surfactants, called Oleo-Furan Surfactants (OFS), which provide

hundredfold improved tolerance to hard water, thereby enabling simplified and more functional cleaning product formulations while utilizing plant-based resources [2]. Catalytic reaction development for the OFS technology has focused on efficient synthesis of surfactant structures from starch-based furan molecules and natural oils, such as those from soybean and coconut. Selective design of OFS structures enables tunable function, such as foaming, micelle stability, and cold water function. Current and future work is focused on scaling the surfactants technology for application in cleaning and personal care products, agrochemicals, and oil recovery. [1] Foley, P., Kermanshahipour, A., Beach, E., Zimmerman, J., Chemical Society. Reviews, 2012, 41, 1499-1518. DOI: 10.1039/C1CS15217C [2] Park, D. S.; Joseph, K. E.; Koehle M.; Krumm, C.; Ren, L.; Damen, J. N.; Shete M. H.; Lee, H. S.; Zuo, X.; Lee, B.; Fan, W.; Vlachos, D. G.; Lobo, R. F.; Tsapatsis, M.; Dauenhauer, P. J. ACS Central Science 2016, 2 (11), 820-824. DOI: 10.1021/ acscentsci.6b00208

New Methyl Ester Ethoxylate Derived from C18 Fraction of Palm Oil for Liquid Laundry Detergent Akinori Joko*, Yuka Morimoto, Yukihiro Kaneko, and Norio Tobori, *Lion Corporation, Japan*

Methyl ester ethoxylate (MEE) derived from plant-based oil is an eco-friendly nonionic surfactant. It is well known that MEE made from the C12-C14 fatty acid methyl ester fraction of palm oil has a larger fluid-phase micelle area and foams less than C12-C14 alcohol ethoxylate (C12-C14AE), and is highly detergent against oleic acid, which is found in sebum and can cause clothes to smell even after being washed. However, no study has assessed MEE made from the non-hydrogenated C18 fatty acid methyl ester fraction even though it is the main component of palm oil. Therefore, in order to utilize this main component as a raw material of MEE, we synthesized non-hydrogenated C18MEE (C18:1MEE) from this fraction and studied its washing and phase behavior in water. In this study, we found that C18:1MEE has better solubility even at low temperatures compared with other MEE made from C16-C18 fatty acid methyl ester fractions. Furthermore, X-ray 3D-computed tomography images showed that C18:1MEE can remove carbon particulates, an air pollutant, not only from the surface but also from the inside of clothes more efficiently than C12-14MEE and C12-14AE due to its excellent dispersive ability. These results indicate that C18:1MEE is likely to be suitable for liquid laundry detergents.

Low Foaming Nonionic Surfactants with High Bio-Based Content Scott Jaynes*, *Croda, Inc., USA*

Low foaming surfactants are important components of cleaning products where the generation of foam can diminish performance or cause mechanical issues. These products include household formulations such as auto dishwash products and glass cleaners, as well as I&I formulations used in clean-in-place and bottle wash processes. Alkoxylated nonionic surfactants are widely used in low foam applications because their foaming characteristics can be carefully controlled by balancing EO and PO components. A family of EO/PO derivatized alcohols will be presented along with associated foaming, wetting and cleaning data in order to illustrate how these different components can be fine-tuned to meet application requirements. A new

low foaming blend with very high caustic stability will be introduced. Additionally, low foaming surfactants with high bio-based content will be presented, that are produced using bio-based ethylene oxide. The commercial availability of these high bio-based low foaming nonionic surfactants now provides formulators with the ability to reach sustainability targets that formerly were not accessible in these types of cleaning products.

Force Mapping and Characterization of Surfactant Adsorbed on Flat and Patterned Surfaces Joshua J. Hamon[1], Rico Tabor[2], Brian P. Grady[1], and Alberto Striolo[3], *[1]University of Oklahoma, USA; [2]Monash University, USA; [3]University College London, UK*

In this work, force curve data collected using an atomic force microscope (AFM) on adsorbed surfactants was used to first investigate the assumption of a "naked" AFM tip in surfactant solutions by collecting force maps on a single AFM tip with the tip of a separate AFM probe. A break-through event was observed between the tips, indicating a layer of surfactant was present on at least one if not both tips. Force curves were then collected using the surfactant TTAB adsorbed to flat surfaces of highly ordered pyrolytic graphite (HOPG), silica, and silica reacted with dichlorodimethyl silane. The break-through events were compared through histogram analysis to show that the break-through distance, often reported as the adsorbed film thickness, varied with concentration below the critical micelle concentration (CMC) but was approximately 3.5 nm on all surfaces between 2 and 10xCMC; an unexpected result. Slope mapping, a variant of force mapping, was also implemented on the three surfaces and resulted in a new technique for visualizing adsorbed surfactant in situ. The resulting maps showed patches of adsorbed surfactant whose size increased with concentration below the CMC and eventually reached full surface coverage near and above the CMC.

