



Lab. de Formulación, Interfases,
Reología y Procesos

Tel: ++58(0)274-2402954 fax 2402957
<http://www.firp.ula.ve>



**2000 PUBLICATIONS AND COMMUNICATIONS
BY LAB FIRP ASSOCIATES**

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

Analysis of Polyethoxylated Surfactants in Microemulsion-oil-water systems,

Analytical Chimica Acta **405**, 267-275 (2000).

ABSTRACT: A normal-phase method for the separation of ethylene oxide number (EON) oligomers by high performance liquid chromatography (HPLC) is described. Isocratic HPLC with mixed solvent on silica column allows to separate oligomers up to EON=18. Gradient programming moves the limit up to EON=20. For higher EON values (up to 50) a NH₂ column has to be used, either with isocratic or gradient mode. Detection was performed using UV detector. The partition of surfactant in the oil-water system over the entire concentration range below the CMC was determined. Surfactant-oil-water systems were studied according to the unidimensional scan. The surfactant content in the oil, microemulsion and water phases were determined by HPLC. The addition of a lipophilic alcohol in a Winsor III system produced a decrease in the partitioning coefficient of the surfactant between the water and oil phases.

SALAGER J. L., Formulation Concepts for the Emulsion Maker,

in *Pharmaceutical Emulsions and Suspensions*, F. Nielloud & G. Marti-Mestres, Eds., Drugs and Pharmaceutical Science Series vol. **105**, Chap. 2, pp. 19-72, Marcel Dekker, New York (2000).

ABSTRACT: This is a self-study text on the basic concepts that an emulsion maker should know to handle the intricacies of physico-chemical formulation, whatever the application, pharmaceutical or other. It spans from very simple concepts such as HLB number to complex but up-to-date SAD numerical expression that allows to take into account the effect of all variables (including salinity, temperature and even pressure). A section on experimental methods surveys the formulation scan technique and how to use it in practice. This chapter contains 21 figures, 126 references and 3 tables of numerical data.

SALAGER J. L., Emulsion Properties and related Know-how to attain them,

in *Pharmaceutical Emulsions and Suspensions*, F. Nielloud & G. Marti-Mestres, Eds., Drugs and Pharmaceutical Science Series vol. **105**, Chap. 3, pp. 73-125, Marcel Dekker, New York (2000)

ABSTRACT: It is a self-study text which presents the state of the art in relating the emulsion properties to formulation, composition and emulsification protocol, whatever the application, pharmaceutical or other. The emulsion characteristic properties (type, conductivity, drop size, viscosity and stability) are first analysed. Then the influence of physico-chemical formulation, as SAD, on all emulsion properties is discussed. The case of emulsions containing a large amount

of either oil or water is treated next on a bidimensional map (formulation-composition) that is presented as the general phenomenology map for emulsion properties forecasting. The variations of this map with other variables (phase viscosity, surfactant concentration, stirring energy) is outlined. The last section is dedicated to an introduction on dynamic phenomena leading to transitional and catastrophic inversion of the emulsion. This chapter contains 23 figures, and 118 references.

BRICEÑO M. I.,

Rheology of Suspensions and Emulsions,

in *Pharmaceutical Emulsions and Suspensions*, F. Nielloud & G. Marti-Mestres, Eds., Drugs and Pharmaceutical Science Series vol. **105**, Chap. 16, pp 557-607, Marcel Dekker, New York (2000).

ABSTRACT: This is a self-study text that introduces the reader to basic rheology concepts before describing the main features exhibited by emulsions and suspensions. It starts with the definition of Newtonian and non Newtonian behaviors, particularly those exhibited by dispersed systems as shear thinning, viscoplastic, as well as thixotropic. Viscoelastic behaviors is outlined, with stress relaxation, creep compliance and recovery features. A section on rheometry discusses the typical arrangements used in apparatuses: concentric cylinders, cone and plate, parallel plates, capillary, rolling ball. The following section describes the main rheological characteristics of emulsions and suspensions, and specifies the effects of the different physical variables (internal phase content, particle size and shape, particle or drop size distribution). The bimodal distribution influence on emulsion viscosity is described in details. Physico-chemical phenomena, such as the interparticle forces commanding aggregation and flocculation mechanisms, as well as electroviscous and solvation effects, are discussed as well. The chapter ends with two practical sections in which the reader can find advice on how to avoid common mistakes as far as the interpretation of the data is concerned, how to select the best apparatus in each case, and how the formulation can be related to the product rheology.

