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2003 PUBLICATIONS AND COMMUNICATIONS BY LAB. FIRP ASSOCIATES

SALAGER J. L., MARQUEZ L., MIRA I., PEÑA A., TYRODE E., ZAMBRANO N.

Principles of Emulsion Formulation Engineering,

in *Adsorption and Aggregation of Surfactants in Solution*. Mittal K. L., Shah D. O., Eds., Surfactant Science Series N° 109, Chap. 24, pp 501-524. M. Dekker New York (2003)

ABSTRACT: Emulsion properties depend mainly upon three kinds of variables: physicochemical formulation, composition and manufacturing protocol. The current state of the art allows the interpretation of the effects of these variables on such properties in the framework of a generalized phenomenology that includes temporal changes, either instantaneous or delayed, as they take place in manufacturing processes. The know-how can be readily translated into guidelines and constraints concerning the process operation and equipment design. This approach is referred to as formulation engineering.

SOLANS C., ESQUENA J., FORGIARINI A., USÓN N., MORALES D, IZQUIERDO P. AZEMAR N., GARCIA M. J. Nano-emulsions, in *Adsorption and Aggregation of Surfactants in Solution*. Mittal K. L., Shah D. O., Eds., Surfactant Science Series N° 109, Chap. 25, pp 525-554. M. Dekker New York (2003)

ABSTRACT. Nanoemulsions are defined as a class of emulsions with uniform and extremely small droplet size (typically in the range 20-500 nm). The formation of kinetically stable liquid/liquid dispersions of such small sizes is of great interest from fundamental and applied viewpoints. In this review, nanoemulsion formation, with special emphasis on low-energy emulsification methods, is first discussed. This is followed by a description of nanoemulsion properties, focussing on their kinetic stability. Finally, relevant industrial applications of nanoemulsions in the preparation of latex particles, in personal care formulations, and as drug delivery systems are reported.

ZAMBRANO N., TYRODE E., MIRA I., MARQUEZ L., RODRIGUEZ M. P, SALAGER J. L.

Emulsion Catastrophic Inversion from Abnormal to Normal Morphology. 1. Effect of Water-to-Oil Ratio Rate of Change on the Dynamic Inversion Frontier,

Industrial & Engineering Chemistry Research **42**, (1) 50-56 (2003)

ABSTRACT: The rate of addition of the internal phase influences the catastrophic inversion of emulsions in the direction of change from abnormal morphology to normal one. At low addition rate, the inversion takes place after a small amount of internal phase is added, and it happens through the occurrence of a multiple emulsion morphology. At high addition rate the inversion is delayed and it takes place without occurrence of a multiple emulsion.

MIRA I., ZAMBRANO N., TYRODE E., MARQUEZ L., PENA A. A., PIZZINO A., SALAGER J. L.

Emulsion Catastrophic Inversion from Abnormal to Normal Morphology. 2. Effect of Stirring Intensity on the Dynamic Inversion Frontier,

Industrial & Engineering Chemistry Research **42** (1) 57-61 (2003)

ABSTRACT: The stirring intensity has a complex effect on the catastrophic inversion of emulsions in the direction of change from abnormal morphology to normal one. At both low and high stirring energy, the inversion takes place early, after a low amount of internal phase is added, and through the occurrence of a multiple emulsion. At some intermediate stirring energy the inversion appears to be delayed and it takes place without occurrence of multiple emulsions.

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

Analysis of Polyethoxylated Surfactants in Microemulsion-Oil-Water Systems. Part III. Fractionation and Partitioning of Polyethoxylated Alcohol Surfactants,

Analytica Chimica Acta **477** (2) 293-303 (2003)

ABSTRACT: Oligomer distribution of polyethoxylated alcohol and polyethoxylated nonylphenol surfactants was studied by normal and reverse-phase high performance liquid chromatography (HPLC). A RP8 column is able to efficiently separate these surfactants according to their alkyl chain group (lipophilic) group, while silica and amino columns separate them according to their polyether chain length (hydrophilic group). Polyethoxylated alcohol and polyethoxylated nonylphenol oligomers selectively partition between the microemulsion-oil-water phases of a Winsor III system. Partitioning of these oligomers was analyzed by HPLC with RI detection. The logarithm of the partition coefficient between the water and oil linearly increases with the number of ethylene oxide groups per molecule of oligomer. For the same ethoxylation degree, the partition coefficient of polyethoxylated tridecanol is found to be higher than the one of the corresponding nonylphenol specie. On the other hand, a polyethoxylated nonylphenol exhibits a higher solubilization than the matching polyethoxylated alcohol.