Foam Properties of Alcohol Ethoxylates, Ether Sulfates and Ether Carboxylates Tamra Weemes, Thu Nguyen, and Jamie Thibodeaux, *Sasol Performance Chemicals, USA*

Foaming is an important parameter in a number of application areas such household cleaning formulations, personal care products, paints and coatings, enhanced oil recovery, and oil and gas. Different types of surfactants can generate different types of foams based on their foamability, foam stability, and foam density. These foaming characteristics will also be affected by temperature. In order to select a suitable surfactant for a specific application, it is important to know the foaming properties of different surfactants and how different parameters (surfactant structure, system salinity, temperature, etc.) affect the foam performance of the surfactants. This research focuses on the evaluation and characterization of foam properties for a wide range of surfactants, including alcohol ethoxylates, alcohol ether sulfates, ether carboxylates and sulfonates.

New Surfactants: Gemini and Microbial Type Sunil S. Bhagwat*, V. Dengle, S. Sulakhe, S. Gotmukle, A. Ghumare, and M. Ahire, Department of Chemical Engineering, Institute of Chemical Technology, India

In this paper, we present some of the new surface active molecules synthesized and characterized in our recent work. Lauramidopropyl glyceryl dimethyl ammonium

chloride or LGDMAC is a quaternary ammonium surfactant where glycerol contributes towards the hydrophilic part of the molecule. The CMC is comparable to conventional quaternary ammonium compounds while the C20 is lower. This molecule has antimicrobial activity as well. Sophorose is a sugar which can work as a polar head group. Sophorolipids were prepared microbially by using fatty alcohols instead of usual fatty acids so that the molecule remains a nonionic one. Cationic gemini surfactants were synthesized from fatty acids via amidoamine derivative and these molecules show lower CMC and good antimicrobial activity. Anionic biphosphodiester gemini surfactants and cardanol sulfonate gemini surfactants of various alkyl chain lengths were synthesized and these molecules show a lower CMC, slower dynamics and consequently lower foamability.

EAT 5.1/S&D 5.1: Complex Phenomena at Interfaces

Chairs: Sam Adamy, Church & Dwight Co. Inc., USA; and Ozan N. Ciftci, University of Nebraska-Lincoln, USA

Complex Interfaces: Role in Foam and Emulsion Behavior of Rinse-off Cosmetics Edward DiAntonio[1], Hani Fares[1], Martin S. Vethamuthu*[1], and Seher Ozkan[2], [1]*Ashland Specialty Ingredients G.P., USA;* [2]*Ashland Specialty Ingredients, USA*

This presentation will review progress of how the interface influences the formation and stability of emulsions and foams. The main function of emulsions is to provide moisturization, occlusion or conditioning benefits to substrates such as skin or hair. A key challenge has been understanding and optimizing the factors effecting the stability of emulsion droplets from destabilization mechanisms such as sedimentation/creaming, flocculation, coalescence, and tolerance to temperature and freeze thaw cycles under equilibrium and kinetic conditions. Attention is focused on the effect of polymer molecular structure, interfacial rheology, competitive adsorption and interfacial structure and composition both in bulk formulation and the interface.

