

AFTERNOON

S&D 1: Surfactants in Oil and Gas

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

New Developments in Chemical EOR. Upali Weerasooriya, Gary Pope, The University of Texas, Austin, Texas, USA

Significant advancements have been made in the area of new systems for Chemical EOR. These high performance systems have been designed with special emphasis on cost effectiveness.

Designing Surfactant Formulations for Oil Recovery from a High Salinity Reservoir: Single-well Test. T-P. Hsu, B-J. Shiau, P. Lohateerapara, J. H. Harwell, B. L. Roberts, University of Oklahoma, Norman, OK, USA

Mature reservoirs containing high total dissolved solids (TDS) make the design of a surfactant/ polymer (SP) flood extremely difficult because anionic surfactant solution tends to precipitate and separate by multivalent cations, such as Ca²⁺ and Fe²⁺. The most promising surfactant mixtures incorporated cosurfactants and co-solvents which promote rapid coalescence under Winsor Type III conditions while maintaining solution stability over extended period. The surfactant/polymer formulations were optimized in the sand-pack experiments and coreflood tests using Berea sandstone, site crudes and brines at target reservoir temperatures. The selected surfactants show impressive oil recovery, ranging from 46 % to 89% of the residual oil (Sor) by the flood with total surfactant concentration of 0.5 wt% or less. Based on this success, a field single-well test was conducted at this mature field (a TDS of 185,000 mg/L) in summer of 2011. The test is a technical success and confirms the effectiveness of the high-salinity surfactant-polymer formulation. Approximately 72 % of the residual oil was mobilized using the chemical tracer data. A pilot test at the same reservoir is scheduled to initiate in November of 2011.

Alternative Biofuel from Palm oil-Diesel Based Reverse Micelle Microemulsion. Noulkamol Arpornpong¹, David A. Sabatini², Sutha Khaodhjar³, ¹International Postgraduate Programs in Environmental Management, Chulalongkorn University, Bangkok, Thailand, ²Schools of Civil Engineering and Environmental Science, University of Oklahoma, Norman, Oklahoma, USA, ³Department of Environmental Engineering, Chulalongkorn University, Bangkok, Thailand

Increased environmental awareness and depletion of resources are driving industry to develop viable fuels from renewable resources. Vegetable oil reverse micelle microemulsions (w/o) formed by low-energy emulsification can be considered as an alternative method for reducing vegetable oil viscosity and used as a renewable biofuel. The objective of this research is to formulate reverse micelle microemulsions of vegetable oil and diesel fuel blended with ethanol using various types of surfactants and co-surfactants. Fuel properties such as phase behavior, the stability against crystallization, and kinematic viscosity were investigated. The initial results indicated that addition of surfactants and co-surfactants dramatically affect miscibility between ethanol and palm oil/diesel blend. The kinematic viscosity and crystallization temperature of the systems were also influenced by the structure of surfactant. The unsaturated hydrocarbon surfactant had the greater affect on the kinematic viscosity reduction than the saturated hydrocarbon surfactant with reflectively similar structure. The biofuel crystallization temperature decreased with the addition of unsaturated hydrocarbon surfactant. Co-surfactants with different carbon chain lengths and branched showed less affect on the phase behavior and viscosity of the system.

An Application of the Hydrophilic-Lipophilic Difference Concept in Surfactant Formulations for Enhanced Oil Recovery. P. Lohateeraparp¹, B. Shiao², J. Harwell¹, ¹Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, OK, USA, ²Mewbourne School of Petroleum and Geological Engineering, University of Oklahoma, Norman, OK, USA

The hydrophilic-lipophilic difference (HLD) method is used in formulating microemulsions. The modified HLD equation contains terms for the salinity of the aqueous solution (S), the equivalent alkane carbon number (EACN) of the oil, a surfactant head group parameter (K), the characteristic curvature of the surfactant molecule (Cc), and functions for co-surfactant or alcohol (f(A)) and temperature ($\alpha_T \Delta T$). In this work, the HLD concept has been applied for surfactant enhanced oil recovery (EOR) using a Cc determination method proposed by Acosta (J Surfact Deterg (2008) 11:145–158). Several microemulsion systems that have an optimal salinity close to the original reservoir brine salinity have been designed using this approach. The interfacial tension and the stability of surfactant and surfactant/polymer solutions in brine from studied reservoirs are evaluated at reservoir temperature and compared to predictions from the Acosta method. Finally, one dimensional sand pack and core flood tests are conducted to determine the performance of the microemulsion systems.

Green Agents to Confront Petroleum Oil Spills. Carl Podella, Michael Goldfeld, Advanced BioCatalytics Corporation, USA

Yeast stress protein form protein-surfactant complexes (PSC) with synthetic surfactants. PSCs display enhanced surface activity, compared to the same surfactants taken alone, and activate degradation of organic contaminants by naturally present microorganisms. A suite of agents was developed in response to the Mexican Gulf oil spill. Some of these herd oil spill to oil-absorbing boom, solely due to tangential surface flows emerging from the point of inception of the agent and to the absorbing boom. Others proved efficient as petroleum oil dispersants. Still others serve as heavy duty solid surface washing agents for cleaning ships, equipment, booms, and beach sand contaminated with petroleum oil. They are also applied in cleaning of the ocean chemical cargo tanks and have been certified by the International Maritime Organization (IMO) for these applications worldwide. Accell® Clean DWD dispersant and Accell Clean SWA surface washing agent passed efficiency, toxicology and biodegradability tests by independent certified labs and were included in the US EPA National Contingency Plan (NCP) listings. Yet another product crafted on the same principles, showed an accelerated biodegradation of the total petroleum hydrocarbons (TPH) in ocean water and soil samples.

Optimizing the Formulation of Vegetable Oil Reverse-Micelle-Microemulsion Biofuel at Low Temperature Using Mixed Surfactant Systems. C. Attaphong, L. Do, D. Sabatini, The University of Oklahoma, Norman, Oklahoma, USA

Environmental considerations and current energy shortages have led to increased use of vegetable oil as a source of renewable fuel. Vegetable oil reverse-micelle-microemulsions have been evaluated as an alternative method of reducing vegetable oil viscosity while avoiding the glycerol byproducts and its environmental problems. From our previous study, a nonionic surfactant and cosurfactant systems were formulated to achieve single phase Winsor Type II microemulsion fuels even at low temperature (-20°C). Therefore, the objective of this study is to minimize the amount of surfactant required for single phase microemulsions using the mixed surfactant systems with the goal of formulating cost-effective and temperature-insensitive surfactant systems. In addition to the phase behavior, fuel properties, such as viscosities and combustion properties of non-edible vegetable oil-based microemulsion fuels, have been studied to compare with those of edible vegetable oil-based microemulsion fuels and neat diesel.

Surfactant Enhanced Oil Recovery in Oil-Wet Reservoirs with High Permeability Contrast. Robert Feng Li¹, Aparna Raju Sagi¹, Maura Puerto¹, George J. Hirasaki¹, Clarence A. Miller¹, Mehdi Salehi², Charles Thomas², Jonathan Kwan³, ¹Rice University, USA, ²TIORCO, USA, ³KinderMorgan, USA

Much previous research on surfactants for enhanced oil recovery has emphasized water-wet sandstone formations. However, great potential for increasing recovery exists in carbonate reservoirs, which are often oil wet and have high

permeability contrast. For example, many carbonate formations are fractured with high-permeability fractures constituting a small fraction and low-permeability matrix a large fraction of pore volume. Waterflooding recovers oil from the fractures but not from the oil-wet matrix. In this case both low interfacial tensions and wettability alteration can contribute to recovery, and gravity is an important driving force for flow in the matrix. Moreover, foam can be used for mobility control to assure that the injected surfactant solution sweeps a large portion of the fracture network. Examples are given of laboratory work on selecting surfactants for such applications and of challenges which require continuing research.

Surfactant Structure-Performance Correlation in Chemical Enhanced Oil Recovery. S. Solairaj, C. Britton, D. H. Kim, U. Weerasooriya, G.A. Pope, University of Texas at Austin, TX, USA

It is well known that the oil recovery efficiency of chemical enhanced oil recovery (CEOR) depends on microemulsion phase behavior and interfacial tension (IFT). The surfactants needed to obtain good phase behavior and ultra-low IFT vary greatly with oil characteristics and reservoir conditions. Hence, it is often necessary to test many surfactant formulations before finding a highly effective one. Based on both sound principles and extensive experience, one would expect to find a relationship between the optimum surfactant structure, the oil characteristics, the brine, and the temperature. Salager's equation (Salager et al., 1979, Anton et al., 2008) shows it is possible to correlate some of these variables to classical surfactant structure. We now have many new surfactants with widely different structures and many more good formulations with a wider range of oils, temperature and so forth. Thus, it becomes imperative to study the underlying trend and to identify the most important variables affecting the optimum surfactant structure. A new equation is developed using an extensive data set taking into account the effect of propylene oxide (PO), ethylene oxide (EO), temperature, brine salinity and the equivalent alkane carbon number (EACN) of the oil. The new correlation will help in identifying the most important variables and also to improve our understanding of the relationship among variables affecting optimum surfactant structure. In particular, the new equation can be used to predict the optimum carbon number of the surfactant hydrophobe. Results show that larger hydrophobes are needed as either the temperature or the equivalent alkane carbon number (EACN) of the oil increases. The surfactant formulations used for this study include mixtures of sulfate, sulfonate, carboxylate and non-ionic surfactants. The equation can also be used to predict the optimum number of EOs and/or POs to add to these surfactants. This is a new and highly significant advance in the optimization of chemical EOR processes that will greatly reduce the time and cost of the effort required to develop a good formulation as well as to improve its performance.

TUESDAY

MORNING

S&D 2: Advanced Formulation Design: Models and High Throughput Screening

Chair(s): E. Szekeres, Clorox, USA; and P. Depa, Procter & Gamble Co., USA

Molecular Bases for HLD and HLD-NAC. E. Acosta, A. Boza, S. Kiran, University of Toronto, Toronto, ON, Canada

In this presentation we will show how the Hamaker summation procedure can be used to account for the surfactant-surfactant, oil-oil, and surfactant-oil interactions in micellar systems of different curvatures. The net free energy for the formation of oil-swollen micelles is then used to establish a relation between micelle solubilization radius and the alkane carbon number of the oil solubilized. A comparison between the predictions from this molecular model with the HLD-NAC model provides insights into the molecular bases of the HLD and provides a Bridge between the Windsor

R ratio and the HLD.

How to Cope with Screening the Vast Diversity of Surfactants and Detergents? Standardize and Accelerate.

Michael Schneider, Annie Schnyder, Carine Marcos, Chemspeed Technologies AG, Augst, BL, Switzerland

Surfactants and detergents are pivotal additives throughout the chemical industries. R+D organizations get more and more pressure by:- decrease in number of staff, BUT increase in number of projects and decrease in time-to-market-limited amount and quality of data caused failures in development with substantial delays / failures- significant lack of reproducibility and traceability Chemspeed's EMULSIFIER for fully automated and controlled formulation, application and testing allows to map a wider process space with market proven scalability with inherent quality by design and complete electronic traceability. Case studies from the petrochemical industry, care industry, and agrochemical industry will be presented.

Use of High Throughput Techniques to Aid in the Development of Complex Surfactant Based Formulations. C.J.