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

Emulsion Morphology Follow-up by Simultaneous *in situ* Conductivity and Viscosity Measurements during a Dynamic Temperature-induced Transitional Inversion,

3rd Int. Symposium on Food Rheology and Structure, Zurich, Switzerland, Feb. 9-13, 2003

ABSTRACT: As a water-in-oil (W/O) emulsion stabilized by a non-ionic surfactant is cooled under permanent stirring, the emulsion inverts into an O/W morphology, at or near the phase inversion temperature (PIT) that corresponds to Winsor III phase behaviour. 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 PIT, and correlate with the attainment of extremely fine emulsions, where the best compromise between a low tension and a not-too-unstable emulsion is reached. The measurement of conductivity indicates the occurrence of multiple emulsions in the three-phase zone around the PIT. The system contains Polysorbate 85, a light alkane, and NaCl brine. The transition is interpreted in the formulation-composition bidimensional map, and is related to industrial processes.

SALAGER J. L., ANTON R. E., BRICEÑO M. I., CHOPLIN L., MARQUEZ L., PIZZINO A., RODRIGUEZ M. P.

The Emergence of Formulation Engineering in Emulsion Making - Transferring Know-how from Research Laboratory to Plant,

Polymer International **52** (4) 471-478 (2003)

ABSTRACT: All variables capable of altering the physico-chemical formulation, including temperature, are included in a generalized concept so-called the Hydrophilic-Lipophilic Deviation (HLD), which measures the departure from the reference state at which the surfactant-oil-water system exhibits Winsor III three-phase behavior. The general phenomenology representing the emulsion properties (type, stability, viscosity, drop size) can be qualitatively charted in a three-dimensional map, where each region exhibits definite features. Travelling across the map from one region to another corresponds to modifications in formulation, composition and stirring along a path which can describe the protocol of change in an industrial process dealing with emulsion making, inversion or reworking. Six different path cases, labeled as unit operations, emerge from a systematic categorizing, and allow the interpretation of complex industrial processes such as crude oil dehydration, or the manufacturing of paint, cosmetics, or heavy hydrocarbon emulsions.

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

Hysteresis Behavior in Temperature-induced Emulsion Inversion,

Polymer International **52** (4) 590-593 (2003)

ABSTRACT: Emulsion inversion produced by a change in temperature usually takes place reversibly, i.e., at the same temperature whatever the direction of change. The present study indicates previously unreported hysteresis in a transitional inversion driven by a temperature variation in a nonionic system containing Tween surfactant mixtures. In both directions of the temperature variation, a delay is exhibited with respect to the standard phase inversion temperature of the equilibrated system. The width of the hysteresis region depends on the temperature rate of change. This behavior, which does not happen in presence of alcohol, is attributed to the presence of liquid crystals.

POPRAWSKI J., CATTE M., MARQUEZ L., MARTI M. J., SALAGER J. L., AUBRY J. M.,

Application of the HLD Concept to Microemulsions containing Pine Oil and a Nonionic Surfactant,

Polymer International **52** (4) 629-632 (2003)

ABSTRACT: The phase behaviour of surfactant-oil-water systems containing pine oil and commercial ethoxylated isotridecanols is reported. All Winsor phase behaviour types are observed, depending on the surfactant average ethylene oxide number (EON) and concentration. The technique used is based on the occurrence of the so-called optimum formulation at which a bicontinuous microemulsion phase is in equilibrium with excess water and oil, with an associated minimum in interfacial tension. Optimum formulation is found at a zero value of the hydrophilic-lipophilic deviation (HLD), a numerical expression which takes all formulation variables into account. This HLD relationship is used to determine Equivalent Alkane Carbon Number (EACN) of pine oil and its major components

