

## S&D 1: Industrial Applications of Surfactants

Chairs: A. Taneja, BASF Corp., USA; and B. Grady, University of Oklahoma, USA

**The Deodorant Effect of Novel Dextrin Compounds in Fabric Softener.** R. Hashimoto, R. Adachi, E. Hashimoto, N. Egawa, and H. Takaoka, Lion Corporation, Edogawa-ku, Tokyo, Japan.

In home laundry, consumer awareness for invisible soils like bacteria and bad odor has been increasing. Especially bad odors of sebum and sweat from the human body are concerned. Even for softener, in addition to a pleasant feeling of touch, the deodorant effect for these bad odors has attracted attention as a new function. We focused on inclusion compounds like dextrin which can trap various bad odor components.

We found that novel high molecular dextrin compounds show higher adsorption on cotton clothes after rinsing and a superior deodorant effect than beta cyclodextrin. In addition, it is important that the adsorption ratio was increased by the co-existence of cationic surfactants. And the high molecular dextrin compounds' deodorant effect for various odor components like amine, indole, aldehyde, and fatty acid are studied. As a result, the high molecular dextrin compounds show high performance against medium chain fatty acids known as characteristic key components of sebum odor. The mechanisms of high adsorption on cotton clothes and inclusion selectivity for fatty acids have been investigated, as well.

**Liquid Detergent Compositions Containing Methyl Ester Sulfonate (MES) with Low Temperature Stability.** A. Morigaki<sup>1</sup>, H. Konnta<sup>1</sup>, T. Ogura<sup>1</sup>, Y. Kaneko<sup>1</sup>, N. Tabori<sup>1</sup>, and O. Glatter<sup>2</sup>, <sup>1</sup>Lion Corporation, Edogawa-ku, Tokyo, Japan, <sup>2</sup>University of Graz, Graz, Austria.

Methyl Ester Sulfonate (MES) derived from sustainable palm oil has already been put to practical use in powder type laundry detergents due to its special features of superior detergency and favorable biodegradability. However, there have been few MES-contained liquid detergents, because MES is separated from the liquid detergents in cold areas in which the temperature drops below 0 degree Celsius. In this study, we investigated to establish new methods of creating MES stability in liquid detergent with low temperatures. It was discovered that the combination of low-molecular-weight sulfonic acids and alkanolamines was useful for improving temperature stability. The

combination proceeds to exchange counter-ions between the Na-ions of MES and the alkanolamine ions in the solution. When this combination was applied to liquid detergent compositions containing MES, the solution showed high stability below 0 degree Celsius. Furthermore, these additives induced the phase transition from hexagonal to micelle and the concentrated MES solution of over 40 % had high fluidity. It can be deduced that this technique is useful for improving the manufacturing process of liquid detergents.

**Cocamide Diethanolamide Alternatives.** G.A. Smith, Huntsman Corporation, The Woodlands, TX, USA.

Cocamide DEA is widely used to build viscosity and foam in low active formulations for a variety of different end use applications. Cocamide DEA is the reaction product of coconut oil and DEA. It is a liquid at room temperature, relatively inexpensive to produce and extremely effective at building viscosity and stabilizing foam. Recently DEA has been classified as possibly carcinogenic to humans and the state of California has listed cocamide DEA under Proposition 65.

Because of the recent legislation, there is a great deal of interest in a low cost alternative to cocamide DEA. A series of primary and secondary amines were reacted with coconut oil under based conditions and the reaction products characterized. Surface properties were determined and compared to cocamide DEA. The ability to build viscosity as a function of salt and foam behavior were also determined.

**The Stabilisation of Reactive Benefit Agents in Laundry Formulations.** D. Duncalf, Revolymex Ltd., Deeside, Flintshire, UK.

This talk will describe the product research we have undertaken to develop responsive protection systems for active agents. These protection systems are able to protect an active agent within a formulation, in order to provide a long shelf life, yet are able to release the active within a very short time in response to a trigger produced when the consumer uses the product.

Modern laundry products are currently facing a number of challenges. Consumer trends are towards quicker washes, lower washing temperatures and lower water usage. Competing

with these trends is the need for outstanding washing performance - which is generally correlated with higher temperatures and higher water use. Consumers also desire a good hygiene effect which is often driven by higher wash temperatures.

These competing needs mean that formulations need to change. They need to incorporate benefit agents which are more reactive so as to be able to clean, bleach and disinfect clothes at lower temperatures, in less time and in reduced water. However the incorporation of active agents into the chemically hostile environment of a laundry product is not trivial.

**The Use of Vegetable Oil Ethoxylates in Beauty and Personal Care Formulations.** G.R. Watkins and G.A. Smith, Huntsman Corporation, The Woodlands, TX, USA.

Beauty and personal care products are generally designed to deliver a function benefit and to enhance the feeling of well-being of consumers by increasing their aesthetic appeal. To this end, many cosmetic formulations are used to clean hair, soften and clean skin, and impart a pleasant odor, make the skin feel smooth and provide moisturizing agents if applicable. In order to have consumer appeal, beauty and personal care formulations must meet rigid aesthetic standards such as texture, consistency, pleasing appearance, fragrance, and ease of application.

Vegetable Oil Ethoxylates are non-ionic surfactants which have been shown to possess the positive attributes described and others. Our research has shown that VOE are very good emollients and have a smoothing, lubricating effect upon application with a high spreading coefficient. Also a good re-fattening or lipid layer enhancing agent on skin (at the interface, the VOE film is birefringent under polarized light) improving skin elasticity. This investigation focused on VOE with 10 & 25 moles of ethylene oxide, with the higher amount of ethoxylation increasing the water solubility. Having the two different levels allows the VOE to enhance all types of beauty and personal care products.

**Improvement of Viscosity by Alcohol Ethoxylate Blends in Laundry Detergent Formulations.** T. Weemes, T. Nguyen, and L. Matheson, Sasol North America, Westlake, LA, USA.

Viscosity control plays an important role in creating a liquid laundry detergent product that meets consumer needs. Beside the reason for the appearance of the liquid detergent, high viscosity

can cause liquid flow and stability problem while low viscosity can cause mechanical loss of the detergent during the machine washing process. Therefore, it is important to formulate a liquid laundry detergent with reasonable viscosity. In this research, the viscosity-salt response of a nonionic alcohol ethoxylate surfactant, a component of liquid detergent formulation, was used as the reference for viscosity alteration. A number of alcohol ethoxylate surfactants were studied to evaluate the effect of the degree of ethoxylation, the alcohol feedstock and the blending of alcohol ethoxylates. It was found that there was a degree of ethoxylation when the viscosity of the formulation reached maximum value. Also, alcohol ethoxylates made from alcohol feedstock of higher molecular weight produce higher viscosity. Thus, blending high- and low-viscosity ethoxylates at a certain blending ratio can create a surfactant mixture that produces desirable viscosity for the liquid detergent formulation.

**Measurement and Application of the Equivalent Alkane Carbon Number of Fragrance Oils.** D. Scheuing and E. Szekeres, Clorox, Pleasanton, CA, USA.

The equivalent alkane carbon number (EACN) of an oil is a key parameter in the hydrophilic-lipophilic difference (HLD) equation. EACN of many oils of interest, including fragrances, may be determined in a relatively simple manner through the use of a model microemulsion system. Differences in the EACN of fragrances, as well as their solubilization parameter at optimum conditions, can be used to guide improvements in formulations requiring fragrance oils.

**What is Industry Hiring Surfactants to Do and Gaps?** L. Minevski, T.L. Phang, and R. Fausnight, ITW Global Brands, Houston, TX, USA.

Starting from a broad industry perspective and then narrowing down to what "job" surfactants are requested to do, we look into the industry uses and needs in respect to surfactants. From packaging to automotive aftermarket uses, there are needs for more cost-effective products as well as the need to satisfy consumers' and customers' needs.

Surfactants do play an important role (1) as active agents in products used in bulk or found on shelves, and (2) as enhancers of processes or performance characteristics of e.g., polymers. We know that some properties of surfactants are to wet, emulsify, thicken, disinfect and make foam but where and how these properties help? Thus,

examples of types of soil and removal, types of surfaces and surface modifications are discussed. We end with discussing a few industry demands and what gaps surfactants need to overcome as industry

is facing ever-changing regulatory and government regulations. Besides these compliances, consumers are asking for recycling and environmentally friendly products.

## S&D 1.1/BIO 1.1: Merging Biology and Surfactants

Chairs: D.G. Hayes, University of Tennessee, USA; G.A. Smith, Huntsman Corp., USA; and D. Solaiman, USDA, ARS, ERRC, USA

**Sophorolipids: Microbial Synthesis and Biotechnological Opportunities.** I.N.A. Van Bogaert and W. Soetaert, Ghent University, Ghent, Belgium.

Sophorolipids are surfactants which are produced by specific yeast species, such as *Starmerella bombicola*. Thanks to the high yields of this biological process (over 400 g/L can be obtained) and the environmentally friendly character of these biosurfactants, they caught the attention of several academic institutes and later on companies. Indeed, sophorolipids are one of the few biosurfactants which are commercially produced and applied.

Although certain microbial biosurfactants are already find applications, their usage range could be further broadened if more structural variants would be available, in this way creating molecules with different physico-chemical properties and functions. Yet, creating variation in a biological controlled process is not as easy as modifying a chemical reaction; rendering the creation of tailored biosurfactants quite a challenge.

We try to tackle this shortcoming by a combined fundamental and applied approach: getting insight into the biosynthetic pathway and its regulation, control and engineer it. In order to achieve this, we *de novo* sequenced the full genome of the yeast and set up extensive transcriptomics and proteomics experiments. We will discuss the identification of the sophorolipid core pathway and will give several examples of how it can be engineered to produce tailored glycolipids.

**Identification of Long-chain Alcohol Oxidase AOX1 from *Starmerella bombicola* and Knocking Out the AOX1 Gene Leads to Improved Alkyl Polyglucoside Production.** F. Takahashi, K. Igarashi, and H. Hagihara, Eco-Innovation Research, Kao Corp., Wakayama-shi, Wakayama, Japan.

Alkyl polyglucoside (APG) has good properties as a cleaner, foamer, and emulsifier, and does not hydrolyze at an alkaline pH. In addition to its advantages as a traditional alkylglucoside surfactant, APG is a low-irritant surfactant that is nontoxic and easily degradable in the environment. Thus, APG is considered an environmentally friendly surfactant. We have been working to develop new APG synthesis methods aimed at decreasing the cost as well as the burden on the environment and

facility, and expanding the structure.

*Starmerella bombicola* glycosylates long-chain omega-hydroxy fatty acids and it also directly glycosylates secondary alcohols. Although it is difficult to directly glycosylate primary alcohols, they are easily converted to the corresponding fatty acid. To redirect unconventional substrates toward APG synthesis, the long-chain alcohol oxidation pathway was blocked at the genome level by knocking out the fatty alcohol oxidase gene. The total gene sequence of the *S. bombicola* AOX1 (2046 bp) was cloned. Knock-out mutants were evaluated by fermentation in 1-tetradecanol. The mutants produced much higher amounts of APG, indicating that the substrate had been redirected toward APG synthesis in those strains.

**Incorporation of Membrane Proteins in the Bicontinuous Microemulsion Phase of a Winsor-III System.** D.G. Hayes<sup>2</sup>, R. Ye<sup>2</sup>, V.S. Urban<sup>1</sup>, S.V. Pingali<sup>1</sup>, and H. O'Neill<sup>1</sup>, <sup>1</sup>Oak Ridge National Laboratory, Oak Ridge, TN, USA, <sup>2</sup>University of Tennessee, Knoxville, TN, USA.

Membrane proteins (MPs) account for approximately 33% of proteins encoded by the human genome, and are targets for 50-60% of therapeutical agents. They are difficult to characterize due to their poor solubility in aqueous media, and therefore account for only 3% of three-dimensional structures within the Protein Data Bank. We have successfully incorporated several different MPs (e.g., cytochrome c, melittin, phtotosystem II, and light harvesting complex I and II) into the middle, bicontinuous microemulsion (Bicont ME), phase of Winsor-III systems at concentrations > 1 g/L, formed using Aerosol-OT / 1,3-dioxolane-based alkyl ethoxylate binary surfactant system. Unlike other surfactant self-assembly systems employed for MP solubilization, the Bicont ME phase is optically transparent, isotropic, and contains surfactant monolayers of near-zero curvature, to reduce denaturation. The MP-laden Bicont ME phases have been investigated by circular dichroism to analyze for perturbations in the MPs' secondary structure, and by small-angle neutron scattering (SANS) to determine structural perturbations of the phase's nanostructure. Via SANS we determined that the incorporation of MPs reduces the average diameter

of the Bicont MEs' nanochannels and increases the surface area per volume of the MEs.

**Surfactants Based on Algae Oil.** G.A. Smith and M. Coleman, Huntsman Corporation, The Woodlands, TX, USA.

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

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

**Superior Characteristics of Biosurfactant Surfactin and Its Application Potentiality.** S. Yanagisawa<sup>1</sup>, T. Nagano<sup>1</sup>, M. Izumida<sup>1</sup>, T. Imura<sup>2</sup>, T. Taira<sup>2</sup>, and D. Kitamoto<sup>2</sup>, <sup>1</sup>New Business Development Division, Kaneka Corporation, Osaka, Japan, <sup>2</sup>Research Institute for Innovation in Sustainable Chemistry, National Institute for Advanced Science and Technology, Tsukuba, Japan.