Tucker, K. Harris, C. Mohler, A. Behr, The Dow Chemical Company, Midland, Mi, USA

In this presentation we will describe various automated formulation and analytical techniques developed internally or commercially available for the characterization of surfactant based formulations, the use of high throughput methods to formulate and characterize the properties of surfactant based formulations and the integration of these tools to generate predictive models. The tools developed allow for the formulation and mixing of high solids/viscosity systems such as liquid laundry detergents. Characterization tools include image capture and analysis, rheology, surface and interfacial tension, foaming and wetting behavior among others. In addition we have developed a series of screening tools and methods such as cleaning performance, suspensibility and water born coatings additive screens related to specific end use applications. The large amount of well controlled data produced lends itself to the generation of empirical models to characterize how components contribute to and interact with each other to give specific physical and performance properties. Examples will be given to show how we have applied these tools to study the phase behavior of multicomponent systems, optimize formulations for specific applications and the use of these tools to aid the development of new surfactants at Dow.

Investigation of Structure-Fundamental/Functional Property Relationships of (Bio)-surfactants for a Rational Design of their Preparation and Use in Food and Non-food applications. Hary Razafindralambo, University of Liege, Gembloux Agro-Bio Tech, Gembloux, Belgium

(Bio)-surfactants are among the most versatile compounds in our planet, either in nature or in biological systems, as well as in manufactured products. Increasing knowledge on the relationships between their structure, fundamental properties, and functionalities in simple, and thereafter in more complicated models, are therefore the key factor on their rational preparation and use for any applications. In the present communication, the effect of different structural entities of (bio)surfactants, especially Carbohydrate-based amphiphilic compounds, including monomeric, oligomeric, and polymeric surfactants, on their interfacial properties at short time (under dynamic conditions) and long time (at the equilibrium), and the impact of such fundamental properties through physico-chemical parameters on the formation and stability of colloidal systems (micelles, foams, emulsions) will be presented. Some perspectives in their applications will be discussed.

Effects of Headgroup Flexibility in Anionic-Nonionic Mixed Micelles. Louis Jackson, Brian Grady, Colby Townsend, Ralph Anglade, University of Oklahoma, Norman, OK, USA

In this study interactions between nonionic surfactants (1) nonyl-,octyl-, and heptylmaltopyranoside (maltoside) mixed with either sodium n-alkyl sulfate or sodium n-alkanecarboxylates were investigated. The mixing behavior of the surfactant systems were evaluated with the one-parameter Rubingh model. Our previous studies showed that an increase in nonionic headgroup flexibility causes less synergistic behavior with respect to mixed-micelle formation which was attributed to a decrease in electrostatic self-repulsion of the ionic surfactant in the mixed micelles caused by a better ability of the flexible molecule to screen charge. Through the evaluation of mixed micelles with the even larger and less flexible maltoside head groups, clarity in proposed wrapping mechanisms and molar ratio dependent molecular interactions will be further evaluated.

Chair(s): E. Szekeres, Clorox, USA; and P. Depa, Procter & Gamble Co., USA

Innovative Approach to Increasing Actives in Solid Product Forms. S. Mohammed, Evonik Degussa Corporation, Piscataway, NJ, USA

Solid product forms exist in many areas within Household Care. These can come as bars, blocks, sticks, tablets, and coated sheet. However formulation flexibility is limited in these systems. Components that are most desirable, typically offer little or no contribution to structure reinforcement of the bulk solid. However these actives and axillaries are very critical to product efficacy. Several successful approaches in structure reinforcement and stabilization have been developed using specific grades of both fumed and precipitated silica. These products function to stabilize liquid or semi liquid components within the solid product form at varying temperatures. These products function by inhibiting the transfer of components throughout the solid form. This approach prevents softening, de-lamination and other stability problems from occurring. This allows the formulator the ability to move beyond current limits, enabling higher levels of actives or axillaries while maintaining a stable product form.

Cellulase Enzyme Technologies and Their Applications in Laundry Products. T.J. Burns, N.E. Prieto, Novozymes North America, Inc., Franklinton, NC, USA

Cellulases comprise a diverse family of enzymes which, in Nature, contribute collectively to the total degradation of cellulose. Today, specific cellulases are used in modern detergent laundry products primarily for effects related to fabric care, whiteness and cleaning. The fabric-care cellulases provide consumer-recognizable benefits to cotton fabrics through repeated wash-and-wear cycles, which is of particular interest to consumers seeking products that extend the useful life of their clothing. Cellulases used for cleaning purposes provide soil-release effects that are a viable alternative to traditional technology based on high doses of surfactants and other actives. This paper will describe the differences between cellulases used in laundry detergents, both mechanistically and in practical use. We will also show how cellulases are used at various stages in a garment's life cycle to deep-clean, to maintain whiteness and brightness, and also to restore a newer appearance. Lastly, new developments and trends will be discussed, demonstrating how cellulase technology for cleaning has evolved to provide modern, relevant applications, and how these enzymes can be used to improve the "sustainability profile" of cleaning products.

Study of the Enzyme Storage Stability in Liquid Detergent with Thermodynamic Analysis. Takayuki Kurokawa, Hirotsugu Ogura, Hiroaki Shindo, Takahiro Okamoto, Hiromitsu Takaoka, Lion Corporation, Edogawaku, Tokyo, Japan

Low temperature washing is one of the biggest challenges in the laundry detergent business because of a sustainable society surge. Utilizing highly functional ingredients like enzymes to achieve satisfactory low temperature detergency is important. We have been studying the utilization of high active protease on commercial liquid detergents, but liquid compatibility was a key issue to be solved. While investigating into enzyme storage stability improvements of formulations, we found thermodynamic analysis by Differential Scanning Calorimetry was a very valuable and useful methodology to predict enzyme stability and design detergent formulations having good compatibility with enzymes. We confirmed T_m (temperature at maximum peak of transition from the folded to unfolded state) correlated highly with storage stability. Generally, residual protease activity is measured after long term incubation, but we can reduce the screening time of stabilizers with this thermodynamic analysis. When we added general enzyme stabilizer like calcium ions in commercial liquid detergents, we observed a T_m shift to the higher value. This means that these stabilizers improve heat stability of protein conformation. We would also like to report other stabilizing mechanisms by another enzyme stabilizer focusing on ΔH (enthalpy).

Biodegradable Fabric Softener Active with Improved Dispersibility. D. Parrish¹, M. Hisamoto¹, J. Hildebrand¹, G. Schick², ¹Evonik Goldschmidt Corporation, Hopewell, VA, USA, ²Evonik Stockhausen GmbH, Krefeld, Germany

Biodegradable fabric softeners derived from triethanolamine (TEA) and fatty acid raw materials have been used globally for over 20 years. Like its predecessors, ester quats are typically synthesized from tallow derivatives. The resulting products, which are solids or pastes at room temperature, must be stored, shipped, and processed at high temperatures, usually at or above 50 °C. Liquid TEA esterquats manufactured from highly unsaturated vegetable oils and tallow oleic fatty acid are not suitable for the manufacture of traditional fabric softener dispersions due to formulation instability. In order to reduce the energy input needed to heat raw materials and the time input needed to cool finished dispersions while allowing for the manufacture of robust, stable products, TEA esterquats which are liquid and formulable at ambient temperatures have been developed. The synthetic procedures and comparative performance results will be discussed.

AFTERNOON

S&D 3: General Surfactants I

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

Interaction of Glycylglycine with Surfactants in Aqueous Medium. Anwar Ali¹, Nizamul Haq Ansari², Nisar Ahmad Malik¹, ¹Jamia Millia Islamia, New Delhi, Delhi, India, ²Zakir Hussain College, University of Delhi, New Delhi, Delhi, India, ³Jamia Millia Islamia, New Delhi, Delhi, India

The partial molar volumes, Φ_v^0 , transfer volumes, $\Phi_v^0(\text{tr})$ of glycylglycine from aqueous to aqueous surfactant, partial molar expansibilities, Φ_E^0 , hydration numbers, n_H , partial molar adiabatic compressibilities, Φ_k^0 , and limiting molar conductivities, Λ_m^0 , were calculated by using densities, ρ , ultrasonic speeds, u , and specific conductivities, k , of 0.02, 0.04, 0.06, 0.08, and 0.10 m (mol kg⁻¹) glycylglycine (Gly-Gly) in 0.005 m aqueous solutions of cetylpridinium chloride (CPC) and cetylpridinium bromide (CPB) at 298.15, 303.15, 308.15, and 313.15 K. Positive Φ_v^0 and $\Phi_v^0(\text{tr})$ values indicate the presence of strong solute-solvent (Gly-Gly — aqueous surfactant) interactions. Higher values of Φ_v^0 and $\Phi_v^0(\text{tr})$ in presence of CPC than in CPB are attributed to the greater charge density of Cl⁻ than Br⁻, resulting in greater interaction of Cl⁻ than Br⁻ with (NH₃⁺, COO⁻) groups of Gly-Gly. The values of $T(\partial^2\Phi_v^0/\partial T^2)_p$ for Gly-Gly are positive, indicating that the solute acts as structure-maker in presence of both the surfactants. Moreover higher values of n_H for Gly-Gly in presence of CPB than in CPC again support that the ions of CPC interact more strongly with (NH₃⁺, COO⁻) groups than do the ions of CPB. Φ_k^0 and Λ_m^0 values for the studied systems also support the above findings.

Staining of Cotton Fabric Before and After Finishing with Admicellar Polymerization. Srinivas Hanumansetty¹, Jayanth Maity¹, Pratik Kothary¹, Jannefer Ma¹, Edgar O'Rear¹, Nantaya yanumet³, ¹School of Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, Oklahoma, USA 73019, ²Institute of Applied Surfactant Research, Norman, Oklahoma, USA 73019, ³Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand

Admicellar polymerization (AP) is used to form polymeric thin films such as polystyrene films on substrates like silica and alumina. Recently, AP has been expanded into the textile area with application of finishes to impart functionality like flame retardancy, anti-microbial activity blocking of UV radiation, and water repellency. We used admicellar polymerization to form thin fluoropolymer films on knit cotton fabrics. Fluoropolymeric films can make cotton a

multifunctional textile material having superhydrophobicity and lipophobicity. Treated cotton fabric with fluoropolymer by AP was compared with commercially available fabrics for performance. The performance of the fabric is tested for water and oil repellency using several testing methods including the drop test method, spray test and contact angle measurements. Fluoropolymer film formation was examined by scanning electron microscopy and elemental analysis. Reflectance measurements of colored stains were also employed to obtain the stain release and stain resistance properties of treated fabric.

Adsorption and Admicellar Properties of Mixed Anionic Extended Surfactants and a Cationic Surfactant. D.

Panswad^{1,4}, D.A. Sabatini², S. Khaodhiar³, ¹Center of Excellence for Environmental and Hazardous Waste Management (EHWM), Chulalongkorn University, Bangkok, Thailand, ²School of Civil Engineering and Environmental Science, University of Oklahoma, Norman, Oklahoma, USA, ³Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand, ⁴Department of Environmental Science, Ramkhamhaeng University, Bangkok, Thailand

Anionic and cationic surfactant mixtures exhibit desirable synergism, but are limited by their tendency to form precipitates. Recently, surfactant based surface modification has attracted much attention. This research evaluates the adsorption and adsolubilization of mixtures of anionic extended surfactant with a cationic surfactant. The mixture of cetylpyridinium chloride (CPC), selected as cationic surfactant, with four anionic extended surfactants were studied. Anionic surfactants studied were alkyl propoxylated ethoxylated carboxylate with average carbon chain length of 16 and 17 or 16 and 18 with 4 moles of propylene oxide groups and either 2 or 5 moles of ethylene oxide groups. The adsorption of anionic extended and cationic surfactant mixtures onto silica was evaluated. Phenylethanol, styrene and ethylcyclohexane were used to evaluate the adsolubilization capacities of these mixed surfactant systems. Results show that the plateau adsorption of mixed anionic extended and cationic surfactant occurred at lower surfactant concentration than that of the CPC alone, although the maximum adsorption capacity of CPC was not enhanced in our mixed surfactant systems. Moreover, these mixed surfactant systems show higher adsolubilization capacity than that of the individual surfactant system.