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

HLD Concept as a Tool for the Characterization of Cosmetic Hydrocarbon Oils,

Polymer International **52** (4) 602-609 (2003)

ABSTRACT: The HLD (Hydrophilic Lipophilic Deviation) concept was applied to several water/*i*-C₁₃En/2-propanol/hydrocarbon oil systems. For each oil, the optimum formulation, corresponding to HLD = 0, was determined by systematically changing the formulation as a monotonous variation of the surfactant ethylene oxide number (EON) scanned variable. The optimum EON value (symbolized as EON*) was accurately pinpointed both by estimating the solubilization and by measuring the interfacial tension with a spinning drop tensiometer. This method allowed the classification of cosmetic hydrocarbon oils such as isoheptadecane, paraffin oil, squalane, squalene and hydrogenated polydecenes in C₃₀, C₄₀, C₄₀-C₅₀, on an equivalent alkane carbon number (EACN) calibration scale based on five linear alkanes covering the liquid range (C₅ to C₁₆).

VAN HECKE E., CATTE M., POPRAWSKI J., AUBRY J. M., SALAGER J. L.

A Novel Criterion for Studying Phase Equilibria of Nonionic Surfactant-triglyceride oil-water Systems,

Polymer International **52** (4) 559-562 (2003)

ABSTRACT: The formulation of macro- and microemulsions through the hydrophilic-lipophilic deviation (HLD) concept based on phase behavior observations, has mostly been applied to mineral oils. The present research reports a similar approach using triglyceride-based oils (seven vegetable oils and one pure triglyceride) and ethoxylated (nonylphenol and isotridecanol) surfactant systems. Formulation scans are carried out by varying the surfactant average degree of ethoxylation, e. g. the ethylene oxide number (EON), at 50°C, 55°C and 60°C. Because these systems do not exhibit a Winsor III phase behavior, the so-called optimum formulation was detected for EON_{0.5}, i.e. the EON value at which the surfactant partitions equally into the aqueous and oil phase, which was found to coincide with the minimum stability of the emulsified system. Experimental EON_{0.5} values ranged from 3.5 to 5.5. as temperature, oil nature and surfactant were altered.

PIERLOT C., POPRAWSKI J., CATTE M., SALAGER J. L., AUBRY J. M.

Experimental Design for the Determination of the physico-chemical Parameters of water-oil-surfactant Systems,

Polymer International **52** (4) 614-618 (2003)

ABSTRACT. An experimental design on a Starks' matrix (7 factors, at three levels) was carried out in order to confirm the correlation expression for optimum formulation of nonionic surfactant-oil-water systems. The linear variation of the average number of ethylene oxide group per surfactant molecule at optimum formulation versus ACN, temperature, salt and alcohol concentration validates the postulated first order model. Moreover, the proposed method for the determination of the 8 coefficients of the model only requires 16 experiments and is an alternative to the classical bidimensional scan strategy.

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

Application of the HLD Concept to the Characterization of Polyglycerol Surfactants,

Comunicaciones Jornadas Comité Español Detergencia, **33**: 49-58 (2003)

ABSTRACT: The phase behaviour of surfactant-oil-water (SOW) systems was studied by

making use of the HLD (Hydrophilic Lipophilic Deviation) concept. The studied systems contain commercial polyglycerol monolaurate non-ionic surfactants, hexanol as a cosurfactant and various oils of the ester type. The water-to-oil ratio (WOR) was equal to 1 and the experiments were conducted at 55°C. Unidimensional formulation scans were performed as a function of the average number of glycerol groups per surfactant molecule (GN) in order to detect to phase behavior transition Winsor type I > III > II. The optimum formulation, for which HLD = 0, was determined from the measurement of the solubilizing parameters. These experiments were carried out first with linear alkanes having a well defined ACN (Alkane Carbon Number). Then, these surfactants were used to emulsify cosmetic oils, in particular esters, which were characterized and classified according to their EACN (Equivalent ACN).