Surfactin (SF) is one of the most promising biosurfactants produced by fermentation under mild conditions with naturally derived raw materials and a type of safe microorganism, *Bacillus subtilis*. It is produced and currently commercially available as sodium salt (Kaneka Corporation). This sustainable product is both human- and environment-friendly. Results of skin irritation test show that it is much milder than other typical surfactants. In fact, it showed no observable skin irritation at generally used concentrations. Moreover, it was degraded almost completely within a week in the biodegradation test.

The structure of SF is unique compared to that of other surfactants. SF has a heptapeptide head group interlinked with a  $\beta$ -hydroxy fatty acid. Due to its unique cyclic peptide structure, it shows

excellent surface and self-assembling properties. It exhibited a dominantly low CMC (critical micelle concentration) value of 0.0003%. It was also found that the molecules spontaneously formed giant aggregations in aqueous solution by freeze-fracture electron microscopy (FFEM). Undoubtedly, it has many interesting potential applications in a variety of fields such as cosmetics and homecare industries.

**Production and Antimicrobial Property of Glycolipid Biosurfactants.** D.K.Y. Solaiman, R.D. Ashby, and J.A. Zerkowski, USDA, ARS, ERRC, Wyndmoor, PA, USA.

Microbial glycolipids such as rhamnolipid (RL) and sophorolipid (SL) are an important class of biosurfactants with excellent surface tension-lowering activity. Besides their surfactant- and environment-friendly properties, however, additional value-added property such as bacteriocidal activity is needed to further heighten their commercial interests. We devised a straightforward production scheme and HPLC analysis method for synthesis and characterization of monorhamnolipid (R<sub>1</sub>L) and sophorolipid (SL) produced from patent-strain *Pseudomonas chlororaphis* NRRL B-30761 bacterium and *Rhodotorula bogoriensis* yeast, respectively. R<sub>1</sub>L and SL were then incorporated into biodegradable poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) films. Tests on acne-causing bacterium (i.e., *Propionibacterium acnes*) and on tomato-rotting causative agent (i.e., *Pseudomonas corrugate*) showed that these glycolipids possessed excellent antimicrobial activity. The finding adds to the antimicrobial spectrum of RL and SL, thus further increasing the potential commercial values of glycolipid biosurfactants.

**Production of Rhamnolipids from Unique Pseudomonads.** G. Deluga, D. Derr, N. Lohitharn, D. MacEachran, J. Ulrich, W. Jordan, and R. Mirani, Logos Technologies, Ashburn, VA, USA.

The promise of biosurfactants has a long and storied history of having commercial potential (1). One of the major classes of biosurfactants is glycolipids that have the potential to replace a number of petroleum based surfactants due their sulfate and phosphate free nature while having superior surfactant properties. This class of glycolipids are characterized by either a mono or di rhamnose head group and a 3-(hydroxyalkanoyloxy)alkanoic acid tail that varies in molecular weight according to a number of factors including feedstock, fermentation time and

Pseudomonas strain. We have developed three strains of Pseudomonads that produce rhamnolipids at high titers.

This presentation will discuss the three strains of Pseudomonads that have been isolated for the overproduction of both mono- and di-rhamnolipids. Each strain has a unique rhamnolipid molecular weight profile for a specific feedstock. Results will be presented discussing how these two variables interact. Data demonstrating a correlation between the molecular weight distribution of the rhamnolipid isolates and the CMC will be presented. These biosurfactants have the characteristics and can meet the cost targets necessary for large scale commercialization.

(1) Desai JD, Banat IM (March 1997). *Microbiol. Mol. Biol. Rev.* 61 (1): 47–64.

**Biosynthesis of Surface-active Lipids.** M. Falkeborg (*Honored Student Award Winner and The Manuchehr Eijadi Award Winner*), R. Gao, S. Song, L.Z. Cheong, X. Xu, and Z. Guo, Dept. of Engineering, Aarhus University, Aarhus, Denmark.

Surface-active lipids find applications in food and pharmaceutical industries and the interest for their economically feasible and ecologically friendly production and derivatization is increasing.

This presentation summarizes our recent progress in 1) production of biosurfactants *via* high-cell density fermentation; and 2) enzymatic synthesis of phosphatidyl saccharides for preparation of nanoliposomes with enhanced stability.

Sophorolipids have received special attention due to their biodegradability, low toxicity, and production from renewable resources. To produce sophorolipids with high time-space efficiency, a high-cell-density fermentation strategy was applied. The nutrient concentration and physical parameters were optimized for enhanced volumetric productivity. The protocol was implemented in a 10-L fermentor and a remarkably high volumetric productivity (>200g isolated sophorolipids/L/day) was achieved.

Derivatization can tailor surface-active lipids to specific applications. Phospholipids are known to form liposomes capable of encapsulating sensitive ingredients; however, drying processes are usually required and cryoprotectants are needed to stabilize the liposomes. To overcome this, an enzymatic method for incorporating sugar moieties into phospholipids was developed. The resulting phosphatidyl saccharides were capable of forming liposomes with increased stability during dehydration.

## S&D 2: Surfactants in Energy I

Chairs: U.P. Weerasooriya, University of Texas Austin, USA; and B.J. Shiau, University of Oklahoma, USA

### Study of Chemical EOR Induced Emulsions and Potential Mitigation Measures.

A. White, M. Gernand, and T. Swanson, Clariant Oil Services, The Woodlands, Texas, USA.

During the application of chemical enhanced oil recovery (cEOR) floods, breakthrough of the injection chemicals periodically occurs. It is generally not possible to predict the quantity and timing of the chemical breakthrough. Some cEOR recommendations use a combination of surfactant and polymer (SP), alkaline, surfactant and polymer (ASP), and variations on these two themes. In the event that chemical breakthrough does occur, these products can greatly contribute to the formation of very stable emulsions, which are quite different from naturally occurring emulsions stabilized by components such as asphaltenes and resins. These emulsions can be both stable water-in-oil (normal) and oil-in-water (reverse) emulsions.

Traditional demulsifiers are often ineffective on emulsions created by chemical floods. Like any emulsion, these induced (i.e. basically synthetic) EOR-based emulsions need to be resolved or broken. Producing dry oil and clean water are requirements that all producers must achieve. Dry oil is needed to meet pipeline and various other transportation specifications, while clean water is needed to meet environmental regulations and operators' own production requirements. This paper addresses the effects SP and ASP treatments have on oilfield emulsions and explores ways to mitigate them and risk manage the cEOR program from a fluid separation process point of view.

**Surfactant Development for EOR.** Z. Mogri and G. Haddix, Shell Chemicals, Houston, TX, USA.

EOR describes a range of techniques that use steam, gas or water to mobilize oil in the pores of reservoir rock. In the case of water, oil recovery can be further improved by adding low concentrations of detergents and other additives. Shell Chemicals, with strong cooperation from Shell Upstream, has developed these detergents – and has the required manufacturing capacity to make them. Shell Chemicals markets the **ENhanced Oil Recovery DETergents** under the ENORDET name. Shell Chemicals offers a range of ENORDET surfactants which by careful formulation can match diverse crudes and reservoir conditions. Technical

developments focus on further extending the range of surfactants to match wider ranges of water compositions and temperatures, thereby enabling the technology to be deployed in even more demanding fields. Our innovations are generally focused on two key classes of molecules – internal olefin sulfonates and alcohol alkoxy sulfates. We make the feedstock for these molecules at our world-scale Geismar plant in Louisiana, using existing processes and equipment. We have substantial manufacturing capability available when it's needed, offering essential security of supply to our customers.

### Gravity Stable Ultra-low Tension Surfactant Floods for Chemical EOR.

J. Lu (*Surfactants and Detergents Division Student Award Winner*), U.P. Weerasooriya, and G. Pope, University of Texas at Austin, Austin, TX, USA.

Classical stability theory can be used to estimate the critical velocity of a miscible flood stabilized by gravity forces. However, stability theory for an ultra-low interfacial tension (IFT) surfactant displacement is not well developed or validated. In this paper, a method for predicting the critical velocity for a surfactant flood is proposed taking into account the microemulsion phase. Vertical upward surfactant displacement experiments were performed and compared with stability theory. The proposed theory and experimental results offer new insight into the behavior of surfactant floods stabilized by gravity forces and how to optimize them by controlling the microemulsion viscosity.

### Investigation into the Effect of pH, Temperature, and Salinity on the Stability and Wetting Performance of Sulfosuccinate Surfactants.

S. Majmudar<sup>1</sup>, N. Jayasuriya<sup>1</sup>, D. Vanzin<sup>1</sup>, and E. Saly<sup>2</sup>, <sup>1</sup>Cytec Industries, Stamford, CT, USA, <sup>2</sup>Cytec Industries, Vlaardingen, The Netherlands.

Sulfosuccinate surfactants are utilized within the oil industry as wetting, dispersing and emulsifying agents. An oil industry concern is hydrolytic stability of these products and the loss of wetting performance of these products over time under varying conditions of pH, temperature and salinity. This paper summarizes the investigation into the wetting performance of these products at a 0.5% concentration in deionized water (DI water) and

brine (i.e. 3.0% NaCl and 3.0% NaCl/0.05% CaCl<sub>2</sub>) solutions. The surfactant solutions were evaluated for wetting performance via surface tension measurements over a period of 28 days at pH 3, 8 and 11 and at temperatures of 23 and 80°C. The appearance of the surfactant solutions was also examined and commentary will be offered as to how this visual screening test impacts final wetting performance. The experimental results indicate that the wetting performances of sulfosuccinate surfactants vary per a given set of conditions. Data from the experimental investigations will be presented and discussed and recommendations offered as to the optimal products for a given set of conditions.

**Effects of Hardness and Cosurfactant on Phase Behavior of Alcohol-Free Alkyl Propoxylated Sulfate Systems.** M. Puerto<sup>1</sup>, G. Hirasaki<sup>1</sup>, C. Miller\*<sup>1</sup>, C. Reznik<sup>2</sup>, S. Dubey<sup>2</sup>, J. Barnes<sup>2</sup>, and S. van Kuijk<sup>2</sup>, <sup>1</sup>Rice University, Houston, TX, USA, <sup>2</sup>Shell Global Solutions, Houston, TX, USA and Amsterdam, The Netherlands.

This presentation describes research related to off-shore surfactant-based Enhanced Oil Recovery, where sea water may be used for injection.

The effect of hardness was investigated on equilibrium phase behavior of blends of **Alcohol Propoxy Sulfates** and an **Internal Olefin Sulfonate**, without alcohol. Hard brines investigated were synthetic **Sea Water**, and 2 and 3\***SW** ion concentrations. Both octane and crude oil systems were evaluated, at ~25 and 50°C.

Optimal blends of four APS surfactants with IOS<sub>15-18</sub> formed microemulsions of high oil solubilization suitable for EOR. However, oil-free aqueous solutions of optimal APS/IOS<sub>15-18</sub> blends exhibited cloudiness/precipitation, making them unsuitable for injection in 2\*SW, 3\*SW. In SW at optimal blend, the aqueous solution of branched alcohol<sub>67</sub>PO<sub>7</sub> sulfate and IOS<sub>15-18</sub> was clear. A salinity map prepared for this blend facilitates selection of injection compositions where injection and reservoir salinities differ.

Branched alcohol<sub>67</sub>PO<sub>7</sub> sulfate was blended with other alkoxyated sulfates, yielding microemulsions with high solubilization and clear aqueous solutions in SW (25°C). Such a blend was found to form suitable microemulsions in SW with a crude oil at its reservoir temperature near 50°C.

**Overview of the Technical Challenges for Chemical EOR (cEOR): A Surfactant Manufacturer's**

**Perspective.** J.R. Barnes<sup>1</sup>, C.G. Reznik<sup>2</sup>, S. van Kuijk<sup>1</sup>, and T. King<sup>2</sup>, <sup>1</sup>Shell Global Solutions International B.V., Amsterdam, The Netherlands, <sup>2</sup>Shell Global Solutions (US) Inc., Houston, TX, USA.

Through oil/water IFT reduction, surfactants can play a role in increasing the volume of crude oil recovered from reservoirs by as much as 50%. If fully realized, surfactant EOR could yield up to 750 billion barrels of oil left in reservoir after water flooding, and could roughly double the current annual surfactant market. To realize this potential and successfully deploy cEOR there are several Upstream and Downstream activities to manage. We shall review the following two areas in this presentation:

1) Surfactant chemistries need to be tailored to each reservoir. The characteristics of a specific surfactant including carbon number, branching, and distribution of components, will impact its ability to form ultra low IFT and mobilize a specific crude oil. We shall discuss these characteristics and how to extend the range of effectiveness of a core set of commercially available surfactants through the use of blends that work across a range of reservoir conditions, crude oil types, temperatures and brine salinities.

2) Surfactant handling and deployment of full scale surfactant EOR will require large volumes that can be easily shipped and handled in the field. Considerations such as achievable active matter content, viscosity/pumpability and options for delivered forms will be covered.

**Novel Extended Surfactant-polymer Formulations for EOR from High Salinity Reservoirs.** M.R. Rojas<sup>1</sup>, A. Raj<sup>1</sup>, B.J. Shiau<sup>2</sup>, and J.H. Harwell<sup>1</sup>, <sup>1</sup>School of Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, OK, USA, <sup>2</sup>Mewbourne School of Petroleum and Geological Engineering, University of Oklahoma, Norman, OK, USA.

