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2002 PUBLICATIONS AND COMMUNICATIONS BY LAB FIRP ASSOCIATES

ROJAS O. J.,

Adsorption of Polyelectrolyte on Mica,

in *Encyclopedia of Surface and Colloid Science*, A. Hubbarb, Ed., pp 517-535. Marcel Dekker New York (2002).

ABSTRACT: The Adsorption of Polyelectrolytes on Mica sounds like a very specific title and it is difficult to envision, at first sight, why mica deserves a separate chapter in the study of adsorption of polymers on solid substrates. What makes mica such a special substrate? What are the driving forces involved in the adsorption of macromolecules on mica? What mechanisms participate in the adsorption phenomenon? What types of interactions and what factors govern systems containing polymers adsorbed on mica? These and other questions will be answered in this discussion which is not meant to be exhaustive, but hopefully will help to understand the intricacies involved in polyelectrolyte adsorption on such special substrates.

MARQUEZ N., BRAVO B., CHAVEZ G., YSAMBERTT F., SALAGER J. L.

Analysis of Polyethoxylated Surfactants in Microemulsions-oil-water Systems. Part II.

Analytica Chimica Acta **452**, 129-141 (2002).

ABSTRACT: Commercial ethoxylated surfactants are always a mixture of oligomers with different ethylene oxide number (EON). The different oligomers were separated by high performance liquid chromatography (HPLC) on an amino column using a mixture of polar and nonpolar mobile phases. Surfactant-oil-water systems were studied according to the unidimensional scan technique. The partitioning of surfactant oligomers in the oil and water phases of Winsor III systems was determined by UV spectroscopy and HPLC. The effect of different salts on the surfactant partitioning is discussed.

SALAGER J.L., MORENO N., ANTON R. E., MARFISI S.

Apparent Equilibration Time required for a Surfactant-Oil-Water system to Emulsify into the Morphology imposed by the Physico-Chemical Formulation,

Langmuir **18** (3) 607-611 (2002).

ABSTRACT: This paper deals with surfactants-oil-water (SOW) system whose formulation corresponds to a Winsor type I phase behavior at equilibrium. When the surfactant is initially dissolved in the oil phase, and the system is immediately stirred, the usual emulsion morphology is the anomalous W/O type, which is not the expected one for a Winsor type I formulation. However, if the SOW system is left to rest and to partially equilibrate during some time, it could result in a normal O/W emulsion upon stirring, as if it were fully equilibrated for several days. The minimum rest time required to produce the normal emulsion morphology is called the apparent equilibration time t_{ape} . It is shown that t_{ape} strongly depends on formulation, and decreases as formulation approaches the boundary between Winsor I and Winsor III phase behavior. In some instances t_{ape} is essentially zero, as if equilibration had taken place

instantly. The apparent equilibration time t_{ape} is found on the surfactant molecular weight and on oil viscosity.

RODRIGUEZ C., UDDIN Md. H., WATANABE K., FURUKAWA H., HARASHIMA A., KUNIEDA H.,

Self-organization, Phase Behavior and Microstructure of Poly(oxyethylene) Poly(dimethylsiloxane) Surfactants in Nonpolar Oil,

J. Physical Chemistry B. **106**, 22-29 (2002).

ABSTRACT: Linear long poly(oxyethylene) poly(dimethylsiloxane) surfactants, formula $\text{Me}_3\text{SiO}-[(\text{Me}_2\text{SiO})_m-2]-\text{Me}_2\text{SiCH}_2-\text{CH}_2\text{CH}_2-\text{O}-[(\text{CH}_2\text{CH}_2\text{O})]_n\text{H} [\text{Si}]_m\text{C}_3(\text{EO})_n$ form reverse micelles in oil such as poly(dimethylsiloxane) and hydrocarbons. The critical micellar concentration (CMC) decreases dramatically with increasing the hydrophilic chain length of the surfactant, whereas the difference in hydrophobic chain length has less influence on the CMC. Hence the segregation of the polyEO chain from nonpolar medium is a main factor to form aggregates in oil. Since the lipophilic surfactants used in this study have very long hydrophilic and hydrophobic chains compared to conventional nonionic surfactants, they also form liquid crystals in non polar medium such as discontinuous reverse micellar cubic and reverse hexagonal phases at high surfactant concentration and even in absence of solvent. Judging from SAXS data, oil penetrates in the palissade layer of surfactant, increasing the preferred negative curvature and relaxing the packing restriction of the hydrophobic chain. Although a normal micellar cubic phase is always changed to a micellar solution upon dilution with water, the present reverse micellar phase coexists with oil in a wide range of composition in the squalane system.

SCORZZA C., GODE P., MARTIN P., MIÑANA-PEREZ M., SALAGER J. L., VILLA P., GEOTHALS G.,

Synthesis and Surfactant Properties of a New "extended" Glucidoamphiphile made from D-Glucose,

J. Surfactants & Detergents **5** (4) 331-335 (2002)

ABSTRACT: We prepared a new nonionic surfactant **8** in which the n-dodecyl chain is attached at C-3 carbon of the D-glucose-based glucopyranose moiety by the linkage $Z = -\text{O}-(\alpha\text{-PP-O})_n$ with $-\text{O}-(\alpha\text{-PP-O})_n$ is a poly-(α -propyloxy) commercial oligomeric mixture (with average $n = 6$). The amphiphilic behaviour study showed that, when compared to the reference compound 3-O-dodecyl-D-glucopyranose ($Z = \text{O}$), compound **8** exhibits : i) a water solubility which is hundred fold higher, ii) a HLB value increase from 8.5 to 12.6 units, iii) a slightly lower CMC.