TYRODE E., PIZZINO A., ROJAS O.,

Foamability and Foam Stability at High Pressures and Temperatures. I. Instrument validation,

Review of Scientific Instruments **74** (5) 2925-2932 (2003)

ABSTRACT: An instrument was designed and assembled with the aim of measuring macroscopic properties of foams (such as foamability and stability) under pressures and moderate temperatures (up to 10,000 bar and 425 K respectively). The device makes use of infrared sensors to detect the foam forefront position as it is generated by gas sparring in the foaming solution. The measurement makes use of a modified dynamic Bikerman protocol to estimate the foamability and stability of the studied solution. Traditional direct observation used in foam experiments at ambient conditions is therefore circumvented and the instrument can be set up in an appropriate place and monitored remotely so as to reduce the risks involved in high-pressure, high-temperature operations.

Data from the infrared system allows not only following the dynamics of foam phenomena but also the relative foam quality along the column, and the presence of air pockets in the case of unstable or pulsating foams. A series of fluorosurfactants (cationic, anionic, and nonionic) were used to validate the instrument and the effect of temperature on foamability, foam stability and foam quality is discussed. Finally synergistic effects were observed with respect to the foam behavior of different mixtures of the studied surfactants.

SALAGER J. L., ANTON R. E., FERNANDEZ A., SCORZZA C., USUBILLAGA A., SABATINI D.,

Guidelines for Enhancing Solubilization in Microemulsions,

94th American Oil Chemist Society Annual Meeting, Kansas City, May 4-7, 2003.

ABSTRACT: The co-solubilization of oil and water by an amphiphile in a microemulsion structure essentially depends on the physicochemical formulation, and its magnitude can be related to conformational factors dealing with the molecular organization at the oil/water boundary. The solubilization is usually studied along a formulation scan, in which the affinity of the surfactant/alcohol amphiphile mixture is continuously changed in some way. 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. Comparison are carried out between optimum formulation systems, on the basis of the value of the solubilization parameter (SP), i. e., the weight of oil/water solubilized in the microemulsion per gram of surfactant. With alkanes and classic anionic and nonionic amphiphiles SP values about 10 g/g 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 an excessive length of the tail group, say beyond n-hexadecyl, ends up in precipitation or liquid crystal formation instead of enhanced solubilization. Solubilization enhancing can be attained by introducing some bridging intermediate between the bulk phase and the surfactant layer, according to the so-called lipophilic and hydrophilic linker effects, or with block copolymer additives, which are both able to modify an extended zone in the oil and water domains close to their boundary. The grafting of a linker group 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 even better results since the single molecule structure inhibits selective partitioning. Its solubilization ability strongly depend of the size of the intermediate polarity extension. Extended surfactants are able to solubilize a diversity of oil phases, particularly synthetic di- and triglyceride oils for which an unmatched SP value above 10 g/g can be attained. Recent results show that additional features such as biocompatibility and temperature insensitivity can be attained with glucidic extended surfactants.

ALLOUCHE J., TYRODE E., SADTLER V., CHOPLIN L. SALAGER J. L.,
Single and Two Step Emulsification to Prepare a Persistent Multiple Emulsion with a Surfactant-Polymer Mixture,

Industrial & Engineering Chemistry Research **42** (17) 3982-3988 (2003)

ABSTRACT: The regions corresponding to different emulsion morphology occurrence 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. In such systems the most external emulsion is found to be unstable when the formulation effect is produced by a single surfactant. The use of a proper surfactant-polymer mixture allows to strongly inhibit the mass transfer and to considerably lengthen the equilibration between 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. The application of the results to emulsion making technology is discussed.

LARA M. A., RODRIGUEZ-MALAVAR A., ROJAS O., HOLMQUIST O., GONZALEZ A. M., BULLON J., PEÑALOZA N., AURAUJO E.,

Black liquor Lignin Degradation by *Trametes elegans*,

International Biodeterioration & Biodegradation **52**, 167-173 (2003)

ABSTRACT: The white rot fungus *Trametes elegans* was used for direct treatment of spent black liquor from pulping processes with the aim to degrade solubilized lignin which is the primary organic by-product from the chemical digestion of lignocellulosic raw materials. The enzymatic activity of *T. elegans* and the resulting degradation was confirmed by UV/VIS spectrometric and size-exclusion chromatography (SEC) measurements on

incubated and control samples of both industrial and synthetic black liquors. Opposing polymerization and depolymerization reactions occurred after treatment of the black liquor with *T. elegans* in liquid media. It is noteworthy that these effects, which originate from lignolytic enzyme systems, occur after the direct treatment of the black liquor even if no nutrient are added. The effect of the suspension pH and incubation time on the lignolytic action of *T. elegans* is also presented.