Effect of Emulsifiers on the Interfacial Tension of Fat-reduced W/O Emulsions Added with a High Behenic Stabilizer Marisol Cordova-Barragan[1], Jaime D. Pérez-Martínez[1], and Elena Dibildox Alvarado[2], [1]*Lab. Biopolímeros Alimentarios, Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, Mexico;* [2]*Universidad Autónoma de San Luis Potosí, Mexico*

Soy lecithin and monoglycerols from rapeseed and palm oils were studied in their effect on the interfacial tension in fat-reduced W/O emulsions added with a high behenic stabilizer (HBS). The interfacial tension of the emulsion was measured with each emulsifier and with the blend of them, all added to the oil phase, composed of palm oil, palm stearin and palm kernel oil. The emulsifiers blend decreased the interfacial tension of the emulsion from 11.7 to 2.1 dynes/cm (p

Surfactant Effects on Fat Crystallization at the Oil-water Interface Nicole Green*[1], Stephen R. Euston[2], and Dérick Rousseau[1], [1]*Ryerson University, Canada;* [2]*Heriot-Watt University, United Kingdom*

We have previously shown that the addition of water to shear-crystallized fat+oil systems can form encapsulated droplets surrounded by Pickering crystal shells in the presence of certain lipophilic emulsifiers. We further explored the interfacial behaviour using a temperature-controlled drop shape tensiometer to monitor the onset and progress of crystallization over time. A single water drop in an oil+fat+emulsifier medium was observed from 80°C to room temperature. The emulsifiers studied were glycerol monostearate (GMS), glycerol monooleate (GMO), glycerol dioleate (GDO), and polyglycerol polyricinoleate (PGPR). The complex branched molecular structure of PGPR prevented any interfacial crystallization. Results for the glycerol-based emulsifiers were concentration-dependent: GMS shells grow thicker with the inclusion of more emulsifier or fat, whereas higher concentrations of GMO allow for fat crystal “satellite” attachment. Experimental results are compared to coarse-grained

simulations of GMO and PGPR at a tristearin/water interface.

Characterizing Adsorption Kinetics and Wetting Behavior of Polyelectrolyte Complexes (PECs) Claire Dentinger* and David Scheuing, *Clorox, USA*

A wide variety of different pairs of oppositely charged polymers can interact electrostatically and form polyelectrolyte complexes (PECs) in solution. Under appropriate synthesis conditions these will form stable colloidal particles with dimensions on the order of 100 nm in diameter. PECs are also able to electrostatically adsorb to solid surfaces and in some cases can modify the properties of the solid surface. FTIR measurements are used to characterize the adsorption kinetics of PECs to solid surfaces under different solution conditions and contact angle is used to understand how PECs' adsorption can modify the wetting characteristics of a surface.

Physical Modification of Faba Bean Proteins Significantly Improves Interfacial and Emulsifying Properties of O/W Emulsions Yan Ran Tang and Supratim Ghosh*, *University of Saskatchewan, Canada*

Protein concentrates from pulses has shown the ability to stabilize oil-in-water emulsions. In this research, faba bean protein concentrates were centrifuged to remove the insoluble fraction, and the supernatant with soluble proteins was utilized for efficient emulsification at pH2 and pH7. Prior to emulsification, the protein solutions were either homogenized or heat treated to investigate the effect of physical modification on interfacial and emulsifying properties. 5wt% oil-in-water emulsions were prepared with 0.5wt% soluble faba bean protein (SFBC) using multiple passes through a high-pressure homogenizer. The resulting emulsions were stored for 30 days and characterized by visual observation, droplet size, charge, creaming velocity under accelerated gravitation and microstructure. At pH2, all emulsions were extremely stable with lower creaming velocity, while at pH7, cream layer separation was observed after 30 days storage. All freshly prepared emulsions had an average droplet size in the range of 0.3 to 0.5 um, which was not significantly affected by pH or types of protein modification. However, after 15 days, droplet size of heat-treated protein-stabilized emulsions significantly increased due to droplet and protein aggregation. Zeta potential of the oil droplets decreased with protein modification, indicating interfacial protein aggregation upon modification due to exposure of hydrophobic groups. These results were explained by interfacial rheology and structural changes of the proteins under different pH and physical modifications. Overall, SFBC showed great potential for improved emulsification and long-term stability of oil-in-water emulsions for food applications.

Crystal-melt Interfacial Energy Effects on the Surface Nucleation of Triglycerides Alejandro G. Marangoni*, *University of Guelph, Canada*

Triacylglycerols (TAGs) nucleate from the melt or solution to form homoepitaxially stacked molecular lamellae, resulting in the formation of thin anisotropic crystalline nanoplatelets. A modified 2D Gibbs-Thomson equation for the formation of a "TAG island" nucleus on a surface was used to estimate the surface energy of the nanocrystals as 70mJ/m2. This value of this surface energy strongly depends on the radius of the surface nucleus. When height and diameter

of the nucleus were similar, the value of this surface energy was ~10mJ/m2, which is typical of TAGs. The surface energy of TAG nanocrystals was then modulated by addition of specific emulsifiers, which allowed the controlled change, both increase and decrease, in nanoplatelet thickness in the range 20-30nm, by homoepitaxial growth of single 4nm molecular lamellae.