Disinfection Promoting Effect and its Mechanism of Zinc Complex in Laundry. Toshiaki Majima, Yasuyuki Morita, Masahiko Ohtani, Tomonari Suekuni, Takayasu Kubozono, Tomomichi Okano, Lion Corporation, Edogawaku, Tokyo, Japan

Recently, consumers have come to pay much attention to the hygiene of laundry, and their desire to remove "invisible stain" such as bacteria and odor from laundry are increasing. We have searched for materials to increase the disinfecting effect of laundry detergent. Zinc methylglycinediacetate complex (Zn-MGDA) increased disinfecting activity of laundry detergent with a common bleach activator, alkanoyl oxybenzene sulfonate (OBS). Zn-MGDA had no activity without OBS, and the chemical interaction between Zn-MGDA and OBS was not observed. We assumed that Zn-MGDA and OBS worked independently on bacteria, and Zn-MGDA promoted some effect of OBS. We confirmed that Zn-MGDA promoted damage of bacterial cell membranes from OBS. In addition, Zn-MGDA was superior in membrane permeability, so we analyzed the action of Zn-MGDA in cell membranes. Zn-MGDA promoted membrane permeation of organic peracid which was derived from OBS, and Zn-MGDA inhibited activity of intramembranous enzymes which could degrade organic peracid. We also want to report the structure-activity relationship in similar zinc complexes. Zn-MGDA is composed of naturally-occurring metal ion and biodegradable ligand, and works even at low temperature and low concentration. Therefore Zn-MGDA is the new eco-friendly detergent ingredient.

Properties of Guar Gum and Effect of Surfactants. L. Ciemnomolonski, S. Adamy, Church & Dwight, Co. Inc., Princeton, NJ, USA

The effects of anionic, cationic, nonionic and green surfactants on the properties of guar gum, such as adsorption and rheology, were studied. The structural properties of the surfactant and effect on guar gum are also discussed.

Low Temperature Synthesis of Fatty Acid Amide (Erucamide) from Fatty Acid and Urea Using Micro-emulsion. Rajinder Pal Singh, Neeraj Praphulla Awasthi, Avinash Sharan Khare, Harcourt Butler Technological

Institute, Kanpur, Uttar Pradesh, INDIA

ABSTRACT A new method for synthesis of fatty acid amide using water-in-oil micro-emulsion has been studied in the present paper. Recently a method for the synthesis of erucamide has been reported using erucic acid and urea at atmospheric pressure, however, the drawback is poor color of the product and formation of byproducts due to high temperature processing. In the present study the stable micro-emulsion was prepared by optimization of the conditions which were obtained using 46 % (w/w) of iso-amyl alcohol, 40 % (w/w) of soy bean oil, 7 % (w/w) of surfactant (sodium lauryl sulphate) and 7 % (w/w) of water. The optimum conditions for above prepared erucamide were 1:4 molar ratio, 240 min reaction time, 115 C temperature with 20 ml microemulsion. The outcome of the present study is that we can improve upon this method to get yield comparable to any other commercial method with lighter colour and minimum formation of any side reaction product.

Biocide and Preservative Boosting with Use of Chelating Agents. P. Kincaid, W. Parry, AkzoNobel Functional Chemicals, Chicago, IL USA

Biocides such as quaternary ammonium compounds are used for disinfectants in the I&I industry and preservatives in the personal care industry. Bacteria and fungi growth can further be reduced with the use of chelating agents in conjunction with the biocide. Chelates like ethylenediaminetetraacetic acid (EDTA) have long been used as a biocide boosting agent. Cell membranes are composed of metal ions which strengthens the cell wall, hindering the activity of the biocide. A chelating agents removes the metal ions from the cell wall improving biocide penetration of the membrane. A biobased chelating agent, glutamic acid diacetic acid (GLDA), was found as an effective biocide booster that reduces . A small addition of GLDA can greatly reduce biocide loading. A reduction of biocide loading greater than 90% was seen with GLDA loadings as little as 1200 ppm. GLDA is efficient in boosting biocide effectiveness on gram positive, gram negative, and fungi. New eco-friendly formulations can take advantage of improved boosting with GLDA. The flexibility added allows for cost savings and a smaller eco-footprint.

Hydroxyl-modified Cationic Lipids with Carbamate as Gene Delivery. Weihong Qiao, Zhibo Zheng, Wenhui Qu, Dalian University of Technology, Dalian, Liaoning, China

Hydroxyl-modified cationic lipids 1, 2, 3 and 4 were designed and synthesized. Liposomes (lipid/DOPE=1/1, m/m) were prepared by conventional thin film evaporation and ultrasonic method. Size and Zeta potential of lipoplexes were tested at different mass ratios which were 1/1, 2/1, 3/1, 4/1, 6/1 and 8/1, respectively. The transfection and cytotoxicity were investigated at the ratios above. Gene transfection efficiency of liposomes 1, 2 and 3-DNA complexes was approximately equal to that of Lipo2000-DNA complexes, and a lower cytotoxicity compared with Lipo2000. And relationship of Size, Zeta potential, structure and transfection was discussed.

Crystallization and Polymorphism in Binary Mixtures of Capric and Lauric acid. Stine Rønholt¹, Jacob Judas Kain Kirkensgaard², Kell Mortensen², Dérick Rousseau³, Jes Christian Knudsen¹, ¹Department of Food Science, Faculty of LIFE Sciences, University of Copenhagen, Copenhagen, Denmark, ²Department of Basic Sciences and Environment, Faculty of LIFE Sciences, University of Copenhagen, Copenhagen, Denmark, ³Department of Chemistry and Biology, Ryerson University, Toronto, Ontario, Canada

Capric (C10) and lauric (C12) acids provide enhanced skin and cornea penetration as well as a greater affinity for lipids in the upper skin layer compared to commonly used penetration enhancers [doi:10.1248/bpb.31.1766 and 10.1081/DDC-120015355]. In this study, combined X-ray diffraction (XRD) and differential scanning calorimetry (DSC) is used to characterise the crystallization and thermal phase behaviour of pure and mixed C10 and C12 systems. In parallel, polarized light microscopy (PLM) is used for morphological visualization. In agreement with previous related studies, complex phase behaviour with the existence of several overlapping peaks in the DSC spectra were found [doi:10.1016/j.chemphyslip.2008.09.006]. The liquid-solid phase transition temperature was strongly dependent on blend composition. Structural XRD data following these phase transitions and their polymorphic characteristics as a function of blend composition and temperature revealed structural information about lamellar packing and crystallization. PLM showed different crystal morphologies and crystallization behaviour due to changes in the lamellar packing of the fatty acid chains in agreement with the XRD data. We discuss this complex polymorphism in

relation to the solid-state miscibility behaviour of binary blends.

WEDNESDAY

MORNING

BIO 4/S&D 4: Biobased Surfactants

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

Use of Enzymes to Prepare Biobased Surfactants: Overview. D.G. Hayes, University of Tennessee, TN, USA

Biobased surfactants, employed as emulsifiers, wetting agents, plasticizers, and agents for lowering surface and interfacial tension, are becoming increasingly popular for use in foods, cosmetics, pharmaceuticals, and other industries. This trend is driven by the increase of cost for petroleum, the enhanced environmental sustainability provided through use of renewable resources, and the increased abundance of bio-based feedstocks resulting from development of biorefineries. Although most biobased surfactants are manufactured by chemical means, their preparation via bioprocessing is very attractive for future employment due to further enhancement of sustainability and potential savings in energy, downstream purification, and disposal costs. This presentation provides an overview of current research and development to prepare biobased surfactants via enzymatic reactions in nonaqueous media using enzymes such as lipases and glucosidases.

Vegetable Oil Based Surfactants: Physical Chemistry and Performance Properties. George Smith, Huntsman Corporation, The Woodland, Texas, USA

Modern surfactants are based on either naturally derived or synthetic feedstocks. Natural surfactants are typically based on alcohols derived from coconut or palm kernel oil whereas synthetic surfactants are based on ethylene derived from gas, oil and coal. This presentation will discuss the physical chemical properties of surfactants based on vegetable oils like soy and canola as low cost, locally grown alternatives to conventional natural and synthetic based surfactants. A series of vegetable oil based surfactants were prepared by reacting different natural oils like soy and canola with polyols derived from glycerin. The properties of vegetable oil derived surfactants have been compared to more conventional natural alcohol ethoxylates (AE). In general, vegetable oil surfactants have a lower CMC, cloud point and foam potential than AEs due to the longer alkyl chain length. Surface and interfacial tension depend on the alkyl chain distribution and the degree of polymerization on the polyol. Vegetable oil derived surfactants show good detergency in single surfactant and multi-component systems.

Rhamnolipid Production and Applications. M. Sodagari, Y. Chen, S.S. Dashtbozorg, N. Callow, L.-K. Ju, The University of Akron, Akron, OH, USA

Rhamnolipids are among the best known and studied biosurfactants produced by bacteria. The glycolipid biosurfactants have many potential industrial, environmental and medical applications. The common aerobic fermentation for rhamnolipid production is complicated by the highly foaming nature of the fermentation broth. We have proposed to develop an alternative production route via denitrifying *Pseudomonas aeruginosa*. Highly productive strains have also been selected. The denitrification route, nonetheless, has also met various challenges. We will present our recent work with a productive strain by both aerobic and denitrifying processes. Under aerobic conditions about 70 g/L of rhamnolipids can be produced at the volumetric productivity of 0.35 g/L-h and specific productivity of 0.023 g/g-h, with

a yield of about 40% from vegetable oil. Further improvement on volumetric productivity will require more fundamental breakthroughs in foaming control. A process to collect and purify the rhamnolipids from the fermentation process has been developed. We have explored applications of rhamnolipids in modification of fungal morphology, affinity foaming for enzyme purification, reduction of bacterial attachment for biofilm formation, and inclusion in wound dressing. We will briefly describe some results of these applications.

Cyanophycin–based Lipo–dipeptides as Biosurfactants. J.A. Zerkowski, D.K.Y. Solaiman, ERRC, ARS, USDA, Wyndmoor, PA, USA

Cyanophycin (Cp) is a polypeptide that can be obtained by growing cyanobacteria on renewable feedstocks such as agricultural byproducts. The structure consists primarily of an aspartic acid backbone with pendant arginines, and this beta–Asp–Arg dipeptide can be isolated enzymatically. We propose that it can serve as a useful building block for the construction of surfactants. This presentation will describe the synthesis and surfactant properties of several structural variants of the Cp dipeptide with hydrophobic chains, derived from fatty acids, attached. One, two, or three lipophilic chains can be attached at varying sites while still retaining a charged unit to aid water solubility.

Fermentative Production and Interfacial Properties of Glycolipid Biosurfactants, Cellobiose Lipids by *Cryptococcus Humicola*. Tomohiro Imura, Tomotake Morita, Tokuma Fukuoka, Dai Kitamoto, Research Institute for Innovation in Sustainable Chemistry, National Institute for Advanced Science and Technology (AIST), Tsukuba, Ibaraki, Japan

Biosurfactants (BS) produced by a variety of microorganisms show unique properties compared to petroleum–based synthetic surfactants. The numerous advantages of BS have prompted applications including the food, cosmetic, and pharmaceutical industries. Among BS, glycolipid–type BS are promising, because they are abundantly produced by yeast fermentation and show unique surface–active and self–assembling properties. Cellobiose lipids (CL) have also been promising, due to the high antimicrobial activity. Recently, *Cryptococcus humicola* was reported to produce a new type of CL. The new CL is an asymmetric bolaform surfactant that has two different polar heads at opposite ends of the hydrophobic core, and is thus attractive from the viewpoint of interfacial properties. However, little is known on the properties of bolaform biosurfactant, due to the low production yield. We thus focused our attention on the improvement of CL production using different strains of *Cr. humicola*, and on the interfacial characterization of the glycolipids. *Cr. humicola* JCM 1461 efficiently produced the CL, tetra–acetylated cellobiose bearing 2–hydroxy–hexadecanoic acid. The present CL exhibited not only a high surface activity but also unique supramolecular gel formation in various solvents.