TYRODE E., MIRA I., ZAMBRANO N., MARQUEZ L., RONDON-GONZALEZ M., SALAGER J. L.

Emulsion Catastrophic Inversion from Abnormal to Normal Morphology. 3. Conditions for Triggering the Dynamic Inversion and Application to Industrial Processes,

Industrial & Engineering Chemistry Research **42** (19) 4311-4318 (2003)

ABSTRACT: The catastrophic emulsion inversion from abnormal to normal morphology is produced in different conditions, as far as the experimental protocol is concerned. Far from optimum formulation, the inversion is found to take place when the fraction of the dispersed phase, which may be a single phase or an inner emulsion of a multiple emulsion, reaches a critical packing value. Near optimum formulation a so-called low-tension streaming-bicontinuity regime is found to happen instead of an emulsion morphology. The phenomenology is used to interpret the emulsification of viscous oil in industrial processes.

BROUILLET F., BULLON J., CARDENAS A., SANCHEZ J., MARTI-MESTRES G., BRICEÑO M. I.,

Modification of Droplet Size and Distribution of Parenteral Emulsions by Tangential Microfiltration,

J. Membrane Science, **221**, 199-206 (2003)

ABSTRACT: In this work we studied the modification of the droplet size and distribution of stable parenteral emulsions (PEs) by microfiltration. The intravenous nutrition through PE needs to be conducted using very fine emulsified fat droplets, which have to be for health reasons at a mean diameter under 1 micrometer. In this work we used membrane microfiltration to decrease the fat particle mean diameter and distribution. The PE filtration was possible without coalescence, because of the high stability of the PE prepared by using an emulsification method never applied before to this type of emulsion. The membrane filtration process was carried out by using ceramic membranes with different pore sizes (0.8, 1.2 and 1.4 micrometer of mean pore radius). The results obtained showed that the shearing forces and trans-membrane pressure had a fundamental influence on the emulsion droplet size distribution and that depending on the membrane type or operating conditions used, the mean droplet size and distribution could be effectively decreased.

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

Development of New Methods for the Preparation of W/O/W Multiple Emulsions.

1st Annual European Rheology Conference (AERC 2003), Guimaraes, Portugal, Sept 11-13, 2003

ABSTRACT: This work deals with the development of new routes for the preparation of w/O/W multiple emulsions. Two strategies were developed on the basis of a Generalized Formulation Concept, thanks to an *in-situ* follow-up method allowing the simultaneous measurement of electrical conductivity and viscosity during the fabrication process. The first strategy deals with a “two-steps-one-batch” process, during which the multiple

emulsion is obtained in a single mixing vessel thanks to the specific positioning of an agitated mobile. The decrease of the interfacial tension in the system through a formulation change allows to considerably reduce the primary emulsion drop size, even in the case of a moderate mechanical energy supply. The second strategy deals with a one step process, in which two opposite curvatures are simultaneously created through the association of both formulation and composition effects. The control and follow-up of the internal phase content allow to envision the possibility of systematizing the protocol of multiple emulsion elaboration as well as the corresponding operating conditions.

DEL GAUDIO L., ALBONICO P., TINUCCI L., BELLONI A., MARQUEZ L.,

Identification of optimum formulation (HLD=0) by Turbiscan.

17th Conference European Colloid Interface Science Society EICS 2003, Firenze, Italy, September 21-26, 2003

ABSTRACT: The phase separation that takes place at optimum formulation (HLD=0) was monitored by using a Turbiscan LAB equipment from Formulacion. Water/dodecane emulsions containing Span-Tween mixtures of variable HLD were prepared by vigorous mixing and their stability profile was determined by transmission and phase separation. The transmitted light output produces a very early information to detect the optimum formulation of the scan.