SCORZZA C., GODE P., GEOTHALS G., MARTIN P., MIÑANA-PEREZ M., SALAGER J. L., USUBILLAGA A., VILLA P.,

An other New Family of "extended" Glucidoamphiphiles. Synthesis and Surfactant Properties for different Sugar head Groups and Spacer Arm lengths,

J. Surfactants & Detergents **5** (4) 337-343 (2002)

ABSTRACT: Following a new four-step route, we prepared a family of "extended" glucidoamphiphiles from D-glucose, D-galactose and xylitol, in which the n-dodecyl chain is attached to the glucidic moiety by the linkage $Z = \text{O-Et-O-Et-O}-(\alpha\text{-PP-O})_n$ where $-\text{O}-(\alpha\text{-PP-O})_n$ is a poly-(α -propyloxy) commercial oligomeric mixture (with average length $n = 6, 10$ and 14). The amphiphilic behaviour study showed that : i) the glucose derivative exhibits a water solubility and a HLB values which are close to those found for the glucose compound with $Z = -\text{O}-(\alpha\text{-PP-O})_n$ (without the Et-O-Et group), ii) all these compounds are strongly more hydrophilic than the corresponding glucidic derivatives with $Z = \text{O}$, iii) the increase of the poly-(α -propyloxy) chain length from $n = 6$ to $n = 14$ tends to slightly reduce the hydrophilicity.

LOPEZ-QUINTELA M. A., AKAHANE A., RODRIGUEZ C., KUNIEDA H.,

Thermotropic Behavior of Poly(oxyethylene) Cholesterol Ethers,

J. Colloid Interface Science **247**, 186-192 (2002)

ABSTRACT: The thermotropic behavior of poly(oxyethylene) cholesterol ether surfactants was studied by differential scanning calorimetry and SAXS. Contrary to what is usually observed in conventional polyEO type surfactant the polyEO cholesterol ether surfactants show a change of the fusion mechanism as the chain length is varied. For long chain lengths ($n > 15$) the usual solid-liquid transition is found, but for short chain length ($n < 10$) the transition goes through a birefringent lamellar phase. The appearance of this liquid crystal (LC) phase seems to be related with the predominance of the cholesterol part in low chain polyEO surfactants. On the contrary, for long polyEO chains the polymer gains in importance and only a solid crystalline structure is observed at low temperatures. An antiparallel packing structure with totally overlapped chains is found for both the solid and the LC phase. The chains seem to be in zigzag configuration, and only for the most large surfactant here studied ($n = 30$) a change of the chain configuration to a much shorter meander configuration is observed.

PEREZ M., ZAMBRANO N., RAMIREZ M., TYRODE E., SALAGER J. L.,

Surfactant-oil-water Systems near the Affinity Inversion. Part XII: Emulsion Drop Size versus Formulation and Composition,

J. Dispersion Science & Technology **23** (1/3) 55-63 (2002).

ABSTRACT: Emulsion drop size depends on the both formulation and composition of the surfactant-oil-water system, as well as the stirring conditions prevailing during emulsification. General trends versus formulation or composition changes are presented. However, it is shown that the effects are not independent and that a proper combination of these parameters allow the attainment of very small drop size, even at low stirring energy. An overall phenomenology is presented on a bidimensional formulation-composition map in which it is easy to select the best emulsification conditions.

FORGIARINI A., ESQUENA J., GONZÁLEZ C., SOLANS C.,

The Relation between Phase Behavior and Formation of narrow size Distribution W/O Emulsions.

J Dispersion Science & Technology **23** (1/3) 209-217 (2002).

ABSTRACT: Water-in-oil (W/O) emulsions of the water/ $C_{12}E_5$ /isooctanol/isooctane system have been prepared at 25°C. Phase behavior studies of the system with constant (2.5 and 6 wt%) isooctanol concentration showed that the surfactant become more lipophilic with the increase in the alkanol concentration. Emulsification was carried out using four low-energy emulsification methods consisting in the slow addition of one or various components to the rest of them, with gentle agitation. Emulsions with low-polidispersity were obtained when the emulsification process started with a single lamellar liquid crystalline phase. If in addition to a lamellar liquid crystalline phase, other phases, such as excess water phase, were present initially, emulsions with intermediate polydispersity were produced. When a lamellar liquid crystalline phase was not involved and the spontaneous natural curvature of the surfactant was not changed during emulsification, high polydisperse emulsions were obtained.

LOPEZ-MONTILLA J. C., HERRERA-MORALES P. E., PANDEY S., SHAH D. O.

Spontaneous Emulsification: Mechanisms, Physicochemical Aspects, Modeling and Applications,

J Dispersion Science & Technology, **23** (1/3) 219-268 (2002).

BULLON J., CARDENAS A., SANCHEZ J., Emulsion Filtration through Surface modified Ceramic Membranes. *J Dispersion Science & Technology* **23** (1/3) 269-277 (2002).

ABSTRACT: In this work was studied the influence of membrane hydrophobicity on the filtration of oil/water (O/W) emulsions which presents a medium content of dispersed phase (30% O/W). The membrane filtration process was realized by using ceramic tubular hydrophilic or hydrophobic membranes with different mean pore size (0.2 μm , 1.2 μm and 1.4 μm of mean pore radius). Hydrophobic character was obtained by modifying superficially the membrane surface with a very thin polymer layer. The results obtained showed that the emulsion viscosity and droplet size distribution depend on the shearing forces and transmembrane pressure. The process operating conditions and the nature of membrane surface / emulsion interaction are the main parameters which control the type and nature of emulsion changes: modification of the mean droplet size, concentration into oleic phase or breaking.

CELIS M. T., GARCIA-RUBIO L. H.,

Continuous Spectroscopy Characterization of Emulsions.

J. Dispersion Science & Technology **23** (1/3) 293-299 (2002).

ABSTRACT: In emulsion polymerization, the formation of particles has an important effect on the rate of reaction and on the final properties of the latex. To investigate particle nucleation mechanisms in emulsion polymerization it is necessary to establish the initial conditions of the emulsified system before the reaction takes place. This research reports on a technique to continuously monitor the droplet size distribution of liquid-liquid emulsions using spectroscopy. The on-line particle characterization methodology is based on an integrated sampling and dilution strategy combined with spectroscopy methods. It is shown that the sampling system integrated with a multiwavelength turbidity detector provides reliable estimates of droplet populations as function of the dispersed phase concentration in emulsions of saturated hydrocarbons. The results provide not only the groundwork necessary for the elucidation of particle nucleation during emulsion polymerization process but also suggests the potential of this combined technology to further our understanding of liquid-liquid emulsions.