BULLON J., BELLEVILLE M. P., RIOS G. M.,

Preparation of Gelatin formed-in-place Membranes: Effects of Working Conditions and Substrates,

J. Membrane Science, **168** (1-2) 159-165 (2000).

ABSTRACT: The preparation of low ultra-filtration membranes, by cross-flow filtration of a protein solution on an α -alumina macroporous ceramic support and further tanning/drying treatments, has been improved. The new operational procedure cut the total manufacturing duration from 5h according to the previous studies, down to only a couple of hours. A study of the effect of the protein/tanning agent couple shows that the best performance is attained with membranes built from proteins having a large molecular weight distribution and then tanned with formaldehyde solution. The optimal concentration of the cross-linking agent depends on the kind of protein used.

AVILA R. M., CARDENAS A., MEDINA A. L.,

Tratamiento del Lacto Suero utilizando la Técnica de Electrodiálisis,

Interciencia **25** (2) 80-84 (2000).

ABSTRACT: The buttermilk serum is a sub product of the manufacturing of cheese and butter. It contains large amounts of proteins and calcium, as well as other components, that make it

attractive as a raw material for beverages. However, it contains acids and salts, which are undesirable for human consumption, and should be removed by a technique such as electro dialysis. In Venezuela, the buttermilk is currently discarded or used only for animal food manufacturing. This paper reports the desalting and deacidizing of buttermilk in a electro dialyser of the Kelf type with 5 cells. The liquids were analysed before and after the treatment to determine the following data: conductivity, pH, calcium, proteins, fat, acid and ashes. The results show that the electro dialysis is an attractive method for desalting and deacidizing. However, the Faraday yield is found to be rather low when the initial salt concentration is low. On the other hand a buffer effect is found to impair the pH change in some cases.

BURGUERA J. L., ANTON-SALAGER R. E., BURGUERA M., SALAGER J. L., RONDON C., CARRERO P., GALLIGNANI M., BRUNETTO M. R., BRICEÑO M.,
On-line Emulsification of Lubricating Oils in a Flow-Injection System for Chromium Determination by Electrothermal Atomic Absorption Spectrometry,
J. Anal. Atomic Spectrometry **15**, 549-555 (2000).

ABSTRACT: A simple and quick procedure has been developed for the on-line preparation of a one phase (micro)emulsion in a flow injection (FI) system for chromium determination by electrothermal atomic absorption spectroscopy (ETAAS) with Zeeman effect background correction. The entire FI system was controlled by a computer, independent of the spectrometer. A 1 ml plug of sample solution was injected in the carrier stream of hexane and was subsequently mixed with streams of 3.8% (m/v) sodium chloride, 5 % (m/v) sodium dodecylsulfate and 5% (v/v) sec-butanol. The flow rates of the carriers, sodium chloride, SDS and sec-butanol streams were 1.0, 0.5, 0.5, and 0.2 ml/min respectively. The sonication of the flowing solutions improved the stability of the emulsion and provided quantitative recoveries. An emulsified sub-sample of 200 microliters was collected in a capillary of a sampling arm assembly. Thereafter, 20 microliters of this sample solution were introduced by means of positive displacement with air through a time-based solenoid injector (TBSI) in the graphite tube atomizer. The furnace program included two drying steps (at 110 and 130°C) to minimize the sputtering of the sample to the atomizer. In all instances, the pyrolysis, atomisation and cleaning temperatures of 1600, 2400 and 2500°C were used to obtain good peak profiles with low background signals without the addition of any chemical modifier. The method provides a linear range for chromium from 7 to 50 microgram/liter and a limit of detection of 4 microgram/liter which correspond to 6 ng/g. The results were precise (0.6 0.8% RSD) and the recovery values found in the analysis of spiked samples ranged from 99 to 12%. The agreement between the observed and certified values obtained from two NIST Standard Certified Materials was good. The described method is satisfactory for determining chromium in new and used lubricating oil samples.

SALAGER J., PEÑA A., PEREZ-SANCHEZ M., RAMIREZ-GOUVEIA M., TYRODE E.,
Formulation Engineering Approach to Emulsion Making,
invited lecture, *13th Int. Symp. "Surfactants in Solution"*, Gainesville, USA, June 11-16, 2000.
ABSTRACT: Emulsion properties depend upon scores of variables, which may be classified in three categories, i. e., physicochemical formulation, composition and manufacturing protocol. In the past ten years the overwhelming number of degrees of freedom involved in emulsion making has been mastered, in particular thanks to the generalized formulation concept, which combines the contributions of all formulation variables. A universal phenomenology may be displayed in a

bidimensional map that reports the emulsion type and properties versus generalized formulation and water-oil composition. The characteristics of this map, such as the inversion line, are found to change with other variables such as surfactant concentration, phase viscosity, and stirring energy. The map can be also used to follow and interpret temporal changes, either instantaneous or delayed, as they take place in a manufacturing process. The know-how can be readily translated into guidelines and constraints concerning the equipment design and process operation, an approach which is referred to as formulation engineering.