SALAGER J. L.,

Formulation Design and Processing of Emulsion Systems,

Conference on New Developments in the Formulation of Dispersion Systems, Royal Society of Chemistry, Manchester UK Sept 29- Oct. 1, 2003.

ABSTRACT: The physico-chemical formulation of most surfactant-oil-water systems can be today expressed as a single generalized concept known as the hydrophilic-lipophilic deviation (HLD). HLD gathers the effect of field variables describing the nature of the components as well as temperature, and measures the (free energy) departure from a reference state often called "optimum formulation" at which the system exhibits a so-called Winsor III three-phase behavior. Equivalence and trade-off between formulation variables can be easily found to design formulation conditions. The generalized formulation is able to qualitatively express the effect of the usual half-a-dozen or so formulation variables (e.g. surfactant HLB, electrolyte type and concentration, oil nature, alcohol type and concentration, temperature, etc) on the phase behavior and emulsion properties. This results in a considerable decrease in the number of degree of freedom to be dealt with by the formulator, down to a manageable level, i.e. three independent variables: one formulation variable and two composition variables, e.g. surfactant concentration and water/oil ratio. Hence, the phase behavior and emulsion properties can be plotted in a 3D representation or three 2D easy to handle maps.

A particularly useful one is the mapping of the system properties in a formulation-WOR 2D plot, because it gathers the two variables that matter most in the design of an industrial process, and it allows the representation of a general phenomenology for emulsion properties such as type, stability and viscosity. Moreover this representation segregates two kinds of inversion (transitional and catastrophic) and allows the description of hysteresis, and its consequences as far as the emulsion properties are concerned.

Moving in the 2D map or its 3D extensions can be done in a few different ways, so-called unit operations in formulation engineering. The assembly of such operations readily allows

the design of processes involving emulsion systems, as illustrated by some typical industrial cases.

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

Development of New Methods for the Preparation of W/O/W Multiple Emulsions.

Conference on New Developments in the Formulation of Dispersion Systems, Royal Society of Chemistry, Manchester UK Sept 29- Oct. 1, 2003.

ABSTRACT: This work deals with the development of new routes for the preparation of w/O/W multiple emulsions. Two strategies were developed on the basis of a Generalized Formulation Concept, thanks to an *in situ* follow-up method allowing the simultaneous measurement of electrical conductivity and viscosity during the fabrication process. The first strategy deals with a "two steps-one batch" process, during which the multiple emulsion is obtained in a single mixing vessel thanks to a specific positioning of an agitation mobile. The decrease of the interfacial tension in the system through a formulation change allows to considerably reduce the primary emulsion drop size, even in the case of a moderate mechanical energy supply. The second strategy deals with a one step process, in which two opposite curvatures are simultaneously created through the association of both formulation and composition effects. The control and the follow-up of the internal phase content allow to envision the possibility of systematising the protocol of multiple emulsion elaboration as well as the corresponding operating conditions.

SALAGER J. L.

Emulsions de Bruts extra-lourds "Orimulsion®".

10èmes Journées de Formulation "Energie et Formulation", Société Française de Chimie, Toulouse France. Nov. 17-18, 2003

ABSTRACT: A la fin des années 70 et au début des années 80, l'exploration à l'est du Vénézuéla de la ceinture bitumineuse de l'Orénoque, gigantesque gisement de pétrole biodégradable s'étendant sur 700 km d'est en ouest et sur 150 km du nord au sud, a indiqué l'existence de réserves considérables d'hydrocarbures (40 milliards de tonnes soit à peu près un tiers des réserves connues de bruts conventionnels). Ces bruts sont à 300 m de profondeur et sont relativement faciles à produire, mais ils sont trop visqueux pour être transportables par oléoduc jusqu'à la côte (300 km) par des méthodes conventionnelles. A la fin des années 70, ces pétroles de densité voisine de celle de l'eau étaient devenus une matière première attractive pour produire des bruts synthétiques par cokéfaction, et, en ce qui concerne leur acheminement vers la côte de la Mer des Caraïbes, le transport sous forme d'une émulsion H/E s'est révélée l'alternative la plus prometteuse, une fois résolu le problème paradoxal de formuler une émulsion à la fois stable durant le transport et facile à casser à l'arrivée.