S&D-P: Surfactants and Detergents Poster Session

Chair: Mike Wint, Amway Corp USA;

1. **Novel Phosphate Ester Replacement for C8-C10 Linear Alkyl Phosphate Esters.** Ryan C. Vikan and Philip C. Benes*, *Nease Co., USA*

A complex mixture of monoester and diester alkyl alcohol ethoxylate phosphoric acid with proven hydrotropic ability in liquid formulations. It is effective as a surfactant in heavy duty alkaline liquid formulations. It is also soluble in high electrolyte systems. It is very useful as solubilizer and corrosion inhibitor in various sanitary and industrial cleaning formulations. As a functional replacement for C8-C10 linear alkyl phosphate esters that are in short supply in commerce it has equal to superior performance for wetting, surface tension reduction, foaming, and caustic stability.

2. **Amide Types of Chemocleavable Surfactants Bearing a 1,3-Dioxolane Ring Derived from Diethyl Tartrate.** Makoto Okumura[1], Daisuke Ono*[2], Shintaro Kawano[3], Hirofumi Sato[3], Motohiro Shizuma[3], and Araki Masuyama[1], *[1]Osaka Institute of Technology, Japan; [2]Osaka Research Institute of Industrial Science and Technology, Japan; [3]Osaka Municipal Technical Research Institute, Japan*

The development of surfactants with excellent surface-active properties, additional functions, or good biodegradability has become desired. Therefore, it has come to be great interest to develop "chemocleavable" surfactants which are designed to decompose into non-surface active species under mild conditions after fulfilling their original functions such as emulsification, solubilization, and micellar catalytic activity. We have been investigating the preparation and properties of a series of acid- and alkali-cleavable surfactants. In this work, amide types of chemocleavable surfactants bearing a 1,3-dioxolane ring were prepared by acid-catalyzed condensation of diethyl tartrate with fatty ketone or aldehyde, followed by a reaction with amine without any expensive reagents or special equipment. We confirmed that they have good surface-active properties. The emulsion stability of these surfactants was almost the same as that of typical surfactant. Biodegradability of the surfactants was evaluated by an oxygen consumption method according to the guidelines which was based upon the OECD301C with activated sludge. Their detergency on artificially soiled cotton cloth was better than the reference detergent in hard water according to the Japan Industrial Standard Method. The reference detergent consisted of sodium n-dodecylbenzenesulfonate, which is a popular component in commercial detergents.

3. **Formaldehyde Free Microencapsulates Improve Detergent Fragrance Delivery.** Terry Crutcher, *Ashland Specialty Ingredients G.P., USA*

Fragrance adds value and allure to detergent products. When fragrance is added to detergents it influences consumer preference and purchase. The fragrance of a detergent may impact the end-user's selection, perception, and experience while using the product, long after the task of cleaning has past. Fragrance makes us feel better about cleaning and serves as an indication to consumers that their homes are clean and refreshed. It is commonly understood that a perfumer's fragrance creation is not what consumers experience from many detergent

products, due to a variety of reasons. The hedonics or bouquet and intensity of many fragrances are altered as a result of being formulated into detergents. Detergent manufactures would like to capture and deliver at the point-of-purchase and in-use an optimal sensorial experience for consumers as close as possible to the perfumer's original fragrance creation, as possible. This research proposes a method of enhancing detergent perfume delivery via fragrance microencapsulation to enhance the usability of the detergent. Further the encapsulation product is formaldehyde free. Residual formaldehyde found in traditional melamine encapsulation technology is of concern today. The study will profile the benefits of fragrance delivery from advanced formaldehyde-free acrylate microcapsules versus traditional melamine formaldehyde microcapsules, and conventional fragrance oil use. Improved fragrance delivery will be discussed for a variety of home cleaning applications.