Synergetic Interactions among Greener Surfactants and Their Synergistic Interactions with Enzymes. P. Somasundaran, J. Wu, S. Lu, M. Chin, NSF I/UCR Center for Particulates and Surfactants, Columbia University, New York, NY, USA

Due to the increasing demand for environmentally benign reagents, greener surfactants are recently receiving the warranted attention. The unique surface activity along with their biodegradability makes this group of surfactants leading candidates as the next generation reagents. One of the unique properties of greener surfactants is the synergistic interactions between each other as well as conventional surfactants. In this work, we selected sugar based greener surfactant alkyl glycosides and conventional surfactant sodium dodecyl sulfonate to explore their potential synergism in mixtures. A range of techniques including surface tensiometry, fluorescence spectroscopy, ultrafiltration, and analytical ultracentrifugation (AUC), were employed to obtain information on the micellization behavior of the mixture. The interaction parameter, monomer concentration, micellar size and shape distribution were obtained for the mixed surfactant system as a function of total surfactant concentration as well as mixing ratio to obtain a full understanding of their aggregation behaviors. Interestingly, coexistence of two types of micelles was identified for the first time and a model is proposed to explain such coexistence based on the interactions between the two types of surfactants. Since enzymes are used along with surfactants, Interactions between a surfactants and enzymes also have been studied. Interestingly, even enhancement of surface activity was observed which was attributed to be the result of micelle/protein interactions that induce a more flexible structure that is more conducive to lowering reaction–energy barriers. These findings are useful for optimizing the composition of mixed surfactant systems and enhancing the synergetic efficiency of the system to achieve more effective and economical formulations.

Sophorolipids and Sophorolactone: Properties and Application Potential. D.W.G. Develter, Ecover Belgium NV, Belgium

Glycolipids can be produced by bioconversion of native and renewable feedstocks such as rapeseed oil. Sophorolipids for example are currently finding their way to the detergent market. These attractive surfactants combine green oleochemistry with an impeccable environmental profile and excellent hard surface cleaning. A new to literature sophorolipid species is described. The interesting physicochemical behaviour of sophorolactone, their surface modification properties and some accompanying promising applications are reported.

Formulating with Bio and Biobased Surfactants. E. Acosta, M. Baxter, University of Toronto, Toronto, ON, Canada

Formulating or reformulating products to incorporate bio or bio-based surfactants is, in most cases, not a trivial task. In this presentation we will explain the use of the HLD-NAC framework to characterize the hydrophobicity of bio and bio-based surfactants and the design of surfactant mixtures to achieve specific performance targets. Literature examples of formulations used in pharmaceutical and environmental applications will be used to illustrate these principles. Finally, an example on the characterization and use of surfactants extracted from waste biomass will be discussed.

Home Care Cleaning Products based on Renewable Materials with Novel Added Benefits. P. Stuu, Purac, Purac, Gorinchem, Zuid-Holland, the Netherlands

Within the home care area there is a clear and continuous trend towards more safe and sustainable ingredients and detergent formulations. Consumers expect safer products and more environmentally friendly products. The origin of more and more raw materials for home care and industrial products can be found in renewable feedstocks like sugars and starches. From these feedstocks, biobased products like lactic acid and derivatives can be produced. They bring added benefits and have a positive impact on CO² emission reduction. Next to this, these products are generally biodegradable and safe for humans and the environment. Lactic acid is currently used in a wide variety of home care products because of its functional benefits in cleaning, descaling and anti-bacterial properties. Current products include toilet bowl cleaners and dish wash products. Recently a novel product for the home care and industrial cleaning market has been developed. This novel product is solid, is mixable with other ingredients like surfactants and perfumes and can be molded into different shapes. During usage the material gradually hydrolyses, delivering lactic acid and other cleaning actives to the substrate. This way, longer lasting cleaning benefits are obtained by a renewable, functional material.

Modified Activated Sludge Oil Phospholipids as Potential Bio-based Surfactants. P.J. Pham, R. Hernandez, W.T. French, W. Holmes, Dave C. Swalm School of Chemical Engineering Mississippi State University, Mississippi State, MS USA

Phospholipids extracted from activated sludge oil comprise about 20–25%. ³¹P-NMR revealed that the phospholipid profile consists of a variety of phospholipids with phosphatidylethanolamine (PE) present in majority (17–18%) followed by phosphatidylglycerol (4%) and phosphatidylcholine (5%). Chemical modification of the phosphatidylethanolamine head group was primarily accomplished by the acylation/acetylation reaction that involved acetic anhydride and an organic base, triethylamine to convert it into an acetylated form (NAC-PE). The potential as bio-based surfactants of these low polarity phospholipids were explored.

Achieving Effective, VOC Compliant, All-Purpose Cleaner Formulations Using Biorenewable Surfactant Blends. Molly I. Busby, Kirsten K. McNally, Dow Chemical Corporation, Midland, MI 48674, USA

The cleaning industry continues a drive to minimize carbon foot print by using raw materials from biorenewable sources; however, biorenewable surfactants often don't provide optimum cleaning performance by themselves. We have investigated blends of alkylpolyglucosides with DfE compliant non-ionic surfactants as a way to increase use of

biorenewable surfactants in cleaning formulations. The resulting surfactant blends displayed multifunctional properties, excellent alkaline stability, solubility, degreasing, fragrance coupling and ease of formulation. These surfactant blends are suitable for concentrates to minimize shipping costs, conserve energy, provide shelf stability and minimize pollution. Examples of the use of these surfactant blends with solvents, alkaline agents, and chelants to prepare VOC compliant formulations for all purpose, hard surface, and carpet cleaners to meet the 2012 target will be discussed.

New Cyclic C–Glycoside Surfactants Derived from Carbohydrates. Neil A. Burns, P2 Science, Inc., New Haven, CT, USA

P2 is commercializing a new, patent pending, class of cyclic C–glycoside surfactants, made via a highly efficient, one-pot process. The chemistry adheres closely to the principles of green chemistry, including atom economy, step economy, and the use of renewable feedstocks, carbohydrates and renewable vegetable oils. Carbohydrate–based surfactants are an important class of nonionic surfactants that include alkyl polyglucosides (APGs), sorbitan esters (tradenames SPAN and Tween), and methyl ester glucosides (MEGs). In addition to being renewable, carbohydrate–based surfactants have a number of favorable attributes including desirable detergency properties and low toxicity. However, current carbohydrate–based surfactants are generally unstable in due to the use of either a base–labile ester linkage (SPAN, Tween, and MEGs), or an acid–labile O–glycoside linkage (APGs) in their structures. P2's C–glycosides replace these traditional bonds with a more stable *Carbon – Carbon* bond. The resulting family of surfactants, is extremely stable across a wide range of pH and temperature conditions, while performing as extremely efficient surface tension reducers over a full range of HLB's. Applications include household and I&I cleaning, personal care, cosmetics and a range of industrial applications including oilfield, emulsion polymerization, lubricants and agrochemicals.

EAT 4/S&D 4.1: Dispersions, Emulsions, and Foams

Chair(s): A. Wright, University of Guelph, Canada; and C. Rojas, AMCOL, USA

Role of Conformation and Interactions of Hybrid Silicones at Various Interfaces. Ponisseril Somasundaran¹, Parag Purohit¹, Somil Mehta², ¹Columbia University, New York, NY, USA, ²Dow Chemicals, Mumbai, Maharashtra, India

Hybrid silicones are unique due to their distinct simultaneous hydrophobic and hydrophilic properties. Behavior of non-ionic and ionic silicone polymers at various interfaces suggested conformational transition of silicone chains from a linear to a coiled form, that are controlled by interfacial concentrations and interactions with bulk phases. At the oil-water interface, functional groups of silicone polymers interact with water phase whereas siloxane backbone interacts with the oil to form O/W emulsion, with the size distribution and charge of it attributed to play an important role in modifying properties of substrates such as fabrics. With a bimodal droplet distribution of silicone emulsions, the nano-sized droplets can penetrate deeper into the substrate to provide bounciness, while macro-sized droplets can coat the top layer leading to friction reduction. Using Atomic Force Microscopy, we observed the treated cellulose fibers are uniform, well stacked and smoother than the untreated fibers. Spectroscopic analysis of treated fibers using Raman spectroscopy indicates a decrease in fiber stress as a function of modification of silicone polymer and the interaction pH. Our study demonstrates that behavior of hybrid silicones at various interfaces can be tailored by selecting appropriate functional modifications.

Effects of Phase Behavior on Spontaneous Formation of Emulsions/Nanoemulsions and on Emulsion Destabilization. C.A. Miller, Rice University, Houston, Texas USA

Knowledge of equilibrium phase behavior is important for understanding various aspects of emulsion behavior. Recent results using dynamic light scattering are presented showing how both initial morphology and drop size of emulsions/nanoemulsions formed on diluting a w/o microemulsion made with an anionic surfactant differ greatly depending on salinity of the brine used for dilution. The differences are directly related to the effect of salinity on oil-brine-surfactant phase behavior. Possible applications in forming aqueous dispersions of nanoparticles and in

detergency are discussed. The effect of phase behavior in breaking of emulsions is reviewed for emulsions stabilized by surfactants and by compounds such as asphaltenes in crude oil. When solid particles contribute to emulsion stability, addition of suitable inorganic salts or surfactants can often alter the particles' wettability, causing them to leave the interface, which can destabilize the emulsion. Recent examples of this mechanism are shown.

Enzyme-Triggered Aroma Release from Emulsions. B.C. Wong, R.J. Elias, J.D. Lambert, J.N. Coupland, The Pennsylvania State University, University Park, PA, USA

Fine (d~200 nm) sodium caseinate-stabilized eicosane-in-water emulsions were equilibrated with ethyl octanoate (EO) at 28°C as either supercooled liquid droplet emulsions or crystalline solid lipid nanoparticles. Porcine trypsin (0.25%) was added to digest the protein and the destabilization of the dispersions and headspace concentration of EO were measured over time. In the absence of enzyme, liquid droplet emulsions had a lower headspace concentration of EO than solid droplet emulsions (0.5µL/mL vs. 3.5µL/mL). When the liquid droplets were treated with protease there was a steady increase in both droplet size and solid fat content over time as the caseinate was digested and the supercooled droplets began to coalesce and crystallize. After a delay there was a sudden increase in headspace EO associated with the complete crystallization of the eicosane. Solid droplet emulsions were destabilized by protease but there was no corresponding change in solid fat constant or headspace EO. This model system study demonstrates the use of supercooled liquid droplet emulsions as delivery vehicles for hydrophobic solutes with release triggered by the action of digestive enzymes. While the present work is focused on flavor release there are potential applications for nutrient as well as pharmaceutical compound delivery.