RAMIREZ M., BULLON J., ANDEREZ J., MIRA I., SALAGER J. L.,

Drop Size Distribution Bimodality and its effect on O/W Emulsion Viscosity.

J. Dispersion Science & Technology **23** (1/3) 309-321 (2002).

ABSTRACT: The research work on why and how distribution bimodality tends to reduce the viscosity of a particulate suspension is reviewed. The transfer of the corresponding concepts to emulsions requires some statistical tools, and becomes particularly easy with probability scale plotting which is reviewed. Viscosity reduction can be attained for different kinds of fine and coarse emulsion associations. The results are shown to depend on the characteristic of the base emulsions as well as on the way they are mixed.

ROJAS O., ERNSTSSON M., NEUMAN R. D., CLAESSION P. M.,

Effect of Polyelectrolyte Charge Density on the Adsorption and Desorption Behavior on Mica,

Langmuir **18**, 1604-1612 (2002).

ABSTRACT: The XPS (ESCA) method was employed to quantitatively determine polyelectrolyte adsorption on the mica basal plane from low ionic strength solutions. Particular emphasis was given to the effect of the polyelectrolyte charge density. By combining the results obtained from XPS and surface force measurements it was possible to analyze the cation exchange at the surface that occurs as a result of polyelectrolyte adsorption. AFM-imaging was used to obtain information on the structure of the adsorbed layer when the polyelectrolyte coverage was low. Further, the desorption of preadsorbed polyelectrolyte layers by addition of inorganic salt and by addition of an anionic surfactant was investigated by XPS and some complementary surface force measurements. The results demonstrate

that the lower the polyelectrolyte charge density is, the easier it is to remove the polyelectrolyte from the surface. The surfactant, which by itself does not adsorb to the mica surface, is more efficient in this respect than the inorganic salt. This observation can be rationalized by considering that the surfactant and polyelectrolyte form complexes with each other. Thus, the surfactant brings negative charges into the adsorbed layer that reduces the affinity to the surface. However, high charge density polyelectrolytes are removed to a very limited degree even when the surfactant concentration is above the critical micellar concentration, which is explainable by the poor solubility of the polyelectrolyte-surfactant complexes formed.

ARAUJO E., RODRÍGUEZ-MALAVAR A. J., GONZÁLEZ A., ROJAS O. J., PEÑALOZA N., BULLÓN J., LARA M. A., DMITRIEVA N.

Fenton's Reagent-Mediated Degradation of Residual Kraft Black Liquor.

Applied Biochemistry & Biotechnology **97**, 91-103 (2002).

ABSTRACT: In this work, the effect of Fenton's reagent on the degradation of residual Kraft black liquor was investigated. The effect of Fenton's reagent on the black liquor degradation was dependent on the concentration of H₂O₂. At low concentrations (5 and 15 mM) of H₂O₂, Fenton's reagent caused the degradation of phenolic groups (6.8 and 44.8%, respectively), the reduction of reaction medium pH (18.2%), and the polymerization of black liquor lignin. At a high concentration (60 mM) of H₂O₂, Fenton's reagent induced an extensive degradation of lignin (95-100%) and discoloration of black liquor. In the presence of traces of iron, the addition of H₂O₂ alone induced mainly lignin fragmentation. In conclusion, Fenton's reagent and H₂O₂ alone can degrade residual Kraft black liquor under acidic conditions at room temperature.

PEÑA A. A., HIRASAKI G.,

Combined NMR-CPMG Technique to Characterize water-in-oil Emulsions,

Proceedings 3rd International Conference on Petroleum Phase Behavior and Fouling. pp 336-342, AIChE 2002 Spring Nat. Meeting, New Orleans, March 10-14, 2002

ABSTRACT: This paper reports results from the implementation of a combined pulse magnetic field gradient spin echo (PGSE)/Carr-Purcell-Meiboom-Gill (CPMG) experimental technique to characterize emulsions of water dispersed in refined and crude oils. The basis of the method can be summarized as follows: the drop size distribution of the tested emulsions can be resolved from both PGSE and CPMG measurements, but the latter is usually faster and thus more suitable to follow the transient behavior. In addition, the CPMG test provides a direct and accurate measurement of the relative amounts of water and oil present in the emulsion. However, the interpretation of the CPMG data requires knowing the average magnetization relaxativity at the water-oil interfaces. The PGSE measurement is independent of this property. Therefore, the combination of the two methods allows simultaneous determination of the drop size distribution, the surface relaxativity and the water-oil ratio.

LOPEZ-MONTILLA J. C., HERRERA-MORALES P., SHAH D. O.,

New Method to Quantitatively Determine the Spontaneity of the Emulsification Process,

Langmuir **18** (11) 4258-4262

ABSTRACT. A method to quantitatively determine the spontaneity (S) of the spontaneous emulsification process using a laser diffraction particle size analysis technique is presented. The method was experimentally tested by studying the rate of increase of the specific interfacial area (cm² mL⁻¹ s⁻¹) and the equilibrium specific interfacial area for different systems formed by the surfactant Brij30 dissolved in linear alkyl oils (C8-C16) when brought in contact with ultrapure water. The experimental results confirmed the effectiveness of the proposed method, and they also suggest that the oil chain length of the linear alkyl oils has an important effect on the driving force of the spontaneous

emulsification process in these systems. Finally a molecular spontaneous emulsification mechanism is proposed for the systems studied.

MARQUEZ N., GRACIAA A., LACHAISE J., SALAGER J. L.,

Partitioning of Ethoxylated Alkylphenol Surfactants in Microemulsion-Oil-Water Systems: Influence of physicochemical formulation variables,

Langmuir **18** (16) 602-6024 (2002).

ABSTRACT: The partitioning of ethoxylated alkylphenol surfactant species between oil and water depends on all physico-chemical variables which are likely to alter the balance of affinity of the surfactant for the oil and water phases. Experimental data indicate how the logarithm of the partitioning coefficient varies with the oligomer characteristics (degree of ethoxylation, alkyl chain length), the phase nature (oil alkane carbon number, aqueous phase salinity) and co-surfactant (n-pentanol) content.