4. **Cationic Polyacrylamide/Cationic Gemini Surfactants Hybrid Material for Enhanced Oil Recovery in Carbonate Reservoirs.** Muhammad Sha Kamal and Syed S. Hussain, *King Fahd University of Petroleum and Minerals, Saudi Arabia*

The chemical enhanced oil recovery methods comprise the use of chemicals including alkaline, surfactants, and polymers. However, such technique faces great challenges due to severe reservoir conditions such as high temperature and high salinity which results in degradation of injected chemicals. Considering the local reservoirs conditions, variety of gemini cationic surfactants were synthesized and characterized by NMR, FTIR, and elemental analysis. The short-range thermal stability was investigated by thermogravimetric analysis and long-range thermal stability was assessed through aging surfactants followed by structural elucidation. Rheological studies were done by Discovery hybrid rheometer. The surfactant was then mixed with the commercial cationic polyacrylamide and the oil recovery efficiencies of surfactant and surfactant-polymer hybrid system were evaluated by core-flooding tests. Thermogravimetric analysis revealed remarkable short-range thermal stability and decomposition in the original structure was not seen down to 250 ^{o}C. The structure elucidation results of the aged sample displayed unique long-range thermal stability by survival of original structure after putting the sample at 90 oC for 10 days. It was observed that interfacial tension decreased by increasing length of spacer of the gemini surfactants and temperature. The spacer moiety showed great influence on the physico-chemical properties of cationic gemini surfactants. The critical micelle concentration of the surfactants as well as corresponding surface tension values exhibited excellent surface properties that are comparable with the commercial surfactants. The oil recovery efficiencies using surfactant and surfactant-polymer hybrid system were 9 % and 23 %, respectively.

5. **A New Approach to Measure the Adsorption Density of Surfactant on Carbonate Rock Using TOC Analysis.** Muhammad Sha Kamal and Abdullah S. Sultan, *King Fahd University of Petroleum and Minerals, Saudi Arabia*

Surfactants are used in chemical enhanced oil recovery to lower the interfacial tension between water and oil. Measurement of surfactant concentration is a challenging task and various

analytical methods such as ultraviolet-visible spectroscopy, high performance liquid chromatography (HPLC) and titration is used to measure the concentration of the surfactant in effluent. In this work, we used a new method based on total organic carbon (TOC) analysis to measure the static and dynamic adsorption of the rock. 2g of crushed carbonate rock and surfactant solutions at different concentration were conditioned in a hot-water shaker for 24 hours at desired temperature and equilibrated for another 24 hours. TOC was used to generate a calibration curve at different surfactant concentrations. Conditioned samples were analyzed using TOC again and corresponding adsorbed amount was determined from calibration curve. In this work, adsorption of anionic, non-ionic, and amphoteric surfactants on carbonate rock surface was evaluated using static adsorption and dynamic adsorption tests. Effect of surfactant concentration, surfactant type, temperature, salinity, and type of salinity was studied. Nonionic and anionic surfactants were found to have higher adsorption on carbonate compared to amphoteric surfactant. Adsorption of most of the investigated surfactants was increased by increasing the salinity and temperature. As method is based on organic carbon analysis, any CO3- ions transferred from rock to solution will not affect the measurement. Detail experimental procedure and approach will be discussed.

6. **Investigating the Effects of Controlled Lateral Confinement Width and Surface Chemistry on Surfactant Adsorption onto Silica using AFM.** Joshua J. Hamon[1], Brian P. Grady[1], Alberto Striolo[2], and Rico Tabor[3], *[1]University of Oklahoma, USA; [2]University College London, United Kingdom; [3]Monash University, USA*

Controlled lateral confinement was investigated using force curve data collected on surfactant adsorbed to patterned surfaces using an atomic force microscope (AFM). Confinement was induced using nano-trenches with silica at the bottom, and walls of either pure polymethyl methacylate (PMMA) or a copolymer of PMMA and methacrylic acid (MAA) to vary hydrophobicity. From the force curves we showed that surfactant adsorbed within trenches were affected by the polymer chemistry but there was no observable effect caused by the trench dimensions down to 30 nm of confinement. Pillar type structures were also used to induce confinement through a lack of surface area and various pillar shapes were used in the mapping to study the effects of the pillar edge proximity on the adsorbed surfactant. Comparisons were then made between the trench and pillar results to images and values collected on flat surfaces. The ultimate goal of this research is to compare the results found using these nano-structures with molecular dynamics simulations performed using similar geometric confinement.