La chute du prix des bruts conventionnels dans les années 80 changea la donne, et la Compagnie nationale *Petróleos de Venezuela* décida d'utiliser l'expertise acquise en matière d'émulsions de bitume pour développer un combustible émulsifié capable de concurrencer le charbon comme source d'énergie pour les centrales thermoélectriques. Ainsi naquit l'orimulsion® (ou émulsion de brut de l'Orénoque), dont la combustion fut testée pour la première fois en 1985. La première formulation commercialisée à la fin des années 80 comportait 70% de brut sous forme de gouttes d'environ 15 mm dispersées dans de l'eau contenant des sels de magnésium, l'émulsion étant stabilisée par un surfactif nonionique polyéthoxylé. Les recherches universitaires et industrielles qui suivirent dans les années 90

réussirent à produire les connaissances fondamentales et le savoir-faire pratique nécessaire pour faire évoluer la formulation et la fabrication en fonction de contraintes croissantes, tant du point de vue de la performance comme combustible que des spécifications plus exigeantes du point de vue de la stabilité du produit et des risques de pollution.

On retrace pas à pas comment l'adaptation de la formulation physico-chimique combinée à de nouveaux procédés d'émulsification en régime transitoire a permis l'évolution jusqu'à la quatrième génération d'Orimulsion®, plus stable, moins coûteuse, plus calorifique et à la fois moins visqueuse. On peut dire que cet effort de recherche, justifié par une production projetée pour 2004 de 10 millions de tonnes par an, probablement le record mondial actuel en matière d'émulsion, avec un potentiel considérablement plus élevé, a jeté les bases du génie de la formulation des émulsions, et bénéficiera de nombreuses autres applications, des émulsions alimentaires aux peintures, en passant par les produits cosmétiques et pharmaceutiques.

BURGUERA J. L., AVILA-GONZALEZ R. M., BURGUERA M., ANTON R., SALAGER J. L., BRACHO C. L., BURGUERA-PASCU M., BURGUERA-PASCU C., BRUNETTO R., GALLIGNAMI M., PETIT de PEÑA Y., *Optimum phase-behavior formulation of surfactant-oil-water systems for the determination of chromium in heavy crude oil and in bitumen-in-water emulsion, Talanta, 61, 353-361 (2003)*

ABSTRACT: An oil-in-water formulation was optimized to determine chromium in heavy crude oil (HCO) and bitumen-in-water emulsion (Orimulsion-400®) samples by transversally heated electrothermal atomic absorption spectroscopy (TH-ETAAS) using Zeeman effect background correction. The optimum proportion of oil-water mixture ratio was 7:3 v/v (70% of oil as the internal phase) with a nonionic surfactant concentration (Intan-100) in the emulsion of 0.2 % w/w. Chromium was determined in different crude oil samples after dilution of the emulsions 1:9 v/v with a 0.2% w/w solution of surfactant in order to further reduce the viscosity from 100 to 1.6 cP and at the same time to bring the concentration of chromium within the working range of the ET AAS technique. The calibration graph was linear from 1.7 to 100 $\mu\text{g Cr l}^{-1}$. The sensitivity was 0.0069 s $1 \mu\text{g}^{-1}$, the characteristic mass (m_0) was of 5.7 pg per 0.0044 s and the detection limit (3σ) was of 0.52 $\mu\text{g l}^{-1}$. The relative standard deviation of the method, evaluated by replicate analyses of three crude oil samples varied in all cases between 1.5 and 2.6%. Recovery studies were performed on four Venezuelan crude oils, and the average chromium recovery values varied between 95.9-104.8, 90.6-107.6, 95.6-104.0 and 98.8-103.9 % for Cerro Negro, Crudo Hamaca, and Boscan crude oils and for the Orimulsion®-400, respectively. The results obtained in this work for the Cerro Negro, Crudo Hamaca, and Boscan crude oils and for the Orimulsion®-400, following the proposed procedure were of 0.448 ± 0.008 , 0.338 ± 0.0004 , 0.524 ± 0.021 , and $0.174 \pm 0.008 \text{ mg Cr l}^{-1}$, respectively, which were in good agreement with the values obtained by tedious recommended standard procedure (respectively: 0.470 ± 0.05 , 0.335 ± 0.080 , 0.570 ± 0.021 , and $0.173 \pm 0.009 \text{ mg Cr l}^{-1}$).