We investigated the properties and performance of several alkyl-propoxy sulfate extended surfactants (APS) for chemical flooding design, particularly for high salinity reservoirs in Oklahoma. The use of the hydrophilic-lipophilic difference (HLD) equation and characteristic curvatures (C<sub>c</sub>) of the surfactants were extended to the estimation of optimal salinities for mixtures of various surfactant system. The novel mixtures exhibit ultralow IFT, high coalescence rates near the optimum (Windsor type III microemulsion), and stability in synthetic and reservoir brines from NE Oklahoma (TDS up to 180,000 ppm). The HLD



equation-based estimations of optimal salinities for the mixtures were in excellent agreement with the experimental data prepared in reservoir brine. Compatibility of the optimal formulations with several polysaccharides, celluloses and polyacrylamides was also studied. Based on the EOR performance in sand-pack and core flood studies, the SP formulations showed residual oil recoveries between 50-60 % at reservoir conditions, using 0.5 PV slugs with 0.2-0.3 wt. % of total surfactant concentration. The new formulations show promising performance to be used in high salinity reservoirs such as those in Oklahoma and Texas.

**Latest Developments in Chemical Enhanced Oil Recovery as Applied to Different Reservoir Environments.** U.P. Weerasooriya and G.A. Pope, University of Texas, Austin, TX, USA.

Chemical EOR formulations have been developed to handle different reservoir environments that include mild to harsh conditions. These conditions include mild to high temperatures, salinities, and hardness ions. These formulations were developed using phase behavior experiments which were subsequently verified by core floods. The new chemicals employed in the formulations have both commercial and cost viability.

**Designing Surfactant Formulations for EOR: Investigation of Equivalent Alkane Carbon Number**

**(EACN) for Crude Oils.** W. Wan, J. Zhao, T. Hsu, J. Harwell, and B.J. Shiau, University of Oklahoma, Norman, OK, USA.

To facilitate screening of EOR surfactants, the concept of equivalent alkane carbon number (EACN) assigns a single "alkane analog" value to characterize the global properties of a complex hydrocarbon mixture such as crude oil. Thus, it would be helpful to know EACN of specific crude oil before finalizing the surfactant formulations for field implementation. In this endeavor, the EACN was estimated from an empirical correlation. The values of EACN for a variety of hydrocarbons mixtures have been determined previously using common EOR surfactants. In addition, we extend our efforts to include several extended surfactants and successfully demonstrate their ability to generate ultra-low IFT middle-phase microemulsions. In this study, the EACNs for crude oils from different mature oil fields are obtained using various surfactant formulations. The estimated EACNs for these crude oils are from 6.0 to 11.3. We compared the EOR potential for both conventional surfactants and extended surfactants using three different crude oils. The resulting EACN values for three targeted crude oils measured from both conventional surfactants and extended surfactants are quite similar, yet the extended surfactant system typically does not need short-chain alcohol as additive to improve their EOR performance.

**S&D 2.1: Impact of Surface Modification in Household and Hard Surface Cleaning Applications**

*Chairs: D. Stott, Church & Dwight Co., Inc., USA; and J. Shulman, Dow Consumer and Industrial Solutions, USA*

**Development of a High Performance Low Streak Degreaser.** J. Wates<sup>1</sup>, M. Dery<sup>1</sup>, A. Slikta<sup>2</sup>, and B.H. O<sup>3</sup>, <sup>1</sup>Akzo Nobel Surface Chemistry, Brewster, New York, USA, <sup>2</sup>Akzo Nobel Surface Chemistry, Chicago, IL, USA, <sup>3</sup>Akzo Nobel Chemicals, Deventer, The Netherlands.

Many commercially-available surfactant-based cleaners exhibit excellent degreasing performance, but they leave visible residues behind after drying, which can result in an unattractive streaky appearance and limits the types of surfaces these formulations can be used on. Glass cleaners are generally much lower streaking but they cannot remove tough grease and so they are only effective on lightly soiled surfaces. Numerous so-called multi-surface cleaners have been introduced in an attempt to fill this gap in performance but current commercial products do not meet the target of combining heavy duty grease removal and low streaking in the same formulation. This presentation describes the development of a surfactant-based cleaner that combines excellent degreasing with very low streaking.

**Multi-benefits from Household and Industrial Cleaners Using Surface-Modifying Polymers.** T.J. Futterer<sup>1</sup>, F. Lambert<sup>2</sup>, K. Karagianni<sup>2</sup>, and C. Orizet<sup>2</sup>, <sup>1</sup>Solvay, Cranbury, NJ, USA, <sup>2</sup>Solvay, Aubervilliers, France.

Household and industrial cleaners like hard-surface cleaners and dish wash & fabric detergents have to provide more and more benefits beyond detergency on a growing variety of surface types. Many desired benefits like easy cleaning, fast drying, shine or anti-scaling can be achieved by changing the surface properties by depositing the right polymer from a cleaning product onto the respective surfaces.

This presentation is discussing the deposition mechanisms and structure-property relations of charged synthetic and natural polymers. The impact of the surface energy (hydrophobic-hydrophilic) and the chemical nature of the polymer (charge, pKa, complexation behavior) on the deposition and the resulting surface properties are described. As one example, we show monolayer deposition of charged acrylate copolymers onto e.g. glass, ceramics, stainless steel and plastics and demonstrate some of the resulting benefits, like fast

drying via instant and complete drainage of aqueous film, easy cleaning via reduced soil adhesion, spot-free and anti-fog via complete wetting. Some of the methods utilized in the present work are Ellipsometry, Quartz-Crystal-Microbalance, Contact-Angle measurements and cleaning tests.

**Observing the Effects of Temperature and Surface Roughness on Cetyltrimethylammonium Bromide (CTAB) Adsorption Using Quartz-Crystal Microbalance with Dissipation.** J. Hamon, B. Grady, and A. Striolo, University of Oklahoma, Norman, OK, USA.

The effects of temperature and surface roughness on mass and viscoelasticity of an adsorbed surfactant layer were monitored using the quartz crystal microbalance with dissipation (QCM-D). Adsorption isotherms at 20, 30, 40, 50 and 60°C and at two different roughnesses on gold were measured using cetyltrimethylammonium bromide (CTAB). All isotherms displayed an increase in mass and dissipation as surfactant concentration was increased to its CMC and, for isotherms above the Krafft temperature of CTAB, roughly 25°C, adsorption reached a peak followed by a slight decrease to a plateau at the equilibrium adsorption value. As the temperature was increased the same trend observed with increasing concentration was seen, but adsorbed mass was decreased at equilibrium. Adsorbed mass and dissipation were both decreased further by increasing substrate roughness, where a decrease in the peak height above the equilibrium value was also observed. Previously, our group reported a large peak at the CMC for rough surfaces at room temperature which was attributed to impurities; in this work the peak is much smaller which we attributed to the fact that helium sparging and ultrasonic degassing of the surfactant solution was performed prior to contact with the substrate surface in this series of experiments.

**Use of Tailor Made Amorphous Silica Technology to Enhance Coatings.** S. Mohammed and M. Nargiello, Evonik Industries, Piscataway, NJ, USA.

With ongoing scrutiny and sensitivity in industry to move towards less hazards in the workplace, more emphasis is placed on suitable amorphous technology to replace crystalline

technology. Amorphous silica character is highly adaptable and flexible to be modified in both powder and pre-dispersed forms. Due to this high flexibility, numerous engineered types of technologies have been developed over the decades to provide functional solutions to many coatings problems.

Amorphous silica technology has been developed to address functionalities including: rheological control, suspension of pigments and fillers, reinforcement of coatings film, impart scratch resistance, impart hydrophobicity - water repellency – anti-corrosion benefits, carriers of trace actives into coatings for homogenous distribution, flow control and charge enhancement of powdered coatings, and gloss reduction of liquid systems.

This paper will address how amorphous silica technology is differentiated and engineered to create specially tailored solutions to enhance the performance of coatings. Particle technology and modifications which will be addressed and performance attributes will be highlighted for each of the types of tailor made modifications. A short discussion of the importance of proper dispersion and homogenous distribution within a coatings matrix will be reviewed.

**Soy Flour Derivatives in Laundry Applications.** A. Hudson, J. Glover, J. Steffens, and R. Klare, Surface Chemists of Florida, Inc., Jupiter, FL, USA.

Defatted soy flour is a coproduct in the processing of soybeans to obtain the more economically valuable oil. It contains a high level of globular proteins which have value in food and nonfood applications, but for most of these applications must be separated from undesirable components by known processing methods.

We will present methods to prepare soy flour derivatives that have efficacy in laundry products as soil antiredeposition agents, dye transfer inhibitors and antisoiling additives. The methods involve minimal processing steps and waste streams. Modifications that increase both the anionic functionality and the cationic functionality of the inherently amphoteric proteins will be presented. Solubilizing with surfactants compatible with laundry products is shown to improve the solubility and efficacy in laundry products and facilitate separation from insoluble materials in the soy flour. New methods for analyzing surface properties will be presented and the properties will be related to their function in laundry detergents.

**Solubilization of Mixed Anionic Extended Surfactants and a Cationic Surfactant.** D. Panswad<sup>1</sup>, S. Khaodhiar<sup>2</sup>, and D.A. Sabatini<sup>3</sup>, <sup>1</sup>Ramkhamhaeng University, Bangkok, Thailand, <sup>2</sup>Chulalongkorn University, Bangkok, Thailand, <sup>3</sup>University of Oklahoma, Norman, OK, USA.

Mixture of anionic and cationic surfactant can exhibit greater synergism than other mixed systems but its limitation is the tendency to form insoluble complexes. In this research, mixture of anionic extended surfactants and a cationic surfactant have been evaluated for precipitation, surface tension and solubilization of three organic solutes (phenylethanol, styrene and ethylcyclohexane). Four carboxylated based anionic extended surfactants (C167-42, C168-42, C167-45, and C168-45) were mixed with a pyridinium based cationic surfactant (cetylpyridinium chloride, CPC). Precipitation phase boundaries of mixed anionic extended surfactant and cationic surfactant showed significant reduction in precipitation region compared to that of a conventional mixed surfactant (SDS/DPC). CMC of mixed surfactant systems were much lower than that of individual surfactant systems. Finally, it was concluded that these mixed surfactant systems can achieve higher solubilization capacity than the individual surfactant system and conventional mixed surfactant system while requiring lower electrolyte addition. This result points to the favorable formulation potential of these mixed systems.

**Characteristic Curvatures of Nonionic Alcohol Ethoxylates: Effects of Alcohol Structure and Catalyst Type.** T. Nguyen and W. Sorensen, Sasol North America, Westlake, LA, USA.

The characteristic curvature (Cc) of a surfactant has been a useful tool in selecting surfactants for formulations in detergency and enhanced oil recovery. Nonionic alcohol ethoxylates are always an important component in detergency formulations. They are currently used more in surfactant flooding formulations in enhanced oil recovery due to their salt tolerance. In this study the Cc of nonionic alcohol ethoxylate surfactants were determined based on the hydrophilic-lipophilic deviation (HLD) concept for nonionic surfactants. It was found that alcohol structures and catalyst types used to synthesize alcohol ethoxylates affect the Cc of alcohol ethoxylates with a similar degree of ethoxylation. A more branched alcohol ethoxylate was found to have more negative Cc value than a less branched alcohol ethoxylate. Alcohol

ethoxylates made with KOH catalysts were found to have more negative Cc value than those made with low alkalinity narrow-range NRE catalyst. The findings of this work are useful not only in the selection of the right alcohol ethoxylate but also in the synthesis of an alcohol ethoxylate with the desirable Cc value for a certain formulation application.

**Novel Chemistries from Itaconic Acid for Detergent Formulations.** Y. Durant, A. Augustiniak, B. Jiang, and J. Shaw, Itaconix, Stratham, NH, USA.

Itaconic acid has intrigued formulation chemists for many years with the potential to improve product performance using the unique functionality of the dicarboxylic acid groups. This potential was limited historically by an inability to manufacture commercial products due to the limited reactivity of the vinyl bond of itaconic acid. From metal ion chelation and threshold inhibition to

antiredeposition and dispersion we will discuss the novel chemistries and the unique functionality enabled by the ability to polymerize, esterify and further modify itaconic acid.

Polymers of itaconic acid are used in a range of detergent and personal care applications. Low-molecular weight linear itaconic acid polymers have excellent calcium binding capacity and are gaining broad use as replacements for phosphates, NTA, EDTA and lesser-performing chelants. Beyond their unique performance, these polymers have favorable low toxicity, are 100% bio-based, and are readily biodegradable. With this excellent environmental profile, sodium polyitaconate with an Mw=4000-5000 g/mol was the first polymer accepted onto the EPA's CleanGredient list for Design for the Environment products and is approved by the Natural Products Association as a certified ingredient in natural products.

### S&D 3: General Surfactants

Chairs: S. Adamy, Church & Dwight Co., Inc., USA; and M. Tsumadori, Kao Corporation, Japan

**Effect of Dialkyl Ammonium Cationic Surfactants on the Microfluidity of Membranes Containing Raft Domains.** M. Uyama<sup>1</sup>, K. Inoue<sup>1</sup>, K. Kinoshita<sup>1</sup>, R. Miyahara<sup>1</sup>, H. Yokoyama<sup>2</sup>, and M. Nakano<sup>2,3</sup>, <sup>1</sup>Shiseido Research Center, Yokohama, Kanagawa, Japan, <sup>2</sup>Kyoto University, Kyoto, Japan, <sup>3</sup>University of Toyama, Sugitani, Toyama, Japan.

TRPM8 (transient receptor potential melastatin 8) is a thermosensitive cation channel that is highly expressed in cold sensory neurons and is activated by cold stimuli (threshold: ~25°C) and cooling agents, such as menthol and icilin. It has been reported that TRPM8 localizes in lipid raft microdomains and the menthol- and cold-mediated responses of TRPM8 are potentiated when the association of the channel to the microdomains is prevented. From this perspective, in this study, we focused in this study on the effects of several surfactants. Treatment of TRPM8-transfected HEK293 cells with dialkyltrimethyl ammonium chloride enhances the menthol-induced Ca response. To evaluate the physicochemical effects of surfactants on membranes, we used liposomes comprising of phosphatidylcholine, sphingomyelin, and cholesterol as models of cell membranes containing raft domains; the microfluidity of the domains was characterized by fluorescence spectrometry using DPH and Laurdan. Among several surfactants, dialkylammonium-type cationic surfactants most efficiently increased the microfluidity. It is therefore concluded that dialkylammonium cationic surfactants potentiate the menthol-mediated responses of TRPM8 by increasing the microfluidity of the lipid raft domains where the ion channel localizes.