SALAGER J. L., SCORZZA C., FERNANDEZ A., ANTON R. E., MIÑANA M., USUBILLAGA A., VILLA P.,

Enhancing Solubilization in Microemulsions. From Classic trends to Novel "Extended" Surfactant Structures,

14th International Symposium "Surfactants in Solution", Barcelona Spain, June 9-14, 2002

ABSTRACT: In a formulation scan the highest solubilization of oil and water is attained at the so-called optimum formulation for Winsor III phase behavior, in which a bicontinuous microemulsion is in equilibrium with both oil and water excess phases. All tested systems are compared in such an optimum formulation, on the basis of the value of the solubilization parameter (SP), i. e., the volume (ml) of oil/water solubilized in the microemulsion per gram of surfactant. With alkanes and classic anionic and nonionic amphiphiles SP values about 10 are common, and could be pushed up to 20-30 with short branched oils and long tail surfactant mixtures not requiring alcohols. Increasing the size of the surfactant hydrophilic and lipophilic groups usually increases SP at first, but the excessive growing of the hydrocarbon "tail" beyond a C16 linear backbone ends up in precipitation instead of enhanced solubilization. Further solubilization improvement is attained with both lipophilic and hydrophilic "linker" varieties, or with block copolymer additives, which are able to modify not the interface but the bulk phase region which is in direct contact with the interfacial layer. The grafting of a linker group, sometimes called "spacer arm" because it is located in between the hydrophilic and lipophilic moieties, results in a so-called "extended" surfactant structure. Such molecule produces equivalent solubilization as the surfactant/linker combo and often better results since selective partitioning cannot take place. Such extended surfactants display a considerable solubilization ability for a variety of oil phases, particularly synthetic di- and triglyceride biocompatible oils for which an unmatched SP value above 10 ml/g can be attained. Recently synthesized sugar-based extended surfactant exhibit similar values with additional features such as full biocompatibility and temperature insensitivity.

ANTON R.E., TORRES R., SALAGER J. L.,

Estimation of the Interfacial Hydrophilicity in pH sensitive surfactant-Oil-Water Systems from the Attainment of Optimum Formulation by the dual Scan Technique.

14th International Symposium "Surfactants in Solution", Barcelona Spain, June 9-14, 2002

ABSTRACT: The relative amount of fatty acid and soap in an aqueous phase directly depends on the pH of the bulk phase and can be straightforwardly calculated from the dissociation equilibrium. When such an aqueous phase is in equilibrium with an interface, or with both an interface and an oil phase, the relative amount of undissociated acid at interface is much higher than its counterpart in the aqueous bulk phase, because of the stronger hydrophobic effect on the acid. The hydrophilicity resulting from the interfacial acid/soap mixture can be estimated by a double scan technique, which consists in

attaining a Winsor III phase behavior (or minimum interfacial tension) with the same water/oil and temperature conditions, on the one hand with the acid/soap mixture, and on the other hand with a known surfactant mixture of ethoxylated nonionic blend. Since the interfacial hydrophilicity of both systems must be the same at optimum formulation, the nonionic scan provides the equivalent HLB value of the acid/soap mixture which is adsorbed at interface. The experiment is repeated with several fatty acids and optimum pH conditions. The results indicate that the acid/soap mixture at interface systematically contains much more undissociated acid, i. e., has a lower HLB, than the acid/soap mixture in the bulk. This is equivalent to say either that the interfacial pH is lower than the pH in the bulk water, or that the acid dissociation constant at interface is much lower than it is in the bulk. This is the reason why in alkaline enhanced oil recovery, the minimum interfacial tension of an acid/oil/water system is attained at a pH as much as 3 units higher than the PKa of the acid in water.

RODRIGUEZ C., ANDEREZ J. M., FORGIARINI A., SALAGER J. L.,

Quasi-periodic Formation-collapse in Bikerman's type foaming experiment,

14th International Symposium "Surfactants in Solution", Barcelona Spain, June 9-14, 2002

ABSTRACT: In a typical Bikerman's foaming experiment a continuous jet of gas is fed in a foaming liquid and the resulting foam accumulates in a graduated glass column. The foam height in the column tends to steadily increase until the foam starts collapsing at the top. At some time a dynamic equilibrium is reached between the foam formation and collapse rates. The equilibrium height is some kind of measurement of both the foamability of the liquid and the foam stability. The present work reports that in certain circumstances the typical Bikerman's equilibrium does not happen. Instead, a quasi-periodic pattern so-called pulsating foam decay takes place. In such instance, the foam column first steadily grows, then suddenly collapses, then the foam rises again, then collapses again and so forth. The quasi periodicity indicates that some critical condition should be met for the sudden collapse to happen. This dynamic foaming behavior of nonionic surfactant solutions is analyzed as a function of the main experimental conditions: gas flow rate, bubble size, surfactant hydrophilicity, surfactant concentration, and aqueous phase viscosity (increased by adding carboxymethyl cellulose). The conditions for the occurrence of pulsating foam regime are outlined and discussed.

MARQUEZ L., ANTON R. E., GRACIAA A., LACHAISE J., RONDON M., SALAGER J. L.,

Morphology Changes during Phase Inversion of Micro and Macroemulsions. Experimental Results and Modeling,

14th International Symposium "Surfactants in Solution", Barcelona Spain, June 9-14, 2002.

ABSTRACT: A change in physicochemical formulation or temperature is able to produce the so-called transitional inversion of an emulsion, whereas a change in composition (water-to-oil ratio) can only trigger the catastrophic inversion type. Characteristic variations of the system conductivity indicate that there are three cases of morphology change as inversion takes place. Transitional inversion occurs according to a continuous and reversible mass transfer from and/or to a microemulsion phase, provided that the time scale of the change is long enough. On the other hand, catastrophic inversion is found to take place in a way that depends on the direction of change. From normal emulsion type to abnormal one, a perfect delay condition results in an extremely broad hysteresis zone with an abrupt catastrophic ending whenever it happens. Contrariwise, from abnormal to normal regions, multiple emulsions materialize and a Maxwell multistate condition allows the interpretation of the experimental results. The three types of inversion are located in the formulation-composition bidimensional map and are discussed according to catastrophe theory framework. Applications of this general know-how to emulsion manufacturing is outlined, particularly the conditions to produce miniemulsions.