BRICEÑO M. I., JOSEPH D. D.,

Self-lubricated Transport of Aqueous Foams in horizontal conduits,

International Journal of Multiphase Flow, 29 (12) 1817-1831 (2003)

ABSTRACT: The flow characteristics of aqueous foams were studied in a thin flow channel and a round pipe instrumented for pressure gradient and flow rate measurement. The

quality of the foam was varied by controlling the volumetric flow rate of liquid and gas, and different flow types were identified and charted. Uniform foams move as a rigid body lubricated by water generated by breaking foam at the wall. A lubrication model leading to a formula for the thickness of the lubricating layer is presented. The formula predicts a layer thickness of 6 to 8 μm in the channel and 10 to 12 μm in the pipe. The thickness depends weakly on foam quality. An overall correlation for the friction factor as a function of Reynolds number which applies to both channel and pipe is derived. This correlation is consistent with a model in which a rigid core of foam is lubricated by laminar flow of water in the range of measured thickness.

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

Propriétés amphiphiles des tensioactifs de la famille du monolaurate de polyglycérol et application à la préparation de microémulsions à base d'esters gras,

Oléagineux, Corps Gras et Lipides **10**, 382-386 (2003)

ABSTRACT: Polyglycerol fatty esters are nonionic, vegetable-based and totally biodegradable surfactants. The phase behaviour of the water-oil-polyglycerol monolaurate systems was studied by the HLD (Hydrophilic Lipophilic Deviation) concept. This allowed to characterize the surfactants of the polyglycerol monolaurate family, and to establish a classification of several ester oils according to their EACN value.

MEDINA A. L., COVA J. A., VIELMA R. A., PUJIC P., CARLOS M. P., TORRES J.

Immunological and Chemical Analysis of Proteins from *Eisenia foetida* Earthworm.

Food and Agricultural Immunology **15** (3-4) 255-263 (2003)

ABSTRACT. Previous studies have demonstrated the fibrinolytic and antibacterial activities of proteins from the earthworm *Eisenia foetida* (Ef), but their use as a food supplement for animals and humans is still being considered. We studied proteins from this worm in order to determine chemical composition (protein, fat and heavy metal levels), electrophoretic profile in SDS-PAGE and 2D gels, induction of humoral immune response in mice and toxicity in human cell line. Chemical analysis revealed 61.8, 11.3, and 8.7 g% of proteins, fat and ash, respectively. Levels of heavy metals were low and similar to tunny fish. Sixteen bands were obtained by SDS-PAGE with a molecular range of 6.9-205 kDa while twenty-three spots were observed following 2D gel electrophoresis. After three immunizations with *Eisenia foetida* lysate, high titer antibodies were produced without causing immediate hypersensitivity reactions. Good cell viability was observed when Ef proteins were added to a human cell line. These results suggest that Ef proteins are safe for feeding animals intended for human consumption.

AVILA R., BURGUERA J. L., SALAGER J. L., BRACHO C. L.

Las micelas en química analítica. Aplicaciones en la espectroscopía de absorción atómica.

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ABSTRACT: En este trabajo se explican, de manera breve, varios fundamentos teóricos relacionados con las micelas, es decir, qué es un surfactante, en qué consisten y como se forman estas estructuras, etc. Además, se muestran algunas aplicaciones que tienen las micelas en la espectroscopía de absorción atómica (AAS). Estas se utilizan en AAS, principalmente para cambiar algunas propiedades físicas de la muestra, como la viscosidad o la tensión superficial, lo que puede ser empleado para optimizar la eficiencia de nebulización y mejorar la mojabilidad de superficies sólidas, entre otras cosas. Con este

trabajo no se pretende realizar una extensa revisión del tema, sino, ilustrar con ejemplos prácticos, la utilidad de estas estructuras en la mencionada área.