**Photoinduced Demulsification of Emulsions Using a Photoresponsive Gemini Surfactant.** Y. Kondo, K. Fukuyasu, T. Horiuchi, and Y. Takahashi, Dept. of Industrial Chemistry, Tokyo University of Science, Shinjuku, Tokyo, Japan.

This paper reports on the influence of light irradiation on stability of emulsions prepared using a photoresponsive gemini surfactant (C<sub>7</sub>-azo-C<sub>7</sub>) having an azobenzene skeleton as a spacer. When mixtures of *trans* C<sub>7</sub>-azo-C<sub>7</sub> aqueous solution and *n*-octane are homogenized, stable emulsions are obtained in a specific region of weight fraction and surfactant concentration. Fluorescence microscopy

observations using a small amount of fluorescent probes show that the stable emulsions are oil-in-water (O/W)-type. UV irradiation of stable O/W emulsions promotes the *cis* isomerization of *trans* C<sub>7</sub>-azo-C<sub>7</sub> and leads to the coalescence of the oil (octane) droplets in the emulsions, i.e., demulsification. Dynamic IFT measurement shows that UV irradiation to the interface between aqueous *trans* C<sub>7</sub>-azo-C<sub>7</sub> solution and octane brings about an increase in the interfacial tension, indicating that the Gibbs free energy at the interface increases. From this result, the *cis* isomerization of *trans* C<sub>7</sub>-azo-C<sub>7</sub> molecules at the O/W interface due to UV irradiation leads to direct contact between the water and octane phases, because of the reduction of molecular area at the interface, and subsequently makes the emulsions demulsified.

**Heat Induced Gelation and Thermo-coloring Phenomena of O/W Emulsions of a Long-chain Amidoamine Derivative.** T. Kawai, Tokyo University of Science, Shinjuku, Tokyo, Japan.

In recent years thermo-responsive materials have attracted as one of the stimuli-responsive materials for pharmacy, micromachines and pollutant removal. Heat-induced gelation materials, which undergo a thermally reversible transition from a low viscosity solution to a rigid gel upon an increase in temperature, have attracted considerable attention as injectable drug-delivery systems. In this paper, we demonstrate that a long-chain amidoamine derivative (C18AA) acts as a normal organogelator in toluene, exhibiting a phase transition from gel to sol on heating, but changes to a heat-induced gelator upon addition of aqueous LiCl to the toluene gel. Further, we also show the unique multi-layered emulsion of C18AA with an additive of quaternary ammonium salt, tetraoctylammonium bromide (TOAB), which developed the structural color only in the specific temperature region.

**Discovery of the Stable a-gel Formation Generated by the Highly Purified Mono Alkyl Phosphates.** K. Tanaka, S. Kamako, J. Li, S. Hashimoto, and T. Suzuki, Nikkol Group Cosmos Technical Center Co., Ltd., Hasune, Itabashi, Tokyo, Japan.

a-gel is known as one of self-assemblies formed by a specific surfactant. However, the characteristic investigations of a-gel have not been

performed enough because of the instability aspect of that. Moreover, it has not been founded the improvement methods to increase its stability. Long chain mono alkyl phosphates were investigated to demonstrate formation of self-assemblies. In this study, we revealed that hexadecyl phosphate neutralized with L-arginine (R16MP-Arg) has very unique self-assembling behavior in the aqueous system. On the DSC measurement, the krafft temperature ( $T_c$ ) of this material in the water was observed around 50 – 60 C. However, on the visual observation, the aqueous solution of this material remained gel-like structure even below the  $T_c$ . Then this association structure was characterized as a lamellar form by SAXS. In addition, spontaneous swelling was observed below the  $T_c$  without heating and shaking. These results were suggested that R16MP-Arg has different aqueous behaviors compared to other common ionic surfactants. It is considered that R16MP-Arg could form a stable “a-gel” thermodynamically below the  $T_c$ .

**Shear-response Emulsion Prepared Through Discontinuous Cubic Liquid Crystal.** Y. Yamashita<sup>1</sup>, Y. Yamaguchi<sup>2</sup>, and K. Sakamoto<sup>1</sup>, <sup>1</sup>Chiba Institute of Science, Choshi, Chiba, Japan, <sup>2</sup>St. Marianna University, Kawasaki, Kanagawa, Japan.

We had investigated kinetic properties of semi-equilibrium micellar solution, which was obtained by simple dilution from a discontinuous cubic liquid crystal. The discontinuous cubic liquid crystal solution ( $I_1$  solution) abnormally behaves under shearing; it remains stable without any stress (microemulsion), while the oil solubilized in the aggregate becomes squeezed out upon the physical forces (emulsion). The semi-equilibrium structure of the  $I_1$  solution was evaluated by scattering methods and FF-TEM, and the kinetic structural change (aggregate deformation or break-up) was monitored by rheological measurements. We introduce this  $I_1$  solution as a novel sustainable vehicle for several applications, e.g. for cosmetics and pharmaceuticals.

**Phase Behavior and Conductivity Studies of Surfactant/Limonene Systems Incorporating Aqueous Carbonate Solutions.** S. Adamy, Church & Dwight Co., Inc., Princeton, NJ, USA.

Oil-water-surfactant systems, which also include carbonate salts, are highly relevant to cleaning applications. Carbonates are often used as builders in such systems, but also have an impact on the overall phase behavior, being soluble salts. The phase behavior of systems incorporating nonionic

surfactant, d-limonene, and aqueous solutions of either  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ , or  $\text{K}_2\text{CO}_3$  have been characterized in order to discern temperature-dependence and locations of the three-phase regions. It has been found that the phase-inversion temperature is dependent on both salt concentration and cation type. The phase-behavior studies have been supported with conductivity measurements and various theoretical considerations.

**Use of Interfacial Phenomena for Prediction of Foaming and Cleaning in Hand Dishwashing Applications.** J.S. Dailey<sup>1</sup>, A. Kingma<sup>2</sup>, T. Gessner<sup>1</sup>, and S. Patterson<sup>1</sup>, <sup>1</sup>BASF Corporation, Wyandotte, MI, USA, <sup>2</sup>BASF SE, Ludwigshafen, Germany.

Recent work in our labs has focused on using Mixture DOE to optimize foaming and cleaning performance for liquid hand dish formulations. More specifically, we have evaluated mixtures of Sodium lauryl ether sulfate, lauryl dimethylamine oxide, alkylpolyglucoside, cocoamido propyl betaine, and 2-propylheptyl ethoxylates in applications such as the ASTM D4009-92 (Standard Guide for Foam Stability in Hand Dish Detergents). In addition to the performance tests we also evaluated the colloid and interfacial properties (interfacial rheology, surface tension and CMC) for the same mixtures to better understand the impact on the performance and to see if any correlations exist between the application test results and the interfacial phenomena. The interfacial rheology (surface dilatational modulus) was determined with a KRÜSS DSA 100 with an EDM/ODM module. The tests allow us to determine the storage modulus, loss modulus, or surface elasticity which has been shown to correlate positively with stable foam. In the end we have developed multiple models which include # plates cleaned, foam profiles, % Cleaning (Soak Test), surface tension, and CMC. In this presentation we will show that the possibility exists to optimize formulations for multiple performance criteria by using mixture design of experiment.

**Phase Behavior and Characterization of Polyelectrolyte Complexes (PECs).** D. Scheuing and M. Knock, Clorox Services Co., Pleasanton, CA, USA.

PECs can be formed by electrostatic interactions between pairs of polyelectrolytes of a wide variety. Manipulation of the conditions of synthesis can result in stable colloidal particles with dimensions on the order of 100 nm diameter. The molecular weights of the polyelectrolytes and the

types of ionizable groups determine the behavior and utility of the PECs at solid-water interfaces and their interactions with micelles. Light scattering and

FT-IR techniques can be used to characterize the PECs in solution and at interfaces.

### S&D 3.1: Surfactants in Healthcare

Chairs: A. Kaziska, Croda Inc., USA; and T. Zander, Henkel Corp., USA

**The Use of TAED/persalt in Laundry Formulation on Contaminated Fabrics and Washing Machines.** A.J. Theobald, A.J. Mathews, K. Harvey, and H. Blakeley, Warwick Chemicals, Mostyn, Flintshire, UK.

The use of front loading washing machines, high use of non-bleach containing liquid detergents, and cool wash temperatures of typically 86°F or lower has led to concerns over the potential for the persistence of microbiological contamination and malodour generation on both fabrics and within washing machines following the laundry cycle. Studies have shown that levels of 150ppm peracetic acid generated *in situ* from TAED (tetra acetyl ethylenediamine) and persalt were sufficient to reduce the loading of two bacterial strains on fabric and in wash water by greater than 3 log units (>99.9% reduction) in the ASTM E2406-09 and E2274 tests at 86°F with a 12 minute contact time. Results will be presented that illustrate how initially clean automatic washing machines can become heavily contaminated with bacteria and fungi in the detergent drawer, drum seal and sump areas over 20 cycles using standard soiled loads in the absence of bleach containing detergent at low temperature. The studies show that biofilm formation can be controlled only when sufficient concentrations of bleach activator, and hence peracetic acid, are used. The effect on malodour, whiteness revival of dingy white items and the preservation of fabric whiteness will also be discussed.

**Novel Benefits Discovered for Lactic Acid as Antimicrobial Active Against Enveloped and Non-enveloped Viruses.** P. Stuuut and R. Wietting, Corbion, The Netherlands.

Novel formulation and antimicrobial efficacy testing have revealed good anti-virus performance against both enveloped as well as some non-enveloped viruses for some standard detergent and cleaner formulations. The combination of lactic acid with anionic surfactants creates a powerful anti-microbial activity that can be used to tackle a wide range of bacteria, yeasts and virus types. A number of example HPC formulations including lactic acid as antimicrobial active, as well as efficacy data against bacteria, yeasts and enveloped and non-enveloped viruses will be covered.

**Performance Synergy Between Alkyl Polyglycoside**

**Surfactants (APG) and Lactic Acid (LA) in Manual Dishwashing Detergents.** S. Gross<sup>1</sup>, M. Coxey<sup>1</sup>, K. Salmon<sup>1</sup>, and P. Stuuut<sup>2</sup>, <sup>1</sup>BASF Corporation, Wyandotte, MI, USA, <sup>2</sup>Corbion, Gorinchem, The Netherlands.

In this presentation, a performance improvement observed with the use of Lactic Acid as an antibacterial active in manual dishwashing detergents containing Alkyl Polyglycoside Surfactants is introduced. A novel synergy has been discovered in systems using Lactic Acid as *the antibacterial active ingredient* and Alkyl Polyglycoside surfactants as a cleaning enhancer - which in turn provides the opportunity to develop a higher performing technical solution at equal actives while choosing an anti-microbial chemistry in Lactic Acid that has a positive long-term positioning in Home Care applications – specifically Manual Dish Detergents.

Market trends in Manual Dish, test formulations and performance data, as well as antimicrobial confirmation will be presented.

**Sunflower Phospholipids as Drug Delivery System.** S. Shulga, Institute for Food Biotechnology and Genomics, Kyiv, Ukraine.

The success of liposomes as drug carriers has been reflected in a number of liposome-based formulations, which are commercially available or are currently undergoing clinical trials. The transport of nucleic acids through membrane pores is a fundamental biological process that occurs in all living organisms. It occurs, for example, during the import of viral DNA into the host cell or during the nuclear pore complex-mediated transport of mRNA in and out the cell nucleus and has implications in nucleic acid drug delivery and gene therapy.

An engineered DNA – sunflower phospholipids transporter that is able to transfer DNA molecule (genetic information) across a biological membrane is described.

Complexes between the DNA and cationic liposomes obtained from sunflower phospholipids are formed by electrostatic interactions between the positive charged groups of the cationic amphiphile and negative charged phosphate groups of the DNA. Nanoscale particles called lipoplexes are formed as a result of such spontaneous self-associations, which



are located between lipid bilayers.

Here, we report a general and simple method to synthesize both 5- and 3-coupled DNA-lipid conjugates and demonstrate that vesicle pairs displaying complementary DNA can mediate vesicle fusion as demonstrated by both lipid and content mixing.

**Delivery of Sevoflurane Limited by the Presence of Cholesterol in Lipid Bilayer Membranes:**

**Multinuclear, Dynamic NMR *in Situ*.** E. Okamura and Y. Takechi, Himeji Dokkyo University, Faculty of Pharmaceutical Sciences, Himeji, Japan.

The delivery of a fluorinated general anesthetic, sevoflurane (SF, fluoromethyl 2,2,2-trifluoro-1-[trifluoromethyl]ethyl ether) to large unilamellar vesicles (LUVs) is studied by multinuclear, high-resolution solution NMR in combination with the pulsed-field-gradient technique. LUVs consisting of phospholipid/cholesterol in solution are used as a model for fluid cell membranes. Fluorine-19 and  $^1\text{H}$  NMR chemical shifts, the longitudinal relaxation times ( $T_1$ ), and the diffusion coefficients ( $D^{\text{eff}}$ ) are systematically analyzed to quantify how cholesterol modulates the SF delivery to the membrane. All NMR parameters (chemical shift,  $T_1$ , and  $D^{\text{eff}}$ ) show that the SF delivery is limited by the presence of cholesterol in the membrane. This is due to the loss of motional freedom in the rigid membrane environment, as demonstrated by the gradual slowdown of the lipid

mobility with increasing the cholesterol concentration from 0 to 40 mol%.