Salt Release from Fat Crystal-Stabilized Water-in-Oil Emulsions. S. Ghosh¹, M. Nadine², D. Rousseau³,
¹University of Saskatchewan, Saskatoon, Saskatchewan, Canada, ²AgroSup, Dijon, France, ³Ryerson University, Toronto, Canada

Fat crystal-stabilized water-in-oil (W/O) emulsions were developed as a controlled release matrix for the delivery of salt (NaCl). Emulsions were prepared at 70°C by homogenizing 20% (w/w) water, canola oil, emulsifiers and stabilizing fat, which were then cooled with stirring and stored at room temperature. Glycerol monostearate (GMS), glycerol monooleate (GMO) or polyglycerol polyricinoleate (PGPR) were used as emulsifiers and hydrogenated canola oil (HCO) was added as a continuous phase stabilizer. The release of salt from the water droplets towards the external aqueous phase was measured at room temperature and under heating using a conductivity meter dipped into a glass beaker containing DI water and emulsion stirred at 300 rpm for 2 hr. Pickering-stabilized emulsions (GMS-CO) had the highest encapsulation efficiency (only 2.7% of the total salt released) while GMO-HCO-CO emulsion (partial Pickering and network stabilization) showed highest salt release (24%). Interfacial GMS crystals formed solid shells around water droplets preventing diffusion of salt molecules. In the GMO-HCO-CO emulsion, the presence of water droplets with partial or no interfacial fat crystal coverage led to higher salt release compared to GMS-stabilized emulsions. Both GMS and GMO emulsions showed rapid release of their salt load upon melting of surrounding fat crystals. The PGPR-HCO-CO emulsion, with its smaller droplet size distribution compared to the GMO-HCO-CO emulsion, showed much less salt release (3.6%) confirming the significant influence of emulsion stability and droplet size in controlling encapsulation efficiency of salt in W/O emulsions.

The Influence of Alcohol on Foam Behavior. S.T. Adamy¹, C.F. Neller², ¹Church & Dwight Co., Inc., Princeton, NJ, USA, ²Rutgers University, Piscataway, NJ, USA

Control of foam is typically managed by the addition of materials which are either meant to destabilize the foam lamellae by migrating to the film surface and disrupting the film, or by interfering with molecular coherence at the air-water interface. Low molecular weight materials like octanol have been reported to stabilize or destabilize such coherence, depending on the system, resulting in enhanced or reduced foam stabilization. This study examines the effect of various isomers of octanol on the foaming properties of detergent systems containing an anionic and nonionic surfactant. Studies were performed by use of a SITA R-2000 foam tester, which employed an agitator to produce foam. Studies were performed in both a dynamic way, where the volume of foam was monitored during generation, and in a static way, where the collapse of the foam over time was observed. It was found that foam behavior was dependent on a number of factors, including the concentration of the octanol isomer, as well as the presence of other

materials, like salts, in the system. Differences were seen between systems where the octanol was pre-solubilized in the system and when the octanol was added during foam generation. In the case of pre-solubilization, no foam impairment and even slight stabilization was seen, while injecting the octanol during generation resulted in immediate foam collapse.

Bio-compatible Low Salinity Triglyceride Microemulsions and Detergency. L.D. Do, D.A. Sabatini, The University of Oklahoma, Norman, OK 73019, USA

Vegetable oil (VO)-based microemulsions (MEs) have wide applications in pharmaceuticals, foods, consumer and personal care products. Due to the hydrophobicity and bulky structure of VO, formulating bio-compatible, alcohol free and low salinity VO-based MEs is challenging at best. Pioneering study in our group was able to form alcohol free VO-based MEs using extended-surfactants (surfactants with internal polypropoxylate and/or ethoxylate groups) and achieved high canola oil detergency. However, the required salinity concentrations ranged from 8-14 wt% eliminates the practical use of these formulations. In this work, we will present our development on bio-compatible VO-based MEs with mixed surfactant/linker systems at low salinity concentration (<0.9 wt%) with algae and canola as model oils. Effect of biorenewable surfactants (i.e. sophorolipids, chitosan) on VO-based MEs will be discussed. All ME types were achieved using bio-compatible mixed surfactant/linker systems at less than 0.9 wt% salinity and 0 to 0.5 wt% extended-surfactant at ambient temperature; to our knowledge, reported here for the first time. Solubilization enhancement of some hydrophobic drugs using these MEs will be presented. More than 90% canola oil detergency was achieved within 10 minute at low surfactant concentration (150 ppm), demonstrating the effectiveness and robustness of our formulations.

Effect of Emulsifiers on Micro-and Nano-structural Changes of Shear Sensitive Emulsions. M.B. Munk^{1,2}, M.L. Andersen², A.G. Marangoni³, ¹Palsgaard A/S, Juelsminde, Denmark, ²University of Copenhagen, Department of Food Science, Frederiksberg C, Denmark, ³University of Guelph, Department of Food Science, Guelph, Ontario, Canada

Rheological properties of o/w-emulsions made from palm kernel oil were strongly influenced by low-molecular-weight emulsifiers. Addition of lactic acid ester of monoglyceride (LACTEM) yielded highly viscous emulsions. However, viscosity was reduced drastically by stirring at 5 °C, whereas stirring at room temperature caused a large increase in viscosity. The process was reversible since viscosity could be decreased again by stirring at cold temperatures. Mixtures of LACTEM and saturated monoglyceride yielded low-viscosity emulsions which also exhibited a sudden shear-thickening behaviour at room temperature. Addition of unsaturated monoglyceride to LACTEM generated a very firm emulsion that was not sensitive to shear or temperature. Confocal microscopy suggested that increased viscosity was due to fat aggregation. Despite shear-induced structural changes, fat polymorphism in the emulsions did not change, but remained in β form. On the other hand SAXS spectra showed a distinct change as emulsions went from liquids to thick pastes: The intensity of the 001 peak increased dramatically. Transmission electron microscopy suggested that fat did not maintain a globule structure; instead it was converted into large plates. Moreover proteins, which initially were located at the interface of fat globules, seemed to create a thin network in the water phase when emulsions thickened.

Physical Control of Fat Crystallization in O/W Emulsion-type Chocolate under Shear. Kiyotaka Sato, Masashi Ochi, Hironori Hondoh, Satoru Ueno, Hiroshima University, Higashi-Hiroshima, Japan

In general, fat crystallization in oil-in-water (O/W) emulsion occurs under quite complicated conditions, and various external factors are affecting the fat crystallization in oil droplet and at the water-oil interfaces. In this study, we observed the effects of shear on the polymorphic crystallization of cocoa butter in O/W emulsion, which is mimic to ganache-type chocolate. Such type of chocolate is produced without tempering process after formation of O/W emulsion at elevated temperature under high shear. We observed that, without the shear, cocoa butter crystallizes in a metastable form IV. However, the application of shear during the controlling process caused direct crystallization into form V, whose melting point is higher than that of form IV and thereby favored for chocolate. We will present the fat crystallization without and with shear under different crystallization conditions.

Chair(s): B. Lin, Henkel, USA; and J. Pytel, Stepan Co., USA

A General Overview of Crystallization Kinetics in Mixed Surfactant Systems. B.P. Grady¹, A. Maneedaeng², A.E. Flood², K.J. Haller², J.F. Scamehorn¹, P. Lohateeraparp¹, ¹University of Oklahoma, Norman, OK, USA, ²Suranaree University of Technology, Nakhon Ratchasima, Thailand

A well-known fact in the surfactant industry is that mixed surfactant systems often tend to precipitate at a much lower rate and/or at a lower temperature than the pure surfactant system at the same concentration. To correctly understand and quantify crystallization rate in mixed surfactant systems is quite complicated. In general, crystallization kinetics at a given temperature can be quantified according to the supersaturation ratio; i.e. a quantity related to the concentration of crystallizable component relative to the saturation concentration of the crystallizable component. The use of this formula assumes that the two surfactant molecules do not co-crystallize; co-crystallization is extremely unlikely in most systems due to mismatch of the unit cell parameters. Using the pseudo-phase approximation, to apply this formula in mixed surfactant systems requires quantification of the non-micellar concentrations of each surfactant, and some techniques to determine these values will be discussed. Once these concentrations have been determined, the supersaturation ratio can be determined and the crystallization rate can be compared to that in the one-component system. Experiments on the anionic surfactants sodium decyl sulfate, sodium dodecyl sulfate, and sodium octylbenzene sulfonate with added calcium cation will be discussed.

Dissolution of Calcium and Magnesium Soap Scums by Surfactant in the Presence of Chelant. Sawwalak Itsadanont¹, John F. Scamehorn², David A. Sabatini², Sumaeth Chavadej^{1,3}, ¹The Petroleum and Petrochemical College, Chulalongkorn University, Patumwan, Bangkok, Thailand, ²Institution for Applied Surfactant Research, University of Oklahoma, Norman, Oklahoma, USA, ³Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok, Thailand

The solubilities of two soap scum models (calcium and magnesium stearates: $\text{Ca}(\text{C}_{18})_2$ and $\text{Mg}(\text{C}_{18})_2$) were investigated under various solution pHs (4 to 11) and different types of surfactants (methyl ester sulfonate (MES); as an anionic, alcohol ethoxylate 9 (EO9); as a nonionic, and dimethyldodecylamine oxide (DDAO); as an amphoteric) with and without a chelating agent (disodium ethylenediaminetetraacetate or Na_2EDTA). The use of the DDAO surfactant and the chelating agent at pH 11 gave the highest dissolubilities of both studied soap scums whereas both MES and EO9 systems with or without the chelating agent gave much lower solubilities of both studied soap scums. The solubility of calcium soap scum was slightly higher than that of magnesium soap scum.

Nonyl Surfactants in Household Product Cleaning Systems. P.T. Sharko, D. Li, Shell Global Solutions, Houston, TX, USA

Consumers demand effective cleaning at low temperatures and with less physical scrubbing. To respond to these demands we have developed new surfactants based on short hydrophobes capable of attacking oily soils quickly. This presentation will show how surfactants built from linear nonyl hydrophobes can be used to deliver effective cleaning in both hard surface and laundry formulations.

Novel Amphiphilic Copolymers Derived from Soybean Oil. Harjyoti Kalita, Samim Alam, Achintya Bezbaruah, Andriy Voronov, Bret Chisholm, North Dakota State University, Fargo, ND, USA

Vinyl ether-functional monomers containing fatty acid pendent groups were produced from soybean oil (SBO) using base-catalyzed transesterification. The vinyl ether monomers were copolymerized using carbocationic polymerization with a water-soluble vinyl ether monomer to produce novel amphiphilic copolymers. The critical micelle concentrations (CMC) of these surface-active copolymers were measured and the relationship between CMC and copolymer composition determined. The copolymers were investigated for use as a delivery system for iron

nanoparticles as well as a binder system of waterborne coatings. The amphiphilic copolymers are currently being investigated for application as nonionic, biodegradable, polymeric surfactants.

Effect of Counterions on Green Surfactant Properties. L. Pechera, Church & Dwight Co. Inc., USA

For ionic surfactants, counterions affect surfactant properties depending on the degree of counterion binding to the surfactant headgroups, which depend on the polarizability, charge and hydrated radius of the counterions. For nonionic surfactants, the salting-in or salting-out of hydrophobic groups depends on the ionic-charge-to-radius ratio of the electrolyte. Because green surfactants have non-traditional surfactant structures and assemblies, the effect of counterions may be different. In this study, the effect of monovalent counterions Na^+ , K^+ , Li^+ (from Na_2CO_3 , K_2CO_3 and Li_2CO_3) on green surfactant properties such as critical micelle concentration, surface tension and oil-water interfacial tension is evaluated. Selected green surfactants include amino acid surfactants, alkylpolyglucosides, glycolipids, saponins and lipopeptides.