ALLOUCHE J., TYRODE E. C., SATLER V., CHOPLIN L., SALAGER J. L.,

Formulation Tactics for Making Multiple Emulsions with Surfactant-Polymer Mixtures,

14th International Symposium "Surfactants in Solution", Barcelona Spain, June 9-14, 2002.

ABSTRACT: The areas corresponding to different emulsion morphologies have been clearly identified on a bidimensional formulation-composition map. Multiple emulsions spontaneously form when there is a conflict between the formulation and composition effects, and the most external emulsion is found to be unstable when the formulation effect is driven by a single surfactant, a surfactant mixture or a temperature variation. The use of a proper surfactant-polymer mixture allows to freeze the mass transfer and to considerably lengthen the equilibration of both interfaces. As a consequence, the multiple emulsion can be stable enough to be used in encapsulation and controlled release applications. The area where multiple emulsions occur and their characteristics (conductivity and amount of encapsulated external phase) are reported for a system containing a sorbitan ester lipophilic surfactant and a block PEO-PPO hydrophilic polymer, as a function of the formulation and composition, for a single-step process, in which a specific amount of mechanical energy is supplied. An increase in oil viscosity is found to alter the map and to modify the multiple emulsion characteristics. We also studied a single-batch two-step process in which a formulation involving another surfactant-polymer mixture is combined with an original mixing process tactic. The application of the results to emulsion making technology is discussed.

CELIS M. T., GARCIA-RUBIO L. H.,

Effect of Emulsifier on Transmission Spectrum,

14th International Symposium "Surfactants in Solution", Barcelona Spain, June 9-14, 2002.

ABSTRACT: In emulsion polymerization, the formation of particles has an important effect on the rate of reaction and on the final properties of the latex. To investigate particle nucleation mechanisms in emulsion polymerization, it is necessary to establish the initial conditions of the emulsified system before the reaction takes place. This research reports on a technique to continuously monitor the droplet size distribution of liquid-liquid emulsions using spectroscopy. The on-line particle characterization methodology is based on an integrated sampling and diluting strategy combined with spectroscopy methods. It is shown that the sampling system integrated with a multi-wavelength turbidity detector provides reliable estimates of droplet populations as function of the dispersed phase concentration in emulsions of saturated hydrocarbons. The results provide not only the groundwork necessary for the elucidation of particle nucleation during emulsion polymerization process, but also suggests the potential of this combined technology to further understanding of liquid-liquid emulsions.

BRICEÑO M. I., SALAGER J. L., MARCHAL P.,

Linking Physicochemical Formulation and Rheological Behavior of Concentrated O/W Emulsions.

14th International Symposium "Surfactants in Solution", Barcelona, Spain, June 9-14, 2002.

ABSTRACT: It has been found consistently that physicochemical formulation has an undeniable effect on the rheological behavior of dispersed systems and this effect can be usually attributed to the presence of surfactants and other interacting species. In this work, a novel systematic approach to link formulation to rheological behavior is used. We measure the rheological behavior (steady state and dynamic) of stable concentrated O/W emulsions (50 to over 80% internal phase) of a viscous oil for which the physicochemical formulation has been varied in a systematic way, using an anionic and a family of nonionic surfactants along with co-surfactants and an electrolyte. The emulsions preparation procedure consists of diluting a mother, highly concentrated, emulsion with aqueous solutions of surfactants and other relevant compounds in order to alter formulation while maintaining constant other properties, such as droplet size. This procedure ensures that the observed effects can be solely

attributed to formulation. Formulation changes are quantified by means of the Hydrophilic-Lipophilic Deviation (HLD) which is varied in the region that ensures stable O/W emulsions. We found that the rheological behavior can vary from weakly shear-thinning to strongly viscoelastic as the HLD value changes. Further, the rheological measurement helps to infer how the surfactant interacts to produce a specific macroscopic behavior.

CHAILLOUX N., NARDELLO V., SALAGER J. L., AUBRY J.M.,

Applications of the HLD Concept to the Characterization of Cosmetic Oils and Polyglycerol Ester Surfactants,

SFC Eurochem, Toulouse-France, July 8-11, 2002

ABSTRACT: The phase behaviour of surfactant-oil-water systems (SOW) is known to be affected by the so-called formulation variables. More than 40 years ago, Winsor proposed a comprehensive approach through the ratio R which takes into account all the interactions between S, O, and W. Recently, Salager has developed a new concept, the HLD (Hydrophilic Lipophilic Deviation) allowing the characterization of ethoxylated surfactants and oils in a SOW system by taking into account all the formulation parameters. The first step consists in detecting "optimum formulation" i.e. the formulation for which the interfacial tensions are lowest and exhibiting the highest instability. These formulations are characterized by EON* for which $HLD = 0$.

In a second step, through the characterization of the SOW system, stable emulsions can be formulated for different HLD values. In the present work, the surfactants under study were polyglycerol (n = 4, 6 and 10) monolaurates used in cosmetics and exhibiting glycerol chain length distributions according to a Poisson law. For such surfactants, EON* is replaced by GN*. So-called unidimensional formulation scans (glycerol units) were performed with water, hexanol as the cosurfactant, different linear alkanes as the oil and with the ratio $O/W = 1$. Thus, the constant k could be determined and compared with that obtained for polyethoxylated *iso*-C13 alcohols. In a second time, the effect of the alcohol concentration was studied in order to determine the coefficient m. A retrograde transition could be observed due to the partitioning of the surfactant. Then, the influence of the temperature was examined and no effect on the behaviour of the surfactant could be observed. The optimum formulation remains unchanged for a given system. Based on all these results, the system under study could be characterized by the following equation : $HLD = 0,87 - G - 0,30 \times ACN - 3,32 \times a$. Finally, typical ester oils chosen as models have been characterized with the polyglycerol monolaurate in order to predict the behaviour of more complex ester oils used in cosmetics. Thus, several oils could be classified according to their EACN value.