**Monoglyceride and Water System: The Sub-alpha Phase and the Krafft Transition.** F. Wang and A.G. Marangoni, University of Guelph, Guelph, ON, Canada.

The nature of the 13°C thermal transition in of 20% (w/w) glyceryl monostearate:sodium stearyl lactylate (GMS:SSL, 19:1) in water (MGgel) was studied by differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Simultaneous powder XRD-DSC was used to characterize the crystalline structure of the MG-gel at the temperature range from 1 to 75°C. GMS sub-alpha XRD patterns were observed below 13°C. The long-term stability of the sub-alpha phase of the MG gel system was also investigated, which was less than one month at 5, 25 and 45°C. The gel system was also observed by light microscopy. Additionally, this work also examined the Krafft transition of MG-water system. Results suggested that the liquid crystalline lamellar structure of the MG alpha-gel phase could be obtained via two pathways, by incubating the dry GMS-SSL-water mixture above their Krafft transition temperature (57°C), or by melting the GMS-SSL completely (72°C) prior to mixing with water. The nature of the Krafft transitions temperature in these lamellar phase forming lipids is discussed in relationship to the traditional definition of the Krafft temperature in emulsifiers.

**S&D 4: Surfactants in Energy II**

*Chairs: C. Hammond, CESI Chemical, USA; and P. Sharko, Shell Global Solutions Inc., USA*

**Vegetable Oil-based Microemulsion Biofuels Using Renewable Alcohols and Surfactants.** C. Attaphong (*Hans Kaunitz Award Winner*) and D. Sabatini, School of Civil Engineering and Environmental Science, University of Oklahoma, Norman, OK, USA.

Vegetable oil-based microemulsion biofuels are proposed as renewable alternatives to fossil-based fuels. Not only can microemulsification reduce the viscosity of vegetable oil and enhance the miscibility of polar and oil phases, they can also reduce pollutant emissions. From the previous studies, vegetable oil-based microemulsion fuels were formulated by using conventional nonionic surfactant with ethanol and other low molecular weight alcohols. It was found that butanol, which is now a potential bioalcohol for use as engine fuel, cannot be used alone to formulate microemulsion fuels since it was completely miscible with the oil phase. However, butanol is expected to assist solubilization of other alcohols into the oil phase. In order to achieve the ultimate goal of environmental sustainability, butanol and renewable surfactants will be introduced to formulate microemulsion fuels with comparable fuel properties to diesel. The objective of this study is to formulate microemulsion fuels using butanol mixed with other alcohols as polar phases, and using alcohol ethoxylate and sugar-based surfactants as renewable surfactants. Moreover, fuel properties and emission characteristics of the selected systems will be determined. The results from this study will provide useful information for sustainable biofuel development.

**Visualizing Foam Flow in Porous Media for Enhanced Oil Recovery.** S.L. Biswal, Rice University, Houston, TX, USA.

Foam has great potential for mobility control for enhanced oil recovery. In this talk I will describe experiments using micromodels that show the mechanisms by which foam leads to oil recovery.

**Use of Surfactants in Offshore Oilfield.** B. Lee, Shell Global Solutions, Houston, TX, USA.

Drilling offshore requires the use of high performance invert-emulsion drilling mud. The mud functions to cool and lubricate the drill bit, carry cuttings to the surface, stabilize the well bore and control formation pressure critical for well control.

Surfactants serve to stabilize the invert emulsion, control viscosity and enhance oil wetting of cuttings and mud ingredients. A mud is a thixotropic fluid system made with a low toxicity and non-persistent (biodegradable) drilling base fluid. US EPA effluent guidelines limit these fluids to synthetic materials such as internal olefins.

**Tuning Surfactants for Oilfield Applications.** J.M. Fernandez, N. Akaighe, and C. Jones, Sasol O&S, Westlake, LA, USA.

This paper discusses the tuning of surfactant chemistry for application in the oilfield. Specifically, this paper discusses the tuning of surfactants for use in specific applications in fracturing fluids, cementing, production and stimulation. By emphasizing real world application and developing laboratory models to best simulate the end use, many surfactants can be tailored to work in a variety of oilfield applications. In addition to the maximizing the application performance of the surfactant, one must also consider environmental restrictions and the economic feasibility of the chemistry in relation to the application.

Non-ionic surfactants have been well characterized and applied across several industries including detergents for household applications. There exist many parallels between household application and oilfield applications including the desire to maximize surfactancy and minimize foam formation in a variety of conditions such as high temperature and high water hardness. The work profiled here discusses the customization of several surfactants from hydrophobe selection based on chain length and level of branching to the level of ethoxylation and/or propoxylation based on the performance in the specific application.

**Tailoring Surfactants to Prevent Gas Hydrates Agglomeration.** S. Natali, Halliburton, Houston, TX, USA.

The formation of gas hydrates in subsea gas and oil-transportation lines present major economical and safety problems, as they have a tendency to agglomerate, blocking flowlines and stopping production of hydrocarbons. A common way to manage gas hydrates formation is by creating emulsions with the use of anti-agglomerants, which

are surfactants that allow hydrate particles to form, but keep them dispersed in the oil phase. However, this emulsification process can create contaminate-produced water that will require further processing steps downstream. With that in mind, tailoring surfactants to produce emulsions during the transport in the pipeline, but that are subsequently amenable to inexpensive separation, is of great importance. To that end, the HLD modeling framework could be used as a guide to the design and selection of anti-agglomerants, but its use is associated with challenges, such as application under high pressure and dissolution of diverse gasses present in field conditions. In this talk, a review of the state of art in tailoring surfactants to manage the flow of gas hydrates will be presented and challenges associated with the application of HLD to anti-agglomerants will be discussed. In addition, further topics for research focusing on current gaps in our understanding of the phenomena underlying this application will be examined.

**Connecting Laboratory Measurements to Oilfield Reality in Unconventional Shale Stimulation.** B. MacKay, Schlumberger, Sugar Land, TX, USA.

Hydraulic fracturing involves injection of large volumes of particle-laden aqueous slurries into oil-bearing rock strata, cracking the rock and establishing a conductive flow path for eventual hydrocarbon production. Surfactants are applied in these aqueous slurries to improve production by affecting several variables including surface & interfacial tension, wettability, and stability of emulsions that may form between oil and water during fracturing operations. Although it is relatively easy to extract comparative information on different surfactant packages from laboratory testing, it is not clear how to extend this knowledge to enhanced production from a reservoir because access to information on reservoir conditions and geometry is problematic. In addition, the rise of unconventional shale reservoirs as important targets has necessitated new approaches to quantifying rock-fluid interactions in field samples with negligible permeability and porosity. This talk will highlight a new laboratory measurement that is well suited to addressing topics in shale stimulation, and will describe its application to a real production problem.

**Review of Surfactant-based Corrosion Inhibitors.** S. Kiran, Nalco Champion, Calgary, AB, Canada.

The aim of this presentation is to provide a

general overview of the use of surfactants as corrosion inhibitors in oil and gas pipelines. To do so, the molecular structure of a set of anionic and cationic surfactants will first be discussed. This includes the likes of alkoxylated amines, alkoxylated phosphate esters, aromatic amines, imidazolines, and quaternary amines. The mechanism by which they adsorb onto the pipeline surface and protect it will next be explored. This will be illustrated with the aid of interfacial/surface tension and Langmuir adsorption profiles. The influence of internal pipeline conditions (e.g. flow pattern, oil type, pH, salinity, and temperature) on the performance of surfactant-based corrosion inhibitors will lastly be reviewed.

**Challenges of Breaking Emulsions in Chemical Enhanced Oil Recovery.** D. Nguyen, Nalco Champion, Sugar Land, TX, USA.

As the price of oil stabilizes and increases, more and more planned or anticipated enhanced oil recovery (EOR) projects will become reality. While recovering the oil can be a challenge, treating production that results from chemical EOR projects can be an even greater challenge. Produced oil-in-water emulsions (O/W) from chemical flooding differ from conventional crude oil emulsions in that the injected surfactant(s) and polymer at high concentrations concentrated at the oil-water interface. Because the injected surfactants and polymers are anionic, electrostatic and steric effects can result in very stable emulsions. In this study, the effects of alkali, polymers, surfactants, temperature, water cut, shear rate, and salinity on emulsion stability was investigated. Measurements of interfacial properties, such as the interfacial tension, elastic modulus, and zeta potential, at the oil/brine solution interface were also conducted. A qualitative correlation was found between the interfacial tension, elastic modulus, zeta potential, and phase separation. The interfacial tension decreased, zeta potential became less negative, elastic modulus decreased, and the size of oil droplets remarkably increased when a cationic demulsifier or an amphoteric demulsifier was added to the emulsion.

**Interfacial Measurements at Elevated Temperatures/Pressures and Their Application to Crude Oil Behavior.** J. Guo, K. Karinshak, and B. Grady\*, University of Oklahoma, Norman, OK, USA.

The measurement of interfacial properties at a temperature that is above the normal boiling point of the liquid(s) being probed presents

significant challenges. Fundamentally, it is not the temperature that is the issue but rather the pressure. Many of the normal ways we measure interfacial properties cannot be adapted in a safe manner at elevated pressures. Our laboratory has made careful study of a number of different methods, including contact angle and interfacial tension, to determine what we believe is the best

way to make measurements at elevated pressures. One application area where such measurements are needed is clearly in crude oil extraction, transport and certain parts of refining. Various measurements relevant to crude oil, e.g. solids found in crude oil, model oils for crude and crude oil itself will be described in this talk.

## S&D 4.1a: Formulating with Surfactants: Chemical Analysis and High Throughput Experimentation

*Chairs: R. Zehr, Church & Dwight Co., Inc., USA; and L. Minevski, ITW Global Brands, USA*

**Art and Industry: Evaluation of Cleaning Agents for Artists' Acrylic Paints with the Aid of High-throughput Testing.** M. Keefe<sup>1</sup>, B. Ormsby<sup>2</sup>, T. Learner<sup>3</sup>, A. Phenix<sup>3</sup>, A. Behr<sup>1</sup>, T. Boomgaard<sup>1</sup>, K. Harris<sup>1</sup>, and C. Tucker<sup>1</sup>, <sup>1</sup>The Dow Chemical Company, Charleston, IL, USA, <sup>2</sup>Tate, USA, <sup>3</sup>The Getty Conservation Institute, Los Angeles, CA, USA.

In this paper we describe the use of high throughput research (HTR) to prepare and rapidly screen cleaning formulations intended to remove surface dirt from acrylic emulsion paints, with the inclusion of raw materials novel to the field of art conservation. A group of liquid handling tools were utilized to develop stable microemulsion systems from hundreds of water/ mineral spirit/surfactant/co-solvent combinations. The cleaning performance of these microemulsions, along with other aqueous and hydrocarbon based cleaning systems were screened using a separate HTR workflow. In this workflow a HTR robotic device developed for household cleaning applications was modified to closely simulate the process of manual swab cleaning commonly used in standard art conservation practice.

The most promising candidates from the HTR evaluations were then assessed by researchers and practitioners at Tate, London, and by conservators participating in the Cleaning of Acrylic Painted Surfaces workshops. Case studies highlighting the use of these new systems on acrylic, oil and PVA based artwork will also be reviewed. This report is part of an ongoing collaboration between Dow, Tate and the Getty Conservation Institute into the development of improved cleaning systems for acrylic paints and other water sensitive works of art.

**Yellow Color Formation in Alcohol Ethoxylates Due to Oxydative Degradation.** V. Chamupathi and P. Sharko, Shell Technology Center, Houston, TX, USA.

Alcohol ethoxylates are commonly used in many detergent and cleaning formulations. These ingredients are often shipped and stored in large volumes and are prone to degradation if not protected from environmental threats. Normally water-white, these ethoxylates can develop a yellow color if they are stored exposed to the air. Standard analytic techniques have been unable to discern the exact chemical changes responsible for this color

change.

Using advanced liquid-liquid extraction methodology and Centrifugal Partitioning Chromatography (CPC) yellow components were concentrated and isolated from discolored laundry detergent samples containing nonionic surfactants. By using Ion Cyclotron Resonance Mass Spectrometry (ICR-MS) analysis, we were able to assign molecular structures for the isolated color pigments and propose a mechanism for the formation of these colored substances. The mechanism implicates the role of atmospheric oxygen in promoting the color change, emphasizing the need to keep alcohol ethoxylates and formulations containing them protected from atmospheric contamination.

**Opportunities and Pitfalls in Applied High Throughput Experimentation.** E. Theiner, Air Products and Chemicals, Inc., Allentown, PA, USA.

High throughput experimentation (HTE) provides the researcher with the opportunity to examine large data sets in order to observe clear responses and behavior. Large data sets may provide their own problems, however, due to traditional methods of analysis being confounded simply through the amount of information being generated. This presentation will discuss the difficulties endemic in examining the large volumes of information that result from HTE, especially within the realm of multi-variate analysis. Suggestions for handling such data analysis via chemometric methodologies will also be presented in a broad fashion.

**Quadruple Parallel Mass Spectrometry "Extract-Filter-Shoot" Method for Fat Soluble Vitamins in Powdered Supplements and NIST SRM 3280.** W.C. Byrdwell, USDA, ARS, BHNRC, FCMDL, Beltsville, MD, USA.