Solid Oily Soil Removal from Fabrics by Using Extended Surfactants. Jarussri Chanwattanakit¹, John F. Scamehorn², David A. Sabatini², Sumaeth Chavadej^{1,3}, ¹The Petroleum and Petrochemical College, Patumwan, Bangkok, Thailand, ²Institute for Applied Surfactant Research, University of Oklahoma, Norman, Oklahoma, USA, ³Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok, Thailand

The aim of this research was to investigate the detergency performance of solid oily soil by using extended surfactants. Methyl palmitate or palmitic acid methyl ester was selected as a model of solid oily soil and three types of fabrics were studied: pure polyester, pure cotton and polyester/cotton blend (65/35). Branched alcohol propoxylate sulfate sodium salt which has 12-13 carbon number with 8PO and 4PO groups (Alfoterra 123-8PO, Alfoterra 123-4PO) were used in this study. The detergency experiments were carried out in a Terg-O-Tometer at different total surfactant concentrations and temperatures (20 to 50°C) to cover both lower and higher than the melting point of the studied oil (30°C). Furthermore, the re-deposition of removed soils was also investigated. From the preliminary results, for any given types of surfactant and fabric, washing temperature showed significant effects on detergency and soil re-deposition performance and no oily soil re-deposition was found when the washing temperature was lower than the melting point of the studied oil. Additionally, the cotton fabric showed the highest detergency efficiency while the polyester gave the lowest performance.

Development and Validation of Image Analysis in Degreasing Evaluation. A. Devries^{2,1}, E. Theiner¹, K. Yacoub¹, ¹Air Products and Chemicals, Inc., Allentown, PA, USA, ²Purdue University, Wabash Township, IN, USA

Quantifying the amount of soil left on a test substrate is important for cleaning testing and applications. Visual inspection can be roughly accurate, but a more statistically precise method is necessary to ensure repeatability and to potentially allow the use of regression analysis to maximize formulation effectiveness. In this work, we developed an image analysis system that photographs test substrates and quantifies cleaned and soiled area. Results show that the system is precise, accurate, and repeatable in its percent clean calculations.

Reformulation of I&I Autodish Detergents for the Removal of STPP or KTPP. I. Leonard¹, J. Kolpa², ¹Thermphos International, Louvain La Neuve, Belgium, ²Thermphos USA, Red Bank, NJ, USA

Legislation in New York and South Carolina has set the limitation on the phosphorus content of industrial and institutional (I&I) autodish-washing detergents at the same low levels as commercial dish detergents. The vast majority of I&I autodish detergents are based on either sodium tripolyphosphate (STPP) or potassium tripolyphosphate (KTPP). With the legislative maximum level of elemental phosphorous set at 0.5%, many new formulas are needed. Historically, attempts to formulate cost-efficient STPP/KTPP free products failed due to ineffective cleaning or high cost. Recent developments indicate cost effective formulating with low levels of phosphonates together with synergistic phosphate free compounds can provide similar performance characteristics as STPP/KTPP based autodishwashing detergents while maintaining a level of elemental phosphorous below the legal limit.

Next Generation Biobased Builder: Polyitaconic Acid. Y. Durant, Itaconix, Dover, NH, USA

A new line of low molecular weight poly(sodium itaconate), named Itaconix? Dispersant DSP, is now available on a commercial basis, with polymer molecular weights ranging for 3,000 g/mole to 40,000 g/mole depending on the specific grade. Their primary utility is found in home cleaning formulations, leather retanning and pigment dispersant. Their molecular structure provides unusually high binding capacity for metal ions such as calcium and magnesium, at neutral to elevated pH. For comparison, it has the equivalent binding capacity and binding constant to calcium as tri sodium polyphosphate (STPP). Since the phasing out of STPP in laundry and automatic dishwasher detergents, formulators have been using as alternatives sodium citrate, sodium polyacrylate, polyaspartic acid and other lower performance builders. Poly(sodium itaconate) provides a cost effective solution to performance loss encountered by brands since the phasing out of STPP. DSP1K and DSP2K are also effective chelant alternative to EDTA and NTA. Low molecular weight sodium polyitaconic acids are inherently biodegradable, are made from 100% sustainable resources, and are safe to consumer and the environment. In addition to their ability to remediate hard water issues, these low molecular weight additionally have unique soil anti-redeposition properties, antiscaling performance, and corrosion inhibition for soft metals.

AFTERNOON

ANA 5.1/S&D 5: Analytical and Characterization Techniques for Probing Structure/Performance Relationships of Colloidal Systems

Chair(s): Hui Li, Bruker Optics, USA; and D. Scheuing, Clorox Co., USA

Quartz Crystal Microbalance (QCM) studies of C12E6 and CTAB Adsorbed at Interfaces and the Effect of Coadsorbents, Roughness and Temperature. B.P. Grady, University of Oklahoma, Norman, OK, USA

QCM measures the change in frequency of an oscillating quartz crystal and is sensitive to both adsorbed mass as well as the rigidity of the membrane. Gold and silica surfaces were studied. Although we were expecting gold to serve as a hydrophobic substrate, after cleaning procedures the substrate was more hydrophilic than hydrophobic and adsorption was similar for the two surfaces when normalized to the actual surface area. Flat adsorbed morphologies (bilayer or monolayer) have much more rigidity than curved layers and dissipation can be used as an indirect measure of morphology. The introduction of small molecule moieties, both polar and non-polar, were shown to drive the morphology towards a flat morphology, which is easily understood given the ability of a flat morphology to more easily incorporate small molecules. Finally, dissipation and adsorbed amount show a maximum at the CMC for rougher QCM surfaces. This effect is the solid-liquid analogue of the minimum in surface tension that occurs at the air-liquid interface: impurities that above the CMC are solubilized in micelles will adsorb at the surface (either in admicelles or directly to the surface) when the concentration is below the CMC.

Use of Isothermal Titration Calorimetry (ITC) to Evaluate the Adsorption of Surfactant on Iron Oxide. E. Acosta, Z. Wang, University of Toronto, Toronto, ON, Canada

The adsorption of sodium oleate, sodium laurate and sodium dodecyl sulfate (SDS) on iron oxide nanoparticles was followed using total organic carbon analysis of the supernatant solution and via isothermal titration calorimetry (ITC). The adsorption isotherms of sodium oleate and sodium laurate follow a classical S-shape isotherm, while SDS shows insignificant adsorption on iron oxide. The ITC experiments show that there are significant differences in the heat of adsorption in the different regions of the adsorption isotherm. The ITC technique is very useful in characterizing the surfactant-surface interaction. However, this technique cannot be readily used to obtain the adsorption isotherm due to simultaneous adsorption processes taking place during titration.

Surfactant Analysis by Infrared Spectroscopy. Thomas Tague, Bruker Optics, USA

Surfactants, detergents, and other lipid based products have been detected and analyzed by infrared spectroscopy. Very small amounts of surfactants and other products can be readily detected, identified, and quantified using infrared spectroscopy. The middle infrared region (MIR, 400-4,000 cm^{-1}) allows access to fundamental vibrational analysis providing excellent sensitivity and selectivity. The infrared fingerprint of a molecule is unique due to the uniqueness of the reduced mass. Lastly, Beer's Law correlates the absorptivity to concentration allowing for the quantification of chemical species. As the structure of a given surfactant changes, so does the MIR "fingerprint". Examples will be shown that demonstrate the ability of infrared spectroscopy to differentiate and identify surfactants.

A Hard-surface Cleaning Performance Test Method with in-situ Photometric Characterization. D. Li, P.T. Sharko, Shell Global Solutions (US) Inc., Houston TX, USA

Hard-surface cleaners are used in large volume. The recent market trend is an increasing focus on efficiency and speed of cleaning (e.g. good cleansing with less soaking time and minimum reps of mechanical motions). Among the existing performance test methods, few are convenient for measuring the kinetics of the cleaning process. In this talk, we present a hard-surface cleaning performance test method with in-situ photometric characterization. With a mounted digital video camera to record the reflectance of the soiled substrate after each scrubber stroke, we are able to resolve the cleaning performance of the surfactant solutions and kinetics of the process in stroke-by-stroke detail. We believe this method is valuable to surfactant suppliers and hard-surface cleaner formulators in screening surfactant/blends for desired cleaning performances.

Imaging the Polymer Network Structure of Ethylcellulose Oleogels using Atomic Force and Cryo-scanning Electron Microscopy. A.K. Zetzi, A.G. Marangoni, S. Barbut, University of Guelph, Guelph, Ontario, Canada

The GRAS (generally recognized as safe) polymer ethylcellulose has the ability to form oleogels at levels as low as 4%. Polymer organogels have the potential to provide the functionality of high-saturate fats, while possessing the fatty acid profile of the gelled vegetable oil they consist of. Though some attempts have been made to image these types of oleogels, they have been fairly unsuccessful until now. By using a solvent to remove a layer of oil from the surface of the gels, the now exposed polymer network can be imaged. Canola oil, soybean oil, and flaxseed oil oleogels were made using ethylcellulose of various molecular weights. Cryo-scanning electron and atomic force microscopy were used to identify differences in the ethylcellulose polymer network for these different gels. By using these microscopy techniques to establish a connection between microstructure and texture, this will give a great insight into these types of oleogels. We should then be able to modify these oleogels and improve their functionality for use in food products.

Direct Analysis of Surfactants using HPLC with Charged Aerosol Detection. M.A. Plante, B. Bailey, I.N. Acworth, Thermo Scientific, Chelmsford, MA, USA

Surfactants are a diverse group of chemical structures which are widely used in commercial products and are typically composed of an oil-soluble hydrocarbon chain and a water-soluble ionic group. Industrial uses extend from detergents in shampoos and cleaning products, ion pairing agents used in chromatography, and to complex dispersants used for oil spills. Many of these commercial surfactants are mixtures of members of homologous series, and LC is capable of defining these mixtures. HPLC methods for a number of surfactants which contained no UV-chromophores often use RP-HPLC with non-suppressed or suppressed mode conductivity or indirect photometric detection. However, charged aerosol detection (CAD) can measure any non-volatile, and many semi-volatile compounds, typically to low ng sensitivity. Furthermore, as response is similar for all compounds and independent of chemical structure, CAD is ideal for measurement of surfactant species. Generally the reproducibility for methods using CAD is less than 2%RSD. Sensitive methods are described for the analysis of various surfactant classes including anionic alkyl sulfonates (lauryl sulfate), cationic quaternary amines (lauryldimethylbenzylamine), non-ionic block copolymer (Pluronic F-68), and complex mixtures of oil dispersants (Span 80).

Viscous Heating in a Mini-Couette Cell Used in Rheo-XRD and Rheo-NMR Research. F.C. Wang, G. Mazzanti, Dalhousie University, Halifax, NS, Canada

A mathematical model is proposed to describe the temperature increase due to viscous heating in a mini-Couette cell used in Rheo-XRD and Rheo-NMR experiments on triglycerides crystallization. The model is tested with a standard Newtonian rheological oil. The cooling fluid inlet and outlet temperature and the mechanical power delivered to the oil are measured at temperature range of 1-20°C under rotational speeds of 0.1 and 50 rps. The average shear rates corresponding to these rotation speeds are calculated taking into consideration the curvature of the cell and the temperature dependence of the viscosity and the thermal conductivity of the oil. As expected, the oil is almost isothermal at low shear rates, as there is no significant increase in the oil temperature. At high shear rates, there is a high temperature gradient across the oil and consequently a considerable departure from the radial shear rate distribution compared to an isothermal oil. The model is essential for the interpretation of viscometric experiments done under shear flow in small-enclosed cells with high curvature, for understanding the crystallization behaviour of triglyceride mixtures. They also help with the calibration of the rheometer under high shear rate conditions, as well as for the design of industrial shearing crystallizers.

Surfactants and Detergents Posters

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

A Specialty Polymer for Surface Modification.