7. **Fragrance Influence on Stability for Fabric Care Applications.** Matt Vanden Eynden[1], Christelle Tisserand[2], Yoann Lefeuvre[2], Pascal Bru[2], and Gerard Meunier[2], *[1]Formulaction, Inc., USA; [2]Formulaction, France*

Kinetically stable mixtures such as certain liquid dispersions typically do not show phase separation signs during the shelf life of the product. But, addition of fragrance compounds can rapidly cause instability of these materials and can result in cloudiness, flocculation and

eventual phase separation. In order to maintain product integrity these dispersions and emulsions must be analyzed for stability in order to predict the shelf life and optimize the formulation. In this study, we show how a Multiple Light Scattering (MLS) technique can be used to quickly and accurately determine destabilization phenomena such as sedimentation, creaming, flocculation as well as complete phase separation. Quantifying these kinetics will provide insight into long term stability and allow the operator to quickly modify any defect in the formulation rather than wait days or weeks for shelf- and bottle-tests to complete. Here, we will show a stable liquid detergent formulation is modified once a perfume is added as well as an optimized perfume formulation. Overall stability results will show how stability of varying fragrances will affect the short- and long-term stability of these formulations, providing not only a resource for fast formulation optimization but for advanced long-term shelf life studies.

8. **Continuous Production of Sugar Fatty Acid Ester from 100% Biorenewable Materials using Heterogeneous Resin Catalyst.** Tomone Sasayama[1] and Naomi Shibasaki-Kitakawa[2], *[1]Dept. of Chemical Engineering, Tohoku University, Japan; [2]Tohoku University, Japan*

Sugar fatty acid ester (SE) is used as a food emulsifier for bakery and confectionery products, but is industrially produced from refined sugar and fatty acid methyl ester (FAME) via a complicated batch process with homogeneous base catalyst. Especially, one of feedstocks, FAME, is commonly synthesized by refined palm oil and methanol from fossil fuel. Due to the use of FAME, toxic methanol is by-produced during the SE production and must be removed from the final product to meet the standard for food additives. We have already proposed a novel continuous process to efficiently synthesize fatty acid ethyl ester (FAEE) from unutilized biomass, distillate and bioethanol using heterogeneous resin catalyst. Thus, by using not FAME but our FAEE as feedstock, SE can be produced more safely from 100% biorenewable materials without by-production of toxic methanol. In addition, the SE production cost would be reduced by using cheaper crude sugar instead of refined sugar. In this research, SE was produced by the continuous production process using a reactor packed with the heterogeneous resin catalyst from 100% biorenewable materials, FAEE and crude sugar. The SE yield was kept almost constant at 45% in a residence time of 1.5 h at 60°C and atmospheric pressure. The yield was almost the same as that from refined sugar and FAME. Thus, this process using the resin catalyst enabled an industrial SE production from 100% biorenewable materials.

9. **Far-from-Equilibrium Dynamic Interface Spontaneously Generated in Drying and Mixing Processes of Two Miscible Solvents.** Kouichi Asakura*, Haruka Watanabe, Taisuke Banno, and Shoji Takekawa, Keio University, Japan

In near equilibrium conditions, any solutions consist of two miscible solvents do not spontaneously generate interface to make the system divided into some phases. However, during the drying process of a sessile droplet of a binary mixture such as aqueous ethanol solution on a solid substrate, one can see the spontaneous generation of spatial inhomogeneity of the content to induce Marangoni flow, capillary flow, diffusive

transport, and inhomogeneous evaporative loss. The same phenomena are also observed when the sessile droplet of water and ethanol collide with each other.

The interplay of these phenomena in far-from-equilibrium conditions leads to generate dynamic behavior unlike the interface between two immiscible solvents in the equilibrium condition. In the present study, macroscopic and microscopic observations were conducted on the spontaneous generation of the dynamic interface. Some sunscreens contain binary mixture solvent. We assumed that the dynamic behavior is generated during the drying process of applied sunscreen layer to influence on the sun protection efficacy.

A UV-B absorber, ethylhexyl methoxycinnamate (EHMC), was dissolved in a binary mixture of isododecane and ethanol, and the solution was spread on a quartz plate. A reference experiment was conducted by preparing isododecane solution of EHMC. Although isododecane and ethanol are miscible with each other, the dynamic interface was generated during the drying process. Deposited EHMC was more likely to deposited larger area on the quartz plate after the completion of drying when the binary mixture sample was used, and the efficient spreading may be induced by the dynamic behavior.