An 'extract, filter, shoot' method for vitamin D2 and triacylglycerols is demonstrated that employed four mass spectrometers, operating in different ionization modes, for a 'quadruple parallel mass spectrometry' analysis, plus three other detectors, for seven detectors overall. Sets of five samples of powder-filled dietary supplements labeled to contain 25.0 ug/mL (1000 International Units, IU) vitamin D2 with rice flour excipient were

diluted to 100 mL, filtered, and analyzed in triplicate by atmospheric pressure chemical ionization (APCI) mass spectrometry (MS), atmospheric pressure photoionization (APPI) MS and electrospray ionization (ESI) MS, along with an ultraviolet (UV) detector, corona charged aerosol detector (CAD), and an evaporative light scattering detector (ELSD), simultaneously in parallel. UV detection allowed calculation by internal standard (IS), external standard (ES), and response factor (RF) approaches that were not statistically significantly different. APCI-MS analysis by selected ion monitoring (SIM) and two transitions of selected reaction monitoring (SRM) allowed comparison of ES, IS, and RF methods, relative to vitamin D3 as the IS. The triacylglycerol (TAG) composition of the rice flour excipient was also determined by APCI-MS, APPI-MS and ESI-MS.

**Automated Formulation Assessment for High Throughput Research.** J.K. Harris, W. Heeschen, and B. Karl, The Dow Chemical Company, Midland, MI,

USA.

Evaluation and characterization of liquid formulations is typically conducted by visual inspection. Information such as number of phases, phase uniformity, optical clarity and color are key clues in determining the nature of the mixture. However this can be a tedious and laborious task and when amplified by the production rates of typical high throughput formulation devices, it becomes truly daunting. Therefore instrumentation that can automate this task becomes a necessity in order to take full advantage of HT tools. This presentation will describe the creation, implementation and utility of such devices as well as their impact on fundamental research and formulation development. These instruments use digital imaging to collect data on sample thermal stability, including phase formation, precipitation and uniformity. This allows for rapid screening of formulation additive packages as well as the effects of environment and processing.

## S&D 4.1b: Practical Use of HLD and HLD-NAC: How to Obtain Basic Parameters and Use Them to Guide Formulations and Performance

*Chairs: E.J. Acosta, University of Toronto, Canada; and N. Komesvarakul, Sun Products Corporation, USA*

### **Applying the Hydrophilic Lipophilic Deviation (HLD) Concept to Optimize Anionic Surfactant Structure and Cost to Meet Reservoir Conditions for Chemical EOR.**

W. Sorensen<sup>1</sup>, G. Trahan\*<sup>1</sup>, and B. Jakobs-Sauter<sup>2</sup>, <sup>1</sup>Sasol North America, Westlake, LA, USA, <sup>2</sup>Sasol Germany, Marl, Germany.

Chemical EOR surfactant use is expected to grow rapidly as this tertiary recovery method has shown to improve oil production. However, choosing an optimal surfactant formulation is still a time consuming and expensive process for formulators. In this paper we show the use of the Hydrophilic-Lipophilic Deviation (HLD) model for extended alkyl propoxylated sulfate surfactants. This approach can provide several near optimum surfactant candidates based on performance. Formulators can then choose the best system based on other factors such as availability and cost. The HLD concept was used to predict alkyl propoxylated sulfate performance based on the alcohol structure and the degree of propoxylation. The HLD model predicted several possible surfactants with significantly different compositions (e.g. alcohol structure and degree of propoxylation) but comparable behavior under field conditions. Four of the predicted alkyl propoxylated sulfate surfactants were synthesized and their performance was evaluated by the reduction of dynamic interfacial tension (IFT) and the formation of Winsor Type III microemulsions. These materials were further tested by core floods to evaluate their effectiveness in oil recovery.

### **Integrated Free Energy Model (IFEM) for Microemulsions.**

A. Boza and E.J. Acosta, University of Toronto, Toronto, ON, Canada.

This work presents a molecular model that accounts for the lipophilic and hydrophilic interactions associated with the solubilization of oils in micelles. IFEM can be considered as a quantitative approach to Winsor ratio, but it uses a net difference instead of the ratio of the molecular interactions. The lipophilic contributions arise from molecular interactions, which are computed using two van der Waals interparticle interaction potentials. Those potentials were developed using the Hamaker approach and validated using molecular properties. The hydrophilic contributions for ethoxylated surfactants are estimated considering the

dehydration energy of the ethylene oxide groups. The IFEM model reflects the solubilization behavior of alkanes in micelles made of non-ionic surfactants considering variations in surfactant tail size, type of oil, headgroup area, headgroup size and temperature. It also reflects the phase transitions towards Bicontinuous systems. The IFEM solubilization predictions not only coincide with the predictions of the HLD-NAC model, but also match closely experimental data. The IFEM model is simple, computationally inexpensive, and it uses only molecular properties as input data. From the parallelism established between the IFEM and HLD-NAC models, the IFEM model can provide parameters to the HLD-NAC, which would be obtained using solely molecular properties.

### **Application of the HLD Model for the Development of Phase Stable SOW (surfactant/oil/water) Type Hard Surface Cleaner Formulation.**

E. Szekeres, M.M. Knock, R. Khan, R. Zhang, and D.R. Scheuing, The Clorox Company, Pleasanton, CA, USA.

The HLD (hydrophilic-lipophilic difference) model has been applied to design phase stable SOW type ready to use hard surface cleaner formulation based on anionic/non-ionic surfactant mixtures. To represent the fragrance oil typically present in these types of formulations a model oil with EACN = 5.3 was chosen and the WOR (water to oil ratio) was set around 47.5. The HLD equation was used to select the surfactants and to optimize the surfactant mixing ratio. Model predictions were compared with laboratory experimental data. The HLD model was able to guide surfactant selection successfully, and predicted the optimized mixing ratio at low WOR quite well. However, liquid crystalline tendencies, which became more prominent at higher WOR values, shifted the optimized surfactant mixing ratio in the hydrophilic direction. It was concluded that the HLD model is a very useful tool for approximate surfactant selection but laboratory experiments are still needed to fine-tune high WOR formulations.

### **Partitioning of Corrosion Inhibitors Applied in Oil and Gas Pipelines.**

S. Kiran<sup>1</sup>, M. Nace<sup>1</sup>, M. Silvestri<sup>1</sup>, J. Moloney<sup>1</sup>, K. Monk<sup>1</sup>, L. Schmidt<sup>1</sup>, and E.J. Acosta<sup>2</sup>, <sup>1</sup>Nalco Champion, An Ecolab Company, Sugar Land, TX, USA, <sup>2</sup>University of Toronto, Toronto, ON,

Canada.

The partitioning of corrosion inhibitor (CI) products between oil and water is an indicator of their potential to protect a pipeline. To manage the partitioning of these products, a more fundamental understanding of the partitioning of their active components is required. In this work, the hydrophilic-lipophilic deviation (HLD) model is for the first used to evaluate structural influences on the relative partitioning of a series of oilfield actives (alkoxylated amines, alkoxylated phosphate esters, aromatic amines, imidazoline acetates, and quaternary amines) over a range of pHs in terms of their characteristic curvatures ( $C_{c,act}$ ). The additional influence of the physicochemical environment is also studied. A key finding under constrained test conditions is that calculated HLD changes experimentally correlate with active partitioning results at a dosage below the critical microemulsion concentration. It is lastly demonstrated that the characteristic curvature of CI products ( $C_{c,mix}$ ) can be predicted as a function of the incorporated actives.

**HLD and HLD-NAC as Guides in the Formulation Space.** E.J. Acosta, University of Toronto, Dept. of

Chemical Engineering and Applied Chemistry, Toronto, ON, Canada.

The first part of this presentation will summarize the connection between HLD and important formulation properties (interfacial tension, solubilisation capacity, microemulsion drop size and shape, viscosity, emulsion drop size, emulsion stability, contact angle, ternary phase diagrams, and fish diagrams) predicted with the HLD-NAC. The connection between these properties and performance will be discussed for certain products and surfactant-based technologies. Without the use of complicated equations, the purpose of this first part of the talk is to gain a sense for the HLD scale and its impact on formulation performance. During the second half of the talk, we will conduct a small interactive exercise where we will begin with a set of formulation objectives, and how we can use the HLD-NAC to identify a target HLD region, and how to narrow down the surfactants and formulation conditions corresponding to that HLD region. A series of examples of similar exercises conducted in our laboratory will be discussed. The advantages and gaps in the HLD and HLD-NAC frameworks will be summarized.



## S&D 5: Polymer-Surfactant-Enzyme Interactions

Chairs: P. Varanasi, BASF Corp., USA; and T. Smith, Rivertop Renewables, USA

**The Effect of Polymer and Surfactant Mixtures on Spotting and Filming in Automatic Dishwashing.** C. Caires and E. Satchell, BASF Corporation, Wyandotte, MI, USA.

The use of polymers and surfactants are extremely common in automatic dishwashing detergents. The role of the surfactant is to defoam the wash liquor and enhance wetting, while the role of the polymer is typically for preventing mineral and food deposits on kitchenware. We have studied how mixtures of polymers and surfactants in a compact automatic dishwashing detergent affects the formation of spotting and filming on glasses. We will report on the results of this study and show that strong differences in spotting and filming are observed depending on the mixture of polymer and surfactant used.

**Understanding Interaction of Surfactants and Enzymes: The Good, the Bad, and the Ugly.** H. Hellmuth, N. Plath, T. O'Connell, and M. Dreja, Henkel AG & Co. KGaA, Düsseldorf, Germany.

Today's laundry detergents are complex mixtures of various ingredients. Among the most important cleaning actives are surfactants and enzymes. Enzymes have been optimized over many years for pH, temperature and detergent stability. Nevertheless, it is still a challenge to identify the optimum formulation conditions to allow for the full potential of the ingredients. The interplay of surfactants and enzymes can lead to unexpected results, which may be related to structural elements and associative behavior of surfactant molecules. In order to optimize detergent performance and to understand the influence of individual ingredients, we have conducted an investigation of the interaction of surfactants and enzymes in laundry applications. We will show that a double-track approach is most efficient to generate superior results: optimization of the enzyme backbone for both activity and stability, and selecting the best surfactant mix to optimize the matrix conditions.

**Novel Builder for Auto-dish Detergents.** S. Brijmohan, K.T. Selvy, G. Hsu, and C. Cypcar, The Lubrizol Corporation, Cleveland, OH, USA.

'Builders', also known primarily as 'Chelators' are widely used in household products to control water hardness to improve the cleaning

efficiency. Automatic dishwashing formulations normally contain a significant amount of chelator to improve cleaning performance by sequestering Ca and Mg ions from hard water. Regulations banning phosphates from auto-dish detergents have led to significant performance gaps in providing shiny, spot-free glasses after dishwashing. Current P-free technologies used for chelating functionality include polymers like polycarboxylates, polycarboxylate copolymers and small molecules such as sodium citrate, sodium methylglycine diacetate. Some of these technologies suffer from issues such as efficiency, cost-in-use, and lack of multi-functionality. Lubrizol has developed a novel multifunctional polymer that can offer chelation, anti-scaling and anti-spotting properties, thus improving formulation efficiency and simplicity. Auto-dishwashing performance of the builder in powder and gel detergents was tested in hard water conditions. The new polymer was found to be more efficient than the leading acrylate polymers and small molecule builders. It was found that the spotting and filming performance was directly related to the level of the polymer in the formulation. Optimization of automatic-dish detergent formulation in gel and powder format for best performance will be presented.

**Development of a Chelating Dispersant Based on the Adduct of Allyl Glycidyl Ether and Ethylenediaminetriacetate.** S. Backer, E.

Wasserman, J. Shulman, R. Roberts, and A. Bullick, The Dow Chemical Company Dow Consumer and Industrial Solutions, Spring House, PA, USA.

Dow Consumer and Industrial Solutions has been developing and evaluating a series of acrylic copolymers containing a chelating moiety based on hydroxyethyl ethylamine diamine triacetate (HEDTA). The target market for use of these copolymers is rapidly changing as classical phosphate-based formulations are being phased out due to environmental regulations in North America and Western Europe. Currently, no direct performance replacement for phosphates has been identified, and new materials and formulations are currently being developed at all levels of the market in order to meet this need. In order to reduce the levels of biodegradable chelants currently being incorporated in nil-P formulations, we posit that a

strong chelating functionality coupled to a traditional polyacrylic dispersant will show synergistic benefits in anti-scaling. The target monomer, ED3A-AGE, was prepared and copolymerized at various levels with acrylic acid. This paper will cover the design of the new polymer, and applications data obtained from both internal and third-party testing.

**Multi-enzyme Solutions Enhance Low-temperature Performance to Address Consumer Wash Trends.** A.

Lee, J. Shingara, and D. Rhine Showmaker, Novozymes North America Inc., NC, USA.

Approximately 50% of North American consumers report they are washing their laundry using the "Cold" wash cycle. Most types of dirt and stains are complex mixtures and require several cleaning functions to be removed efficiently. Each enzyme class is designed to perform a specific cleaning function; however, with the right multi-enzyme composition you can achieve a significantly higher level of wash performance compared to single-enzyme solutions. A low-temperature detergent formulated with a multi-enzyme solution can deliver a significant performance increase, which is generally not possible using surfactants alone. Data will be shared to support the need for multi-enzyme solutions to fully deliver on low-temperature claims to meet both the manufacturers' and the customers' needs.