Andras Nagy¹, Joerg Peggau², ¹Evonik Goldschmidt Corporation, Hopewell, VA, USA, ²Evonik Industries AG, 45127 Essen, Germany

Hard surfaces often create challenges for easy cleaning, dusting, quick drying and long term shine and protection. When one area is improved, usually others suffer, e.g.: when shine and protection are enhanced, cleaning and spotless drying are negatively affected. With a specialty smart polymer one can overcome these difficulties by creating a chemical structure which will help easier spot- and streak-free cleaning, quick drying resulting in antistatic, glossy surfaces at the same time. Among many advantages this polymer is compatible with alkaline and acidic cleaners, all formulations containing anionic, nonionic, cationic and amphoteric surfactants, aqueous and alcoholic based care and cleaning agents, etc. This polymer is easy to process and can subsequently be added into existing formulations as a performance booster. More details will be presented and benefits are demonstrated in the poster.

Counterion Effects in Microemulsion Formulation.

S. Baradaran¹, P. Lohateeraparp¹, B. Shiau², J. Harwell¹, ¹Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, OK, USA, ²Mewbourne School of Petroleum and Geological Engineering, University of Oklahoma, Norman, OK, USA

This research focuses to formulate a low electrolyte concentration microemulsion by introducing a stronger electrolyte, potassium chloride (KCl), into the system. Studies consisted of microemulsion phase behavior, interfacial tension (IFT), precipitation and phase separation, surfactant adsorption, and one dimensional soil column tests. From the phase behavior test, the results indicated that adding 0.1 wt% KCl decreases approximately 0.4 wt% of the sodium chloride (NaCl) required for microemulsion phase transition (I to III to II) and optimum salinity. At optimal conditions, the IFT between surfactant and oil phases is at a low level of 10-3 mN/m. The low electrolyte microemulsion system shows no surfactant precipitation and less tendency of surfactant phase separation when compared to the conventional system. The surfactant adsorption onto the solid surface in the low electrolyte microemulsion is similar to the conventional microemulsion. Furthermore, the results from column test show a high oil recovery, over 95%, when applying this low electrolyte microemulsion formulation, which is similar to the conventional formulation. The results from this study show a potential application of the low electrolyte microemulsion in surfactant-enhanced aquifer remediation (SEAR), especially in the states that require low electrolyte addition in the injected fluid (e.g., California and Texas).

A Novel Approach of Applying Chelating Agents and Surfactant/polymer System for Improving Oil Recovery.

Sangho Bang¹, Tzu-ping Hsu¹, Prapas Lohateeraparp¹, Jeffrey Harwell^{1,2}, Benjamin Shiau^{1,2}, ¹University of

Oklahoma, School of Chemical, Biological, and Materials Engr. and Mewbourne School of Petroleum & Geological Engineering, Norman, OK, USA, ²Institute for Applied Surfactant Research, Norman, OK, USA

To expand our current low-IFT surfactant system applying for various high salinity reservoirs, we explore improved chelating agents (i.e., non-EDTA system) to eliminate the negative impacts of surfactant precipitation or separation due to elevated total dissolved solids of reservoir brine (e.g. 166,192mg/L~185,000mg/L). We investigated the most critical parameters, including generation of micro-emulsions, high coalescence rate, homogeneity of fluid, precipitation over time and ultra-low interfacial tension (IFT), characterizing the best middle phase microemulsion formulations. We suspect that the added chelating agents stabilize the surfactant solution by changing the rheological properties of the surfactant such as the morphology and rearrangement of micelles. In addition, the stabilizer not only prevents iron (II) precipitation with higher solubilization parameter, but also enhances the polymer as required for better mobility control of crude oil. In parallel, one-dimensional sand-packed column (using crushed Berea sandstone), the proprietary stabilizer improves oil recovery from 59% to 75% of initial residual oil saturation while lowering IFT value from 10-2mN/m to 10-3mN/m. This novel stabilizer has great potential to achieve the stable surfactant formulation and much lower IFT for recovery under high salinity condition.

Anionic Scavengers in Drying Agents for Hard Surfaces.

Andras Nagy¹, Saïid Mohammed², ¹Evonik Goldschmidt Corporation, Hopewell, VA, USA, ²Evonik Degussa Corporation, Piscataway, NJ, USA

In automatic carwashes the cleaning step is usually followed by a water rinse before a drying agent or spraywax is applied to remove residual water, accelerate drying, provide temporary protection and increase the shine of surfaces. However if the rinse step is not complete, residual detergents are carried over to the drying step. If the cleaners contain anionic surfactants, they will neutralize the cationic emulsifiers in the drying agents resulting in insoluble precipitates (soap scum), less efficient and slower drying, foam residue and visible spots on the surfaces upon drying. To overcome these deficiencies, monoalkyl quaternary surfactant additives were used as anionic scavengers. Monoalkyl mono-quaternaries act as sacrificial molecules: they neutralize the anionics, and the resulting complex is water soluble. Monoalkyl di-quaternaries however have an additional benefit: not only they neutralize the anionics, but the resulting complex will have a cationic character which can act as an in-situ quaternary emulsifier resulting in economical and aesthetical benefits: quicker drying, reduced drying agent and rinse water usage, less spots and foam and increased customer satisfaction. The detailed chemistry is presented and the benefits are demonstrated in the poster.

Motor Oil Removal by Multistage Froth Flotation: The Effect of Operational Parameters.

Paweena Kanokkarn¹, John H. O'Haver², Sumaeth Chavadej^{1,3}, ¹The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand, ²Department of Chemical Engineering, University of Mississippi, USA, ³Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok 10330, Thailand

In this present work, a continuous multistage froth flotation unit was used to remove motor oil from water at a low motor oil concentration (500 ppm) using different surfactants - dioctyl sodium sulfosuccinate (AOT), and branched alcohol propoxylate sulfate sodium salt (Alfoterra[®], C145-8(PO)) as a foam generator. To maximize the process performance, the system has to be operated under the low IFT condition with proper air flow rate and feed flow rate in order to obtain high adsorptive transport with low bulk liquid transport. An increase in surfactant concentration can lower the system IFT, but at a very high surfactant condition, it lessens the enrichment ratio, resulting from increasing bulk liquid transport. The highest separation efficiency (surfactant recovery~98%; oil removal~98%; residual factor of surfactant~0.03; residual factor of oil~0.08 and enrichment ratio~20) of the studied multistage foam fractionation unit was observed at an air flow rate of 20 dm³/min, a feed flow rate of 20 cm³/min, foam height of 60 cm, and the number of trays equal to 5 by using Alfoterra[®], C145-8(PO) as foam generator. This is due to the molecular structure of Alfoterra[®], C145-8(PO), which has a higher hydrophobicity than AOT.

Obtaining and Characterization of Brazilian Rose Smectite - Application in the Development of Soaps and Detergents.

Maria das Graças Silva-Valenzuela¹, Flávio M S Carvalho², Isaac Jamil Sayeg², Lucy Gomes Sant'Anna³, Francisco Rolando Valenzuela-Díaz¹, ¹Polytechnic School, University of São Paulo, São Paulo, São Paulo, Brazil, ²School of Geosciences, University of São Paulo, São Paulo, São Paulo, Brazil, ³School of Arts, Sciences and Humanities, University of São Paulo, São Paulo, São Paulo, Brazil

Clays are materials used in the manufacture of soaps and detergents, conferring properties of excipient or vehicle, according to their physical and chemical characteristics. Here, we describe obtaining of pink clay from purification of Brazilian clay, originally classified as smectite. The pink clay obtained was characterized by PXRD, SEM, Laser granulometry. Clay was used in formulations of liquid soaps and detergents. Experimental products of the characterized clay were submitted to tests of pH measure, viscosimetry and stability using three different concentrations of clay: 3%, 6% and 10%. PXRD analysis showed peaks for montmorillonite and kaolinite. The techniques of SEM and Laser granulometry revealed the lamellar structure of clay, and its particle size distribution ranging between 2-9 μm . The pH, viscosimetry and stability measure have indicated that the fresh pink clay can be used in the formulation of liquid soaps and detergents, showing good stability under the conditions of the experiment, and pH = 6.5 -7.0. Viscosimetry tests indicated that lower concentrations (3% and 6%) are most advisable for final application of the pink clay in liquid soaps and detergents. Our results show that this pink clay can be used as a stabilizing agent for emulsions and creams cosmetics.

Novel Polymer-surfactant System for Mitigating Interfacial Tension.

P. Tongwa, Missouri University of Science and Technology, Rolla, MO, USA

Surfactant ?polymer flooding for enhanced oil recovery applications have gained considerable interests in recent years due to their ability to significantly decrease oil-water Interfacial tension, solubilize and release oil and thus increase oil sweep efficiency. They have two major utility: (1) to improve volumetric sweep efficiency and (2) to improve microscopic sweep efficiency. However, due to reservoir heterogeneity, surfactant adsorption, chromatographic separation, and high temperature environments which cause molecular degradation, most conventional surfactants are not applicable. Herein we introduce the design of a novel polymer-surfactant system with significant thermal stability which have potential applications in mitigating oil-water interfacial tension, decrease residual oil saturation and thus increase oil recovery factor.

Tridecyl Alcohol (TDA) Ethoxylates - Optimal Broad Spectrum Vertical and Horizontal Axis Commercial Laundry Surfactants.

Terry Crutcher, James Dailey, Virginia Lazarowitz, Nancy Almasarweh, BASF Corporation, USA

In the consumer and commercial laundry technology markets there are both vertical and horizontal axis laundry systems. Due to the differences in the two laundering processes there is concern that laundry technology developed for one geometric machine design may not be suitable (perform similarly) in the alternate system. Because both vertical and horizontal axis laundry systems can be found in U.S. Industrial & Institutional laundry market research has been conducted to investigate the effect of laundering axis on detergent technology. Tridecyl alcohol (TDA) ethoxylate surfactants were studied in a standard vertical axis laundry laboratory protocol to provide synergistic and optimal broad spectrum cleaning results. The study reveals a clear soil removal synergy for specific analog TDA surfactant compositions. Additionally, the optimal surfactant blend is shown to further enhance the cleaning performance of a built detergent system. The same synergistic surfactant composition is also studied and data will be presented for parallel performance in a standard horizontal axis lab laundry test protocol to confirm or deny a cross over axis concern. The importance of the results extends beyond the immediate discussion of vertical versus horizontal axis detergent performance to a more significant technical and commercial question of the global application of detergent research, in general, as the world engages in diverse laundry practices.

Use of Lactose Monolaurate as an Emulsifier and its Effect on Crystallization of Anhydrous Milk Fat.

Ashwini Wagh, Silvana Martini, Marie Walsh, Utah State University, Logan, UT, USA

Lactose monolaurate (LML) was synthesized in our laboratory to evaluate its potential use as an antimicrobial agent. The objective of this research was to evaluate other functional properties of LML such as emulsification capacity and

crystallization modifier. LML was used as an emulsifier in 20% soybean oil-in-water (o/w) emulsions at concentrations of 0.1%, 0.25% and 0.50%. Highly stable emulsions were obtained when 0.5 and 0.1% of LML were used as emulsifiers with destabilization rates of 0.0018 mm/d and 0.01 mm/day, for emulsions formulated with 0.5 and 0.1% LML, respectively. LML was dissolved in anhydrous milk fat (AMF) to test its efficiency as crystallization modifier. AMF was crystallized at different crystallization temperatures and the induction time (τ) was calculated at each temperature (25-31 °C at intervals of 0.5 °C). LML was dissolved in AMF at 0.025% and 0.050% and τ was calculated at 31 °C. At 0.025% LML the τ was increased to 41.9 ± 3.52 min from 34.2 ± 1.68 ($p < 0.05$). The higher concentration of LML (0.050%) also increased τ in AMF to 43.7 ± 3.98 min ($p < 0.05$). These results suggest that LML can be used to delay the crystallization of AMF.

Adjustment Method of Removal Percentage in Washing Test of Iron (III) Oxide Soiled Cloth Using Probability Density Function.