SALAGER J. L., FORGIARINI A., MARQUEZ L., PEÑA A.,

Emulsion Inversion as a Tool in Industrial Processes.

Plenary Conference 3rd World Congress on Emulsion, Lyon France Sept. 24-27, 2002

ABSTRACT: Emulsion inversion is a complex phenomenon, often perceived as an instability which is essentially uncontrollable, although many industrial processes make use of it. A research effort that started two decades ago has provided the 2D and 3D description, the categorization and the theoretical interpretation of the different kinds of emulsion inversion. A clear-cut phenomenological approach is currently available for understanding its characteristics, the factors which influence it and control it, the importance of fine tuning the emulsification protocol, and the crucial occurrence of organized structures such as liquid crystals or multiple emulsions. The current know-how is used to analyze several industrial processes involving emulsion inversion, e. g., the attainment of a fine nutrient or cosmetic emulsion by temperature or formulation-induced transitional inversion, the preparation of a silicone oil emulsion by catastrophic phase inversion, the manufacture of a viscous polymer latex by

combined inversion and the spontaneous but enigmatic inversion of emulsions used in metal working operations such as lathing, lamination or extrusion.

ALLOUCHE J., TYRODE E., SADTLER V. CHOPLIN L., SALAGER J. L.,

Evolution of Emulsion Properties along a Transitional Phase Inversion Process driven by Temperature Variation.

Paper 094, Proceedings *3rd World Congress on Emulsion*, Lyon France Sept. 24-27, 2002

ABSTRACT: As water-in-oil (W/O) emulsion stabilized by non-ionic surfactant is cooled under permanent stirring, the emulsion inverts into an O/W morphology, at or near the formulation that corresponds to Winsor III phase behaviour case. As temperature changes, the continuous monitoring of both the emulsion conductivity and viscosity, allows the identification of several phenomena which take place during this transition. Two viscosity maxima are found just before and just after the phase inversion temperature, and correlate with the attainment of extremely fine emulsions where the best compromise between low tension and not-too-unstable emulsion is reached. The measurement of conductivity indicates the occurrence of multiple emulsions in the three-phase zone around the phase inversion temperature. The system contains Polysorbate 85, a light alkane cut oil, and sodium chloride brine. The transition is interpreted in the framework of the formulation-composition bidimensional map, and is related to industrial processes.

CELIS M. T., GARCIA-RUBIO L.,

A Rapid Spectrometric Method for Emulsion Characterization.

Paper 099, Proceedings *3rd World Congress on Emulsion*, Lyon France Sept. 24-27, 2002

ABSTRACT: The formation of the particles is the first event that takes place in emulsion polymerization reactions. The locus of particle nucleation and the particle number will be determined by the micellar concentration, the droplet size distribution of the dispersed phase, and of the conditions of the emulsion system before the reaction begins. The droplet size distribution of the emulsion not only affects the final properties of the latex but also determines the properties of the dispersed phase, and reflects the stability of the liquid-liquid emulsion. This research reports a rapid spectroscopic technique for droplet size measurements. It is shown that the combination of sampling and dilution coupled with spectroscopic measurements lead to reliable estimated of the droplet size distribution as function of the dispersed phase concentration. The reported method is simple, fast, applicable to industrial processes, and relevant to further understanding of particle nucleation mechanisms.

PEÑA A., ZAMBRANO N., MARQUEZ L., SALAGER J. L.,

Properties of Emulsions on the Onset of Catastrophic Phase Inversion.

Paper 185, Proceedings *3rd World Congress on Emulsion*, Lyon France Sept. 24-27, 2002

ABSTRACT: The formation of the particles is the first event that takes place in emulsion polymerization reactions. The locus of particle nucleation and the particle number will be determined by the micellar concentration, the droplet size distribution of the dispersed phase, and of the conditions of the emulsion system before the reaction begins. The droplet size distribution of the emulsion not only affects the final properties of the latex but also determines the properties of the dispersed phase, and reflects the stability of the liquid-liquid emulsion. This research reports a rapid spectroscopic technique for droplet size measurements. It is shown that the combination of sampling and dilution coupled with spectroscopic measurements lead to reliable estimated of the droplet size distribution as function of the dispersed phase concentration. The reported method is simple, fast, applicable to industrial processes, and relevant to further understanding of particle nucleation mechanisms.

MARQUEZ L., GRACIAA A., LACHAISE J., SALAGER J. L.,

A Third Type of Emulsion Inversion attained by Overlapping Transitional and Catastrophic Regimes: The Combined Inversion Process.

Paper 180, Proceedings *3rd World Congress on Emulsion*, Lyon France Sept. 24-27, 2002

ABSTRACT: Emulsion inversion has been easily interpreted in a bidimensional formulation-composition map, which segregates the regions where the simple emulsion morphologies, e. g., O/W and W/O, are attained. There are two inversion regimes. When the amounts of oil and water are alike, says from 30 to 70% water, the inversion essentially depends upon the formulation or temperature, and its is called transitional because it displays reversible features associated with a continuous change in phase behavior. Far from unit water-to-oil ratio, the most abundant phase becomes the external phase of the emulsion, sometimes with multiple morphology occurrence in the so-called abnormal regions. The inversion associated with the transition from or into any of these regions is called catastrophic because it displays typical features which have been handily interpreted by a catastrophe theory model. The inversion branches related to the two previous regimes overlap in two map locations, where both regimes could be concomitant, in what is labeled as a "combined" inversion, during which both the formulation (or temperature) and water-to-oil ratio are modified. It is found that such a regime combo is difficult to pinpoint but results in a particularly fine drop size emulsion with no occurrence of multiple morphology.