**Production of High Mole Ethoxylates Using NRE**

**Catalyst.** T. Weemes, L. Matheson, and S. Lyons, Sasol North America, Westlake, LA, USA.

Surfactants containing high numbers of moles of ethylene oxide (EO) are used in household and industrial applications, including cosmetics and personal care, oil and gas recovery, and paints and coatings. Alcohol ethoxylates (AEs) with  $\geq 30$  moles of EO are used as high efficiency emulsifiers and suspension aids. Additionally, there is regulatory pressure to replace 40kt of high mole nonylphenol and octylphenol ethoxylates. AEs in these applications are most often produced using conventional broad range alkaline catalysts like potassium hydroxide (KOH). When alkaline catalyst is used to make high mole AEs, the products will often exhibit dark colors and high polyethylene glycol (PEG) content. We have developed a technique for synthesizing high mole AEs containing up to 150 moles of EO which exhibit unique product characteristics that provide superior performance. This technique utilizes an alkoxylation catalyst that is less alkaline than the conventional catalyst and produces a material with a narrow range ethoximer distribution. Our work has shown that the narrow-range, high mole AE products show reduced by-product formation, improved color, lower PEG, improved production efficiency and good biodegradability. Also, these high mole AEs have very similar surfactant characteristics to high mole nonylphenol ethoxylates making them excellent alternatives to these products.

**S&D 5.1/EAT 5: Suspensions, Emulsions, and Foams**

Chairs: S. Ghosh, University of Saskatchewan, Canada; and A. Ramchandran, University of Toronto, Canada

**Microbeam X-ray Diffraction of Pickering Fat Crystals at the Oil-water Interface.** D. Rousseau<sup>1</sup> (*Timothy L. Mounts Award Winner*), S. Ueno<sup>2</sup>, K. Sato<sup>2</sup>, and G. Mazzanti<sup>3</sup>, <sup>1</sup>Ryerson University, Toronto, ON, Canada, <sup>2</sup>Hiroshima University, Higashi-Hiroshima, Japan, <sup>3</sup>Dalhousie University, Halifax, NS, Canada.

Synchrotron microbeam small angle X-ray diffraction ( $\mu$ -SAXD) was used to probe surfactant and triacylglycerol (TAG) molecular arrangement at the oil-water interface of water-in-oil emulsions stabilized with glycerol monostearate (GMS) and fully hydrogenated canola oil (HCO). The  $\mu$ -SAXD experiments permitted spatial analysis of the polymorphic structure and orientation of surfactant and TAG lamellar planes at different positions around the periphery of the dispersed aqueous droplets. There were 2 key findings from this study: i) the lamellar planes of crystalline GMS were highly aligned at the oil-water interface and ii) GMS templated HCO crystallization, resulting in oriented HCO crystals that extended well into the continuous oil phase. Overall, these findings provided further evidence of the interfacial orientation of surfactants at the oil-water interface and their role on interfacial templating of TAGs.

**Fabrication of Reduced Fat Products by Controlled Aggregation of Lipid Droplets.** B.C. Wu<sup>1</sup> (*Edible Applications Technology Division Student Award of Excellence Winner*), B. Degner<sup>2</sup>, and D.J. McClements<sup>1</sup>, <sup>1</sup>Dept. of Food Science, University of Massachusetts Amherst, Amherst, MA, USA, <sup>2</sup>ConAgra Foods, Omaha, NE, USA.

The creation of high quality reduced-fat food products is challenging because the removal of fat adversely affects quality attributes, such as appearance, texture, and flavor. This study investigated the impact of pH- or calcium-induced droplet aggregation on the microstructure and physicochemical properties of model mixed colloidal dispersions containing 2 wt% protein-coated fat droplets and 4 wt% modified starch (hydroxypropyl distarch phosphate). DIC and confocal microscopy showed that the aggregation state of fat droplets dispersed within the interstitial region between the starch granules can be altered by modulating the inter-droplet electrostatic interactions using either pH adjustment or calcium addition. Systematically

controlling pH and calcium concentration can modulate the microstructure of the mixed colloidal dispersions and obtain a system with a high yield stress and apparent viscosity and other desirable properties. This study has important implications for fabricating reduced fat food products with desirable sensory attributes such as sauces, dressings and deserts.

**Application of the HLD and NAC Models to Predict the Size and Stability of Emulsions.** S. Kiran and E.J. Acosta, University of Toronto, Toronto, ON, Canada.

Emulsions represent surfactant encapsulated droplets of one medium (oil or water) dispersed throughout the other. These mixtures are of growing interest across various applications such as the design of agricultural, coating, crude oil, foodstuff, paint, and pharmaceutical products owing to their tailorable size and stability. It has been demonstrated by a number of past researchers that the above emulsion properties are a function of the underlying phase behavior of related microemulsions ( $\mu$ Es). The first objective of this work is to therefore illustrate how the measured size and stability of emulsions formulated with sodium dihexyl sulfosuccinate (SDHS), toluene, and water vary across a Type I-Type III-Type II phase behavior scan. To do so, the hydrophilic-lipophilic deviation (HLD) model is used to help guide formulation changes. The second objective of this work is to in turn predict the measured size and stability of these emulsions. This is accomplished with the aid of the net-average curvature (NAC) model.

**Experimental Investigation of Sub-micron Water Droplet Formation in Bitumen Froth.** R. Sonthalia<sup>1</sup>, A. Ramchandran<sup>1</sup>, and S. Ng<sup>2</sup>, <sup>1</sup>Dept. of Chemical Engineering & Applied Chemistry, University of Toronto, Toronto, ON, Canada, <sup>2</sup>Edmonton Research Centre, Syncrude Canada Ltd., Edmonton, AB, Canada.

Processes such as centrifugation and inclined settling are currently used to achieve the separation of water and solids from bitumen froth in the oil-sands industry. They are, however, ineffective in removing sub-micron water droplets, which can form a significant fraction of the residual water content in bitumen after separation. The aim of our project is to understand the mechanisms of

formation of sub-micron-scale water droplets, and to suggest remedies to mitigate their production. Our current focus is to assess if the combination of hydrodynamics and interfacial composition/properties could be leading to small droplets. Preliminary experiments were performed in a co-flowing device with an aqueous-bitumen system. We observed the tip streaming of fine threads (<2µm diameter) of the core fluid that produced sub-micron droplets for capillary numbers less than the critical value for primary drop breakup. This implies that there could be mixing conditions where drops could tip stream to produce sub-micron droplets, but not break up. We will also discuss results from a systematic study that is currently exploring the effects of viscosity ratio, bitumen weight fraction and concentrations of asphaltenes and naphthenates.

**Impact of Droplet Size and Emulsifier Concentration on Nanoemulsion Gelation.** V. Erramreddy and S. Ghosh\*, University of Saskatchewan, Saskatoon, SK, Canada.

We show that liquid nanoemulsions (NE) stabilized with ionic emulsifier can be transformed into viscoelastic gels by reducing droplet size. 40wt% canola oil-in-water NE were prepared with different amount of sodium dodecyl sulfate (SDS) or Tween 20 by high-pressure homogenization. During homogenization viscosity of SDS NE progressively increased as the droplet size decreased and beyond a critical droplet radius (65-90 nm), the liquid NE transformed into viscoelastic gel. The yield stress and elastic modulus of the nanogels increased with SDS concentration until 15 times the critical micelle concentration, thereafter decreased steadily till it became liquid beyond 25 times CMC. The repulsive electric double layer on the nanodroplet surface significantly increased the effective oil phase volume fraction such that the nanodroplets kinetically jammed to provide elastic behavior. NE prepared with non-ionic Tween 20 did not show any elastic behavior, as no repulsive barrier was formed. At intermediate concentrations of SDS, depletion attractions by micelles in the continuous phase further improved nanogels' elastic behavior, while at higher concentration SDS micelles acted as depletion stabilizer and their overall charge screened the repulsive interactions among the nanodroplets, leading to gel breakdown. The NE gels possess great potential for use in low fat foods.

**Trends in Structuring Edible Emulsions with**

**Pickering Fat Crystals.** D. Rousseau, Ryerson University, Toronto, ON, Canada.

This presentation proposes a new microstructure-based nomenclature to delineate three classes of fat-based Pickering stabilizers: Types I - III. Type I stabilization results from the solidification of lipids at the droplet surface during cooling of freshly-formed emulsions either via interfacial crystallization, as is commonly observed with high-melting, oil-tending surfactants, with the crystal morphology of the resulting fat crystals consisting of mono- or multilayers, individual crystals or even spherulites. Type II stabilization involves the diffusion or migration of previously-formed micro or nano-scale crystals or particles towards the oil-water interface, with possible species being TG crystals or lipid particles. Emulsion formation and stabilization with Type II species may arise due to the inherent surface activity of the crystal/particle or may require the use of a surfactant layer to aid in emulsification and particle adsorption. Finally, Type III stabilization consists of micron or nano-scale droplets encased within crystalline shells significantly larger than the droplets themselves. These spheroidal crystalline assemblies form due to combined surfactant-TG molecular compatibility (as per Type I above) and shear cooling in a micro-confined environment, the result being agglomerated fat crystal microstructures containing encapsulated droplets.

**Formulation of Lipopeptide Biosurfactant Mixtures for Dispersing Oil Spill in Seawater.** W.

Rongsayamanont<sup>1,6</sup>, S. Soonglerdsongpha<sup>2</sup>, O. Pinyakong<sup>3,6</sup>, C. Tongcumpou<sup>4,6</sup>, D.A. Sabatini<sup>5</sup>, and E. Luepromchai<sup>3,6</sup>, <sup>1</sup>International Postgraduate Programs in Environmental Management, Graduate School, Chulalongkorn University, Patumwan, Bangkok, Thailand, <sup>2</sup>Environmental Research and Management Department, PTT Research and Technology Institute, Ayutthaya, Thailand, <sup>3</sup>Bioremediation Research Unit, Dept. of Microbiology, Faculty of Science, Chulalongkorn University, Patumwan, Bangkok, Thailand, <sup>4</sup>Environmental Research Institute, Chulalongkorn University, Patumwan, Bangkok, Thailand, <sup>5</sup>Schools of Civil Engineering and Environmental Science, University of Oklahoma, Norman, OK, USA, <sup>6</sup>Center of Excellence on Hazardous Substance Management (HSM), Chulalongkorn University, Patumwan, Bangkok, Thailand.

This study aimed to formulate a biocompatible (low toxicity) oil dispersant by mixing lipopeptide biosurfactant, synthetic surfactant and

electrolyte. The lipopeptide biosurfactant was produced by *Bacillus* sp. GY19 using waste glycerol and palm oil as substrates. The biosurfactant was found to be relatively hydrophobic since it could lower interfacial tension values against hexadecane better than toluene. In addition, the biosurfactant was stable under a wide range of temperature, alkalinity, and electrolyte concentrations and was not toxic to brine shrimp, vegetable seed and PAH-degrading bacteria. To improve its surface activity, the lipopeptide biosurfactant was mixed with 0.1-2 % of various synthetic surfactants and/or electrolytes. Biosurfactant mixtures lowered the IFT values of hexadecane and toluene to the range of 0.07-0.46 mN/m when the concentrations of additives increased. The oil dispersion efficiency of various biosurfactant mixtures were later investigated with synthetic seawater and a local seawater sample. When compared with a commercial dispersant, the mixture of lipopeptide, Triton X-100 and  $K_2HPO_4$  dispersed Oman light crude oil and fuel oil at 100% in both seawater samples. Consequently, lipopeptide biosurfactant mixtures have a potential for lowering IFT and showed a great promise for use as an oil spill dispersant.

**N-alkylimidazole as CO<sub>2</sub>-switchable Surfactant.** Z. Zheng, M. Chai, L. Bao, and W. Qiao, Dalian University of Technology, Dalian, Liaoning, China.

Due to global environmental pollution and rich carbon dioxide as a friendly solvent, CO<sub>2</sub>-switchable surfactants as a kind of functional surfactant are more attractive. We found that functionalized N-alkylimidazoles (amidine group existed in the imidazole ring) show the similar switchability compared with long chain alkyl amidines. In the present work, we focus on the switchability of four N-alkyl imidazole compounds synthesized in our lab. They can be reversibly transformed from uncharged to charged species by

exposure to carbon dioxide, reflecting in the repeatedly conductivity increase-decrease cycle in their aqueous solution under alternatively CO<sub>2</sub>/N<sub>2</sub> stimuli. The emulsion prepared by CO<sub>2</sub>-induced imidazole can be stable for more than 5 hours, and be broken by bubbling N<sub>2</sub> for 20 min. The cycle of emulsion-demulsion can be repeated at least 5 times.

**Structure Parameter: Modeling Ice Cream**

**Meltdown Test.** M.M. Warren and R.W. Hartel, University of Wisconsin-Madison, Madison, WI, USA.

A structure parameter has been developed to model the relationship between partially-coalesced fat globules and meltdown rates of ice cream. Commercial vanilla ice cream products were analyzed for their fat content, degree of partial coalescence, mean ice crystal and air cell size, and overrun. The conventional meltdown test, where ice cream melts on a mesh screen, was also studied to measure meltdown rate and percent change in height. The foam that remains atop the mesh screen (Top) after the meltdown test provides great insight into structural elements that affect the behavior of ice cream. The structure parameter was developed utilizing the Top of the meltdown test. Fat destabilization level of the melted ice cream, as determined by the relative number of clusters to initial emulsion droplets, did not predict the drip-through or stand-up properties of the ice cream products. However, the structure parameter (Top cluster density) predicts the behavior (drip-through and stand-up properties) of ice cream products. This parameter accounts for size and number of partially coalesced fat globules and the volume they occupy. By understanding and controlling partially-coalesced fat in ice cream, the structure parameter can model, control, and predict the behavior of ice cream products.

## S&D-P: Surfactants and Detergents Poster Session

Chair: M. Wint, Amway Corp., USA

### 1. Synthesis Characterization and Surface Properties of Cationic Gemini Surfactants. C.K. Mangat and S. Kaur, Guru Nanak Dev University, Amritsar, Punjab, India.