Masaru Oya¹, Emi Shigyo², ¹Institute of Environment and Information Sciences, Yokohama National University, Yokohama, Kanagawa, Japan, ²Graduate School of Environment and Information Sciences, Yokohama National University, Yokohama, Kanagawa, Japan

The method of standardizing the soil removal percentage in washing tests using probability density function reported in 2011 AOCS meeting was developed. Assuming that variability of adhesion power of soil follows normal distribution and the strength of removal action (= rate constant in first-order reaction) shows cumulative normal distribution, mean value of removal load (μ) and standard deviation of removal load (σ) were calculated as washing power parameters from 4 removal percentages obtained from 4-times repeated washing test. Test cloths soiled with iron (III) oxide were prepared and provided in washing test using Terg-O-Tometer under the agitation of 80, 120, 140, 160 rpm. σ values of iron oxide were greater than those of carbon black or mixed soil. The distances between μ values for different agitations were the same as those obtained by washing test of carbon black soiled cloths and mixed soiled cloths. Removal percentage of iron oxide tends to vary greatly according to the condition of soiling procedure, but it was clarified that removal percentage can be adjusted by recalculation with transforming the distribution of adhesion power.

Removal of MgSiO₃ Particles from the Surfaces of AlTiC Coated with Diamond-Like-Carbon.

Aree Pinpiti¹, Sumaeth Chavadej^{1,2}, ¹The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand, ²Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok, Thailand

Hard disk drives (HDD) are used to store data in a computer system. They have a slider or head to write and read information from the disk. This slider is produced from a wafer which is aluminium titanium carbide (AlTiC) and its surface is coated with diamond like carbon (DLC). The Hard Disk Drive industry requires an extremely low level of solid particles on the surface because these particles can cause data losses. The common particles found on the surface of sliders are identified as talcum powder or magnesium silicate (MgSiO₃) which comes from the cosmetic powder used by woman workers during slider manufacture. A surfactant has the unique property of adsorbing onto surfaces or interfaces which can enhance particle removal from surfaces by modifying the particle-surface interaction forces. The objective of this work was to investigate the surface cleaning mechanisms by surfactant to remove talcum powder from AlTiC surface by studying the adsorption isotherm, zeta potential, and contact angle. From the results, the concentration of and type of surfactant affect on the adsorption capacity which, in turn, relates to in the removal performance of talcum powder from the studied surface.

Influence of Linker Molecules on Adsolubilization of Organic Compounds Using Hydrophobic Silica Modified with EO/PO Triblock Copolymers.

Phongsakorn Banjai¹, Pomthong Malakul¹, Manit Nithitanakul¹, John O'Haver², ¹The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand, ²The University of Mississippi, Oxford, USA

Wastewater from chemical industries usually contains various toxic chemicals that consist of organic and inorganic compounds, which potentially harm human and ecosystem. In recent years, adsolubilization process has been found to

be useful in techniques for the removal of toxic organic compounds from wastewater by using solid particles modified with various types of surfactants. EO/PO triblock copolymers are nonionic macromolecular surfactants which have good detergency properties, low toxicity and low desorption. Thus, the purposes of this study were to investigate the influence of linker molecules (lipophilic linker and combined linker) on the adsorption of EO/PO triblock copolymers (Pluronic P123, L64, and 25R4) onto hydrophobic silica and used the modified hydrophobic silica to adsorb various model aromatic organic compounds such as phenol, naphthalene, and 2-naphthol from water. The results showed that the maximum adsorbed amount of EO/PO triblock copolymers and maximum adsorbed amount of aromatic organic compounds were increased by using linker molecules.

Silicone-Free Tire Dressings.

Dave McCall, Vaughan Industries

The job of cleaning a car involves more than just dirt removal. In addition to being free of oily and particulate soil, a cleaned car will be waxed to a high shine and the rubber and vinyl surfaces will be dressed with a gloss agent. The gold standard for tire dressings is silicone. It lays on top of the surface, rather than dissolving into it. It has a high refractive index, yielding very high gloss. Silicone also has some notable disadvantages. It is expensive and the tiniest remaining traces on any surface ruin any subsequent attempts to paint the surface. Hence, silicone-based tire dressings are absolutely forbidden in the auto paint shop. Hence, there is always a need for silicone-free tire dressings. There have been many attempts to produce such a product. None approaches the performance of silicone. In this investigation, new tire gloss formulations are pursued by synthesizing molecules specifically designed to be highly refractive. Specifically, several poly aromatic esters are evaluated as silicone substitutes.

Analysis of Underivatized Surfactants using High Performance Liquid Chromatography.

Marc Plante, Thermo Fisher Scientific, Chelmsford, MA, USA

Surfactants are a diverse group of chemical structures which are widely used in commercial products and are typically composed of an oil-soluble hydrocarbon chain and a water-soluble ionic group. Industrial uses extend from detergents in shampoos and cleaning products, ion pairing agents used in chromatography, and to complex dispersants used for oil spills. Many of these commercial surfactants are mixtures of members of homologous series, and LC is capable of defining these mixtures. HPLC methods for a number of surfactants which contained no UV-chromophores often use RP-HPLC with non-suppressed or suppressed mode conductivity or indirect photometric detection. However, charged aerosol detection (CAD) can measure any non-volatile, and many semi-volatile compounds, typically to low ng sensitivity. Furthermore, as response is similar for all compounds and independent of chemical structure, CAD is ideal for measurement of surfactant species. Generally the reproducibility for methods using CAD is less than 2% RSD. Sensitive methods are described for the analysis of various surfactant classes including anionic alkyl sulfonates (lauryl sulfate), cationic quaternary amines (lauryldimethylbenzylamine), non-ionic block copolymer (Pluronic F-68), and complex mixtures of oil dispersants (Span 80).

Supramolecular Gel Formation from Glycolipid Biosurfactants, Cellobiose Lipids by *Cryptococcus humicola*.

Daisuke Kawamura¹, Yoshihiro Kikkawa², Tomohiro Imura³, Tomotake Morita³, Tokuma Fukuoka³, Hideki Sakai¹, Masahiko Abe¹, Dai Kitamoto³, ¹Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, Noda, Chiba, Japan, ²Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan, ³Research Institute for Innovation in Sustainable Chemistry, National Institute of Advanced Science and Technology (AIST), Tsukuba, Ibaraki, Japan

Biosurfactants (BS) are unique natural amphiphiles produced by microorganisms from a variety of renewable resources. They give not only an excellent surface-activity but also various biological activities. The numerous advantages of BS have prompted applications including the food, cosmetic, and pharmaceutical industries. Among BS, cellobiose lipids (CL) are glycolipid-type BS that are abundantly produced by yeast. Recently, *Cryptococcus humicola* was reported to produce a new type of CL. Interestingly, the new CL has an asymmetric bolaform amphiphiles that could give unique self-assembling properties. In this study, we thus focused our attention on the production and the self-assembling properties of CL obtained by different strains of *Cr. humicola*. Particularly *Cr. humicola* JCM 1461 efficiently produced the CL, tetra-acetylated cellobiose bearing 2-hydroxy-hexadecanoic acid. Moreover, the produced

CL having bolaform structure was found to act as low-molecular-weight gelators (LMWGs) for various solvents such as acetonitrile, 1-pentanol, 1-octanol, toluene, ethanol/water, and 1,3-butanediol/water. The supermolecular fibrous structures that eventually entangle into three dimensional networks were captured by the AFM observation of the ethanol/water and 1,3-butanediol/water gels spin-coated on a silicone wafer.

Microemulsion-Based Semi-Solid Oil Detergency Using an Extended Surfactant: Effect of Washing Temperature.

Thitirat Choke-arpornchai¹, Sumaeth Chavadej^{1,3}, John F. Scamehorn², ¹The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand, ²University of Oklahoma, Norman, Oklahoma, USA, ³Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok, Thailand

The purpose of this research was to examine the use of a single extended surfactant in the microemulsion-based detergency of semi-solid oil. The correlation between the phase behavior of microemulsions and the detergency performance of semi-solid oil removal at various washing temperatures was studied. The extended surfactant system—Alfoterra[®], C145-4(PO)—was selected to form different microemulsions with the semi-solid oil (methyl palmitate). The interfacial tension (IFT) of various microemulsion systems was measured in order to find the best formulation which corresponded to the lowest IFT condition. For detergency testing, the white fabric of polyester/cotton (65:35) blend soiled with the semi-solid oil (methyl palmitate) was tested by using a Terg-O-Tometer at different total surfactant concentrations and washing temperatures (10 °C, 20 °C, 30 °C, 40 °C and 50 °C). The results showed that the highest semi-solid oil removal was at 30 °C. In addition, the re-deposition of the semi-solid oil onto the fabric was less than 5%.

Effect of NaCl on Dissolution of Magnesium Soap Scum in Different Surfactant Solutions.

Darunrat Ratanalert¹, John F. Scamehorn², David A. Sabatini², Sumaeth Chavadej^{1,3}, ¹The Petroleum and Petrochemical College, Chulalongkorn University, Patumwan, Bangkok, Thailand, ²Institute for Applied Surfactant Research, University of Oklahoma, Norman, Oklahoma, USA, ³Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok, Thailand

In general, a sticky stain or filmy layer around sanitary wares results from the reaction between soap and divalent cations in hard water. The existence of soap scum can be removed by applying a proper types and concentrations of surfactant and chelating agent. The effect of added NaCl on the equilibrium dissolution of magnesium octadecanoate (magnesium stearate or $Mg(C_{18})_2$) was investigated for different types of surfactants: hexadecylpyridinium chloride monohydrate (CPC); as a cationic, methyl ester sulfonate (MES); as an anionic, alcohol ethoxylate with 9 ethylene oxide groups (EO9); as a nonionic, and dimethyldodecylamine oxide (DDAO); as amphoteric at various solution pHs. The presence of NaCl improved the equilibrium dissolution of magnesium octadecanoate especially in the DDAO system at a high pH. On the other hand, the addition of NaCl had insignificant effect on the equilibrium dissolution of magnesium octadecanoate for the other systems of MES, CPC and EO9.

Opportunities in VOC Reduction: Performance and Cost Improvements by Eliminating Solvents.

Eric ?Rick? Theiner, Khalil Yacoub, Air Products and Chemicals, Inc., USA

New regulations that are forcing cleaning product manufacturers to reconsider solvent use in their products may benefit both manufacturers and consumers in the long run. Hesitation in revisiting ?tried and true? formulas that rely on the use of solvents must now be overcome and technology is already in place to allow the beneficial replacement of solvents. This poster will present some of the latest work in replacing solvents with surface active materials to show reduction of active materials yet significant performance improvements.

The Use of Nicotinamide as an Anti-crystallizing Agent of Caffeine in Cosmetic Products.

Dong Hyuk Jang, Hwa Young Shin, Changhoon Park, R&D Center, Amorepacific Corporation, Yongin-si, Kyeonggi-do, South Korea

Caffeine is known to promote lipolysis by inhibiting phosphodiesterase activity in adipose tissue. For this reason, it has

been used as a key ingredient in body-slimming products in cosmetic industry. However, because of its poor water-solubility in room temperature and re-crystallizing property in lower temperature, producing products with high dose of caffeine has been limited. In fact, many cosmetic products containing caffeine as a key ingredients showed crystallization when stored in low temperature, and this was often not re-dissolved even when came back to room temperature. Here, we used nicotinamide as hydrotropic agent to resolve this problem. Nicotinamide, also called niacinamide, has been used as solubility enhancer of poorly water-soluble drugs. We found that nicotinamide can prevent crystallization of caffeine in cosmetic formulations in low temperature. Using proper dosage, nicotinamide even can prevent nucleation induced by adding caffeine powder to formulations.