ANTON R. E., ZAMBRANO A., ALAYON M., RISS A., SALAGER J. L.,

Effect of Hydrophobic Clay Particles on the Formulation and Properties of Emulsions,

Paper 165, Proceedings *3rd World Congress on Emulsion*, Lyon France Sept. 24-27, 2002

ABSTRACT: Solid particles are frequently added to emulsified systems, as in foodstuff, paints, drilling fluids, cosmetics and others, and their effect is not always well interpreted, most often because the comparison is not carried out the right way. Emulsion properties (type, stability, viscosity) are known to vary with the physico-chemical formulation according to a general pattern. When a formulation variable is scanned, the value corresponding to Winsor III (three) phase behavior, so-called optimum formulation, coincides with the change in emulsion morphology and a deep minimum in emulsion stability, as well as other characteristics. It is shown how these properties can be altered when hydrophobated clay particles are added to an emulsion. Experiments on systems containing anionic or nonionic surfactants indicate that the effect of added solid particles is (1) a modification of the apparent formulation, as detected by a shift in optimum formulation with associated properties, (2) an improvement in emulsion stability mostly for W/O type because of the particle wettability.

BRICEÑO M. I., SOLORZANO Y., BERTRAND J., SALAGER J. L.,

Emulsification of Concentrated O/W Emulsions in controlled hydrodynamic Conditions: How Formulation and Mixing Efficiency are Linked.

Paper 145, Proceedings *3rd World Congress on Emulsion*, Lyon France Sept. 24-27, 2002

ABSTRACT: The current know-how on mixing concentrated emulsions is far from complete, not only because the influence of the hydrodynamic factors is not well understood, but also because the effect of physico-chemical formulation has been disregarded. The usual approach has been to focus on hydrodynamics and to overlook formulation issues, even though it is well known that the addition of a tiny amount of surfactant can dramatically alter mixing efficiency. Concentrated O/W emulsions are prepared under controlled dynamic conditions, i. e., with in similar flow regime (in the laminar-turbulent transition region) and comparable power consumption. The mixing efficiency is defined as the droplet size reduction produced by a given mixing energy. Formulation changes are referred to as the value of the hydrophilic-lipophilic deviation (HLD) which is varied from zero (at the so-called optimum formulation for three-phase behavior) to about - 10 by changing the polyether chain length of

a nonionic surfactant. It is found that a large increase in the mixing efficiency takes place as the system formulation approaches $HLD = 0$ and as the interfacial tension decreases hundredfold. Near $HLD = 0$ the formulation controls mixing efficiency, whereas its effect vanishes and dynamic conditions become dominant away from optimum formulation

PEÑA A., HIRASAKI G., NMR CPMG-PSE:

A Novel Method to Characterize water-in-oil Emulsions.

Paper 182, Proceedings *3rd World Congress on Emulsion*, Lyon France Sept. 24-27, 2002

ABSTRACT: This paper presents results from the implementation of the pulsed magnetic field gradient spin echo (PGSE) combined with the Carr-Purcell-Meiboom-Gill (CPMG) technique to characterize emulsions of water dispersed in several oils. The drop size distribution can be resolved via PGSE and CPMG, but CPMG is usually faster and therefore more suitable to evaluate the transient behavior. In addition, the CPMG test renders an accurate measurement of the amounts of water and oil that are present in the emulsion. However, the average magnetization relaxivity at the water-oil interfaces must be known to interpret CPMG data. The PGSE measurement is independent of this property. The combined method allows simultaneous determination of the surface relaxivity, the water-oil composition and the drop size distribution of the emulsion.

MONTESI A., PEÑA A., HIRASAKI G., PASQUALI M.,

Viscoelastic Behavior of Polymer-thickened water-in-oil Emulsions.

Paper 184, Proceedings *3rd World Congress on Emulsion*, Lyon France Sept. 24-27, 2002

ABSTRACT: The viscoelastic behavior of emulsions of water dispersed in a lubricant oil base and stabilized with a nonionic surfactant (Span 80, 5 wt%) was determined in steady shear and sinusoidal oscillatory tests. For each water concentration, emulsions with and without polyisobutylene (PIB, $M_w = 2,100,000$ Da) added to the oil phase at its overlap concentration (0.5 wt%) were tested, and the distribution of drop sizes of each emulsion was determined via NMR. It was found that the steady shear viscosity increased noticeably with the water content, and to a significant less extent with the presence of polymer. Similarly, G' , G'' and other related viscoelastic properties were dictated mainly by the dispersed phase content, and not by the PIB present in the oil. Also, emulsions with water content of 60 wt% exhibited local minima in shear viscosity and loss modulus. These maxima, which were not observed in more diluted emulsions, seem to be related to flocculation and to a structural transition in the configuration of drops from diluted to compressed.

PEÑA A., MILLER C.,

Transient behavior of Polydispersed Emulsions undergoing Mass Transfer,

Industrial Engineering & Chemistry Research, **41**, 6284-6296 (2002)

ABSTRACT: Numerical simulations of transport in polydispersed oil-in-water emulsions were carried out for three situations in which the aqueous phase contained surfactant micelles: solubilization of pure oil; Ostwald ripening of a pure oil; and compositional ripening of a mixed emulsion initially containing drops of two pure oils, only one of which was solubilized to a significant extent. Transport was assumed to be controlled by interfacial effects, not by diffusion of micelles in the aqueous phase. The results were compared with published data for changes in drop size distribution in hydrocarbon-in-oil emulsions stabilized by nonionic surfactants for each of the three phenomena. In some cases the published data were supplemented by measurements of interfacial tensions and solubilization rates of single drops of the same oils in solutions of the same nonionic surfactants. Excellent agreement between simulation results and the published data was found for the solubilization and compositional ripening cases with no adjustable parameter. Moreover, accounting for polydispersity was found to be important, i.e., agreement was sometimes not as good when the same transport mechanism was

assumed but with a monodispersed distribution corresponding to average drop size. Although results for the Ostwald ripening case showed that interfacial effects and not diffusion controlled transport, confirming that the same mechanism of transport applied to all three cases, numerical agreement between simulations and experiment was not as good, probably because of additional transport between flocculated drops not accounted for in the theory.

ROJAS O. J., MACAKOVA L., BLOMBERG Eva B., EMMER Å., CLAESSION P.