New pyridinium gemini surfactants have been synthesized by esterification of renewable fatty acids with mercaptoethanol furnishing respective esters (mercaptomethyl decanoate, mercaptomethyl dodecanoate, mercaptomethyl tetradecanoate, mercaptomethyl hexadecanoate) followed by their subsequent treatment with 4-Dimethyl amino pyridine resulting into the formation of title gemini surfactants: 1-(5-(decanoyloxy)-2-hydroxypentyl)-4-((5-(decanoyloxy)-2-hydroxypentyl)dimethylammonio)pyridin-1-ium chloride (9), 1-(5-(dodecanoyloxy)-2-hydroxypentyl)-4-((5-(dodecanoyloxy)-2-hydroxypentyl)dimethyl ammonio)pyridin-1-ium chloride (10), 1-(5-(tetradecanoyloxy)-2-hydroxypentyl)-4-((5-(tetradecanoyloxy)-2-hydroxypentyl)dimethylammonio)pyridin-1-ium chloride (11) and 1-(5-(hexadecanoyloxy)-2-hydroxypentyl)-4-((5-(hexadecanoyloxy)-2-hydroxypentyl)dimethyl ammonio)pyridin-1-ium chloride (12). Their identifications are based on IR,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, DEPT, COSY and Mass spectral studies. Their surface active properties are also evaluated on the basis of surface tension and conductivity measurements. Thermal stability of these long chain cationics Gemini surfactants have been measured by thermal gravimetric analysis under nitrogen atmosphere.

2. Synthesis, Characterization, and Evaluation of the Surface Active Properties of Novel Cationic Imidazolium Gemini Surfactants. P. Patial<sup>1</sup>, A. Shaheen<sup>1,2</sup>, and I. Ahmad<sup>1</sup>, <sup>1</sup>Guru Nanak Dev University, Amritsar, Punjab, India, <sup>2</sup>Punjabi University, Patiala, Punjab, India.

New imidazolium gemini surfactants have been synthesized by reaction of epichlorohydrin with long chain fatty alcohols furnishing products 2-(alkoxymethyl) oxirane followed by their subsequent treatment with imidazole resulting into the formation of 1-(1H-imidazol-1-yl 3 alkoxy) propane-2-ol which on subsequent treatment with 1,2-dibromoethane and 1,3-dibromopropane resulting into the formation of title gemini surfactants: 1,2-bis(1(3-alkoxy 2-hydroxy propyl) 1-H -imidazol-3-ium ) ethane bromide (7), 1,3-bis(1(3-alkoxy 2-hydroxy propyl) 1-H -imidazol-3-ium ) propane bromide (8), 1,2-bis(1(3-alkoxy 2-hydroxy propyl) 1-H -imidazol-3-ium ) ethane bromide (9), 1,3-bis(1(3-alkoxy 2-hydroxy propyl) 1-H -imidazol-3-ium ) propane bromide (10), 1,2-bis(1(3-alkoxy 2-hydroxy propyl) 1-H -imidazol-3-ium ) ethane bromide (11) and ), 1,3-bis(1(3-alkoxy 2-hydroxy propyl) 1-H -imidazol-3-ium ) propane bromide (12). Their identifications are based on IR,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, DEPT, COSY and Mass spectral studies. Their surface active properties are also evaluated on the basis of surface tension and conductivity measurements.

3. Physico-chemical Studies of CTAB and AOT in Mixed Solvents. P. Jamwal<sup>1</sup> and O. Yadav<sup>1</sup>, <sup>1</sup>LPU, Jalandhar, Jalandhar, Punjab, India, <sup>2</sup>Harmaya University, Ethiopia.

From specific conductance measurements critical micelle concentration (CMC), counter-ion dissociation constant ( $\beta$ ), limiting equivalent conductance at infinite dilution ( $\Delta^\circ$ ) and thermodynamic quantities of micellisation ( $\Delta G_m^\circ$ ,  $\Delta S_m^\circ$  and  $\Delta H_m^\circ$ ) and transfer ( $\Delta G_{tr}^\circ$ ) from aqueous solution to mixed solvent have been determined for aqueous solutions of cetyltrimethyl ammonium bromide (CTAB) and bis(2-ethylhexyl) sulpho succinate sodium salt in mixed solvent (water + 1,3-dioxolane or + Diethylene glycol) at 298.15, 308.15 and 318.15 K as the whereby process of micellisation is favoured both by exothermic enthalpy change and entropy gain; positive value of Gibb's free energy of transfer suggests the non-feasibility of micellisation on transferring surfactant from water to mixed solvent. Molar excess volumes of mixed solvent (1,3-dioxolane + DEG) have been determined dilatometrically as a function of composition at 298.15 K and the same have been utilized to extract information about the state of components in pure and mixed state.  $V^E$  values lend additional support to the micellisation behaviour of surfactants in mixed solvent.

4. Green Methodology for the Synthesis of Isomannide-based Non-ionic Surfactants. T. Vijai Kumar Reddy, G. Sandhya Rani, R.B.N. Prasad, and B.L.A. Prabhavathi Devi, CSIR- Indian Institute of Chemical Technology, Hyderabad, Andhra Pradesh,

India.

Sugar fatty acid esters are non-ionic surfactants obtained from renewable, cheap and easily available raw materials. They are largely used in the food, cosmetics and pharmaceutical industries. Generally sugar esters are prepared employing sulphuric or sulphonic acids as homogeneous catalysts which generate huge quantities of effluents. The present work describes a green approach for the synthesis of isomannide-based fatty esters by using water resistant and reusable carbon-based solid acid catalyst derived from glycerol. The mannitol was reacted with decanoic, undecenoic, lauric, myristic, palmitic, stearic and oleic acids under solvent free conditions to obtain corresponding isomannide esters involving *in situ* dehydration of mannitol to isomannide followed by acylation. The optimized reaction conditions for obtaining isomannide esters are: fatty acid to mannitol (1:1.5 mole), catalyst 20 wt%, temperature 180°C and reaction time 12 h. After the reaction, the catalyst was easily recovered by filtration and reused for five times without any deactivation. All the synthesized compounds were further evaluated for their surface active properties such as, critical micelle concentration (CMC), surface excess and the surface tension and the data revealed that isomannide monolaurate exhibited superior properties compared to other esters.

#### 5. Aminosiloxanes in Household Care Applications.

M. Hisamoto<sup>1</sup>, A. Nagy<sup>1</sup>, D. Parrish<sup>1</sup>, and D. Kuppert<sup>2</sup>,  
<sup>1</sup>Evonik Goldschmidt Corporation, Hopewell, VA, USA, <sup>2</sup>Evonik Industries AG, Hanau, Germany.

A new aminosiloxane has been developed for multiple application areas, including hard surface treatment and fabric softening. The special structure of this new polymer will enable the user to clean and protect hard surfaces with higher efficiency while improving their aesthetic appearance. This polymer can also improve fabric softener formulations as a performance additive including softening, rewet and fabric conditioning performance. Formulation procedures and comparative results will be discussed.

#### 6. Modified Polycarboxylate Polymers - Detergent Builders for Improved Anti-Encrustation Cleaning Performance.

T. Crutcher, R. Rigoletto, M. Standish, and P. Shah, Ashland, Inc., Bridgewater, NJ, USA.

Today sodium carbonate is a common alkaline hard water sequestering agent globally used in granular auto dish and powdered laundry

detergents. Unfortunately, in hard water sodium carbonate is converted to calcium carbonate which in a laundry wash solution may precipitate and deposit on to fabrics in the wash cycle. This type of antagonistic soil deposition can dull the appearance of laundered garments over time. Additionally, the texture and feel of garments may be perceived as abrasive to hands and skin. Sodium carbonate is still a natural alternate to phosphate builders due to its cost efficiency. This research paper proposes a solution to the negative effects caused by ash deposition encrustation. The deposition of calcium mineral salts can be alleviated by the addition of modified polycarboxylate polymers. The anti-encrustation benefits of modified carboxylate copolymers were studied in laboratory scale tergotometer test, and also in practical machine laundry studies for consumer perceivable results. Quantification of calcium carbonate on the fabric is measure analytically, spectroscopically, and using other material science imaging techniques. Selected polycarboxylate copolymers are effective builders and are shown to provide anti-encrustation cleaning performance in model detergent systems.

#### 7. Cleavable Surfactants Bearing a Sucrose: Surface-Active Properties and Application in Oil-treating Agent.

D. Ono<sup>1</sup>, Y. Nishida<sup>2</sup>, M. Minamitani<sup>2</sup>, S. Kawano<sup>1</sup>, H. Sato<sup>1</sup>, M. Shizuma<sup>1</sup>, and A. Masuyama<sup>2</sup>,  
<sup>1</sup>Osaka Municipal Technical Research Institute, Osaka, Osaka, Japan, <sup>2</sup>Osaka Institute of Technology, Osaka, Osaka, Japan.

The marine pollution with the oil spill becomes the big environmental problem. The development of the oil spill treatment agent with good biodegradability has become desired. We have been investigating the preparation and properties of a series of acid- and alkali-cleavable surfactants. The chemocleavable surfactants are designed to decompose into non-surface active species under mild conditions after fulfilling their original functions. We have mentioned that the chemocleavable moiety (noncyclic acetal group, 1,3-dioxolane ring or ester) had a positive effect on the various surface-active properties. In this work, one-chain and double-chain chemocleavable nonionic surfactants bearing a 1,3-dioxolane ring were prepared from diethyl tartrate without any expensive reagents or special equipment. A sucrose was used as hydrophilic group. We clarified that they have good surface-active properties, and the decomposition function in acid water. The biodegradabilities of these chemocleavable

surfactants after 28 days were more than 60% by an oxygen consumption method according to the guidelines which was based upon the OECD 301C with activated sludge. We evaluated the biodegradation of heavy oil.

**8. Laundry Detergent Stain Removal Evaluation: Comparing Imaging and Spectroscopic Methods.** R. Zehr, Church & Dwight Co., Inc., Princeton, NJ, USA.

The primary function of laundry detergents is to facilitate the efficient removal of soils and stains from textile garments. The determination of the efficacy of detergent formulations is an important concern for detergent manufacturers.

Detergent efficacy is determined by measuring the change in color of stained fabric after laundering with the assumption that loss of color is proportional to the degree of stain removal. A large set of pre-stained textile swatches are washed under conditions simulating typical home laundry conditions. The color of each stain is measured instrumentally before and after laundering and the difference in color is related to the degree of stain removal. The wide variety of household stains a consumer may encounter is simulated by measuring a large range of stains on different textile substrates. The use of large stain-sets results in a labor intensive process because the stained samples must be sequentially labeled, sorted, and measured pre and post washing. The labor involved can be reduced by leveraging the ability of an imaging system to capture color information from multiple stains in a single image.

My talk will detail the comparison between a commercial imaging system and a spectrometer in the laundry detergent stain removal evaluation role. Similarities and differences between the two methods will be highlighted.

**9. An Investigation on Mechanisms of Soybean Oil Extraction by Aqueous Surfactant Mixtures.** L. Do, T. Stevens, K. Tohren, and D. Sabatini, University of Oklahoma, Norman, OK, USA.

Surfactant-assisted aqueous extraction processing of vegetable oils is a promising green alternative to hexane extraction processing. The extraction efficiency employed aqueous extended-surfactant method has shown to be very competitive to other alternative technologies, owing to the ultralow interfacial tension reduction between the vegetable oils and aqueous extended-surfactant solution at relatively low surfactant concentration. The objectives of this work are: 1) to formulate a

surfactant mixture that can greatly reduce the salinity level from 5% to 0.5% while still achieving ultralow interfacial tension values with soybean oil, and 2) to study the mechanisms of soybean oil extraction by aqueous surfactant method. A response surface experimental design was used to test the significant impacts on oilseed extraction and to develop an empirical model for process optimization. The use of a protease enzyme to demulsify the cream formation after the extraction is also discussed.

**10. Production of High Mole Ethoxylates Using NRE Catalyst.** T. Weemes, L. Matheson, and S. Lyons, Sasol North America, Westlake, LA, USA.

Surfactants containing high numbers of moles of ethylene oxide (EO) are used in household and industrial applications, including cosmetics and personal care, oil and gas recovery, and paints and coatings. Alcohol ethoxylates (AEs) with  $\geq 30$  moles of EO are used as high efficiency emulsifiers and suspension aids. Additionally, there is regulatory pressure to replace 40kt of high mole nonylphenol and octylphenol ethoxylates. AEs in these applications are most often produced using conventional broad range alkaline catalysts like potassium hydroxide (KOH). When alkaline catalyst is used to make high mole AEs, the products will often exhibit dark colors and high polyethylene glycol (PEG) content. We have developed a technique for synthesizing high mole AEs containing up to 150 moles of EO which exhibit unique product characteristics that provide superior performance. This technique utilizes an alkoxylation catalyst that is less alkaline than the conventional catalyst and produces a material with a narrow range ethoximer distribution. Our work has shown that the narrow-range, high mole AE products show reduced by-product formation, improved color, lower PEG, improved production efficiency and good biodegradability. Also, these high mole AEs have very similar surfactant characteristics to high mole nonylphenol ethoxylates making them excellent alternatives to these products.

**11. Automatic Laundry Washing Machine Changes and Impact on Detergent Formulation Chemistry.** J.S. Pell and P.G. Silva, Amway Corporation, Ada, MI, USA.

High efficiency washers are significantly impacting washing machine detergency. There is a larger than anticipated reduction in wash water volumes. Even the low water European machines



wash volumes dropped from 20 liters to 8 liters. We see improved soil removal, however, soil redeposition is becoming more pronounced. This creates a need for improved technology in this

important area. It may also offer potential opportunities as concentration limits may spur consideration of chemistry previously not applied.