Fluorosurfactant Self-Assembly at Solid/Liquid Interfaces,

Langmuir **18**, 8085-8095 (2002)

ABSTRACT: Fluorosurfactants have some unique properties that are advantageously used in a range of applications. Their solutions are commonly in contact with solid surfaces onto which the molecules adsorb. Despite this, the adsorption behavior of fluorosurfactants at solid/liquid interfaces is not sufficiently understood, and there is a need for more information. In this study we focus on cationic fluorosurfactant adsorption on negatively charged hydrophilic surfaces, especially with respect to the adsorbed layer structure, long-range interactions and adhesion forces. To this end we combined results obtained from bimorph and interferometric surface force instruments and ellipsometry techniques. The initial adsorption to the oppositely charged surfaces occurs due to the electrostatic attraction between the charged headgroups and the surface. Further adsorption, driven by hydrophobic interactions, occurs readily as the surfactant concentration is increased. Surface force and ellipsometric experiments indicate that the surfactants self-assemble in the form of bilayer aggregates. The thickness of the bilayer aggregates was found to be consistent with the molecular structure. Further, ellipsometric measurements indicate that no complete bilayers were formed but rather that bilayer aggregates were present on the surface even at concentrations well above the cmc. Surface force data for low fluorosurfactant concentrations demonstrate that upon compression the bilayer aggregates assembled on the isolated surfaces are transformed and as a result monolayer structures build up between the surfaces in contact. The force required to attain bilayer-bilayer contact increases with the surfactant bulk concentration due to an increase in the repulsive double-layer force. The force required to drive out surfactant molecules to achieve monolayer-monolayer contact also increases with surfactant concentration. Above the cmc some additional aggregates are present on top of the bilayer aggregates coating the surface. The adhesion found between the monolayer aggregates is an order of magnitude larger than between the bilayer aggregates. However, it is an order of magnitude lower than the corresponding value for Langmuir-Blodgett monolayer films of similar fluorosurfactants.

BENDITO A. T., ROJAS, O. J., VALECILLOS M. A.

Actividad Superficial de Surfactantes Pulmonares,

Ciencia **10** (3) 300-314 (2002)

ABSTRACT: El proceso de adsorción en la interfase gas/líquido de la región alveolar es fundamental en el desempeño adecuado de surfactantes pulmonares y por tanto la evaluación de preparados exógenos debe incorporar estudios de la actividad superficial. Por esta razón el presente estudio versa sobre la caracterización de la actividad superficial de surfactantes pulmonares (tanto naturales como sintéticos) a los efectos de dilucidar las variables más importantes en la aplicación de los mismos. Se evaluó la tensión superficial (por el método del anillo y de la gota giratoria), así como la movilidad electroforética de surfactantes pulmonares bajo diferentes condiciones de pH. Se demostró la reducción de la tensión superficial por efecto de los surfactantes pulmonares y se evaluó la cinética o velocidad de adsorción. Ambas variables dependen de la formulación empleada. Al comparar el surfactante natural SURVANTA con el surfactante sintético EXOSURF o el DPPC, se observó que el primero produce la menor tensión superficial y se adsorbe a la interfase con la mayor velocidad. Ambos resultados se explican por la presencia de apoproteínas, lípidos y otras especies en los extractos de pulmones de

bovinos con los que se obtiene esta preparación. El conocimiento generado en esta investigación es útil no sólo en cuanto a la aplicación de estos sistemas (formulación, dosificación e interacción con otros componentes existentes en los fluidos alveolares), sino que permite establecer protocolos para comparar en forma rápida la efectividad de diferentes surfactantes exógenos.

SALAGER J. L., ANDEREZ J. M., BRICEÑO M. I., PEREZ M., RAMIREZ M.,
Emulsification Yield related to Formulation and Composition variables as well as Stirring Energy,
Revista Técnica Ing. Univ. Zulia **25** (3) 129-139 (2002)

ABSTRACT. The emulsification yield, i.e., the reduction of drop size when a surfactant-oil-water system is stirred, can be altered by changing (1) the physicochemical formulation variables which are linked to the nature of the water, oil, and emulsifier, (2) the composition variables [surfactant concentration and water-to-oil ratio] and (3) the variables which characterize the mechanical energy supplied by the stirring device. After reporting the general trends found in previous research, the best compromise situations to attain a minimum drop size are located in a three dimensional formulation-composition-stirring space

SALAGER J. L., ANDEREZ J. M., FORGIARINI A.,
Les Mousses - Influence de la Formulation Physico-chimique (in French),
in "*Les Mousses: Moussage et démoussage*", S. Lagerge Ed., Cahier de Formulation vol. 9, EDP Sciences Paris, France pp. 58-91 (2002)

ABSTRACT: In the three steps that span a foam life, there are numerous phenomena which can stabilize it, most of them involving surfactants or other additives, which are dealt with as formulation factors. It is the case of Gibbs elasticity, capillary suction and several mechanisms that delay the drainage of the thin film. Foaming agents can influence in two ways, referred to as efficiency and effectivity. The first criterion corresponds to the smallest amount of surfactant that is able to produce the maximum foamability resulting from the conflict between Gibbs and Marangoni effects. It is often identical to the critical micelle concentration, a well known concept in colloid chemistry. The second criterion deals with the magnitude of the maximum effect, particularly the amount of produced foam in a standardized experiment, often referred to a foamability. After showing that these two criteria are independent from each other, the factors which are susceptible of increasing the effectivity, i. e. the foamability, are analysed: low tension, higher adsorption density, better interactions between adsorbed molecules, interbubble repulsion, phenomena which could delay the film drainage. The most typical cases are analysed. Anionic versus nonionic surfactants, effect of the surfactant molecular structure, shape factor, counter-ion type. Foam boosting effects are discussed next as due to the interaction of nonionic additives (fatty alcohol, acids, amides and others), and ionic species. The effect of electrolyte concentration is shown to be favourable or not, depending on the case. Finally the effect of polymer molecules either adsorbed or in solution, is dealt with, as well as the related association phenomena. The conclusion is that many effects are understood on an independent basis, but that their combination is often a risky business for the foam formulator, much less secure than in the case of emulsions