ROJAS O. J., CLAEISSON P. M., ERNSTSSON M., NEUMAN R. D.,

Desorption of Cationic Polyelectrolyte Adlayer in aqueous SDS Solution,

oral presentation, *13th Int. Symp. "Surfactants in Solution"*, Gainesville, USA, June 11-16, 2000.

ABSTRACT: Association between polymers and surfactants in solution has been the subject of extensive research due to its importance in several fields, both on a fundamental and applied level. The presence of an interface, however, complicates the involved phenomena. This is the case, e. g., of surfactants that are present in, or added to, dispersions in which the particles are stabilized by adsorbed polymers. In this situation the interactions between polymer-covered particles and surfactant molecules play a key role. This study deals with the effect of SDS on the adsorption behavior of a cationic polyelectrolyte preadsorbed on oppositely charged surfaces (mica and silica) in terms of the adsorbed amount, layer thickness and interaction forces as studied by X-ray photoelectron spectroscopy, ellipsometry and surface force techniques, respectively. Regardless of the electrolyte (random cationic polyacrylamide) charge density, the association (for surfactant concentration above the c_{ac}) is a highly cooperative process which produces an expansion of the adsorbed layer and associated long-range repulsion forces. As a consequence, polyelectrolytes preadsorbed on surfaces of opposite charge are readily desorbed by addition of ionic surfactants with the same charge as the surface. The effectiveness of the surfactant in desorbing polyelectrolytes of low-charge density is explained by the conformation of the polymer at the interface which is dominated by long loops and tails (as demonstrated by surface force and ellipsometry measurements). The adsorbed polyelectrolyte is thus easily detached from the surface upon association (driven by hydrophobic interactions) with surfactant molecules.

PEÑA A., VALERO J., CASTRO L., MARQUEZ L. RONDON M., SALAGER J.L.,

Emulsion Catastrophic Inversion. Influence of the Emulsification Protocol,

oral presentation, *13th Int. Symp. "Surfactants in Solution"*, Gainesville, USA, June 11-16, 2000.

ABSTRACT: The influence of the emulsification technique on the emulsion catastrophic inversion pattern is reported in a bidimensional formulation versus composition map. Catastrophic inversion is attained by adding internal phase to an initial emulsion, either O/W or W/O, according to different techniques involving lumpwise or continuous addition of internal phase, different stirring conditions, constant volume or cumulative batch. The hysteresis region location and width are found to depend on the operational mode, i.e. lumpwise or continuous addition, the stirring energy, and the internal phase addition rate. It is found that catastrophic phase inversion is promoted by a high stirring energy or a high addition rate. Contrariwise, a continuous and slow addition rate tends to delay the occurrence of inversion, thus favoring the attainment of a broader hysteresis region, and a high internal phase ratio emulsion. These findings can be readily applied to emulsion making processes.

CREUX P., BOURRIAT P., GRACIAA A., LACHAISE J., SALAGER J.L.,

Enhanced Adsorption of a Fluorocarbon Surfactant on a Hydrocarbon Polymer,

oral presentation, *13th Int. Symp. "Surfactants in Solution"*, Gainesville, USA, June 11-16, 2000.

ABSTRACT: Fluorocarbon surfactants are used in dispersed system applications such as paints, coatings or adhesives, where they are often in contact with hydrocarbon surfaces. However, it is well known that fluorinated hydrophobic tails exhibit a poor interaction with hydrocarbon surfaces, a condition that results in a weak adsorption on such surfaces. This paper shows that the adsorption can be enhanced by the presence of a proper auxiliary surfactant. In order to magnify the hydrophobic interactions, the electrical interactions are dwarfed by using a polypropylene surface with a very low charge and an insignificant catalytic residue. The auxiliary surfactant is selected to be nonionic for the same reason. Its hydrophobic structure contains both hydrocarbon and fluorocarbon groups to provide simultaneous interactions with the fluorocarbon surfactant and the hydrocarbon surface. Electroosmosis experiments reveal that adsorption is enhanced by the presence of the auxiliary surfactant. The procedure optimisation is discussed.

ANTON R. E., BRACHO C. L., DURAN L., PRATO J., SALAGER J. L.,

Flocculation of asphaltic emulsion of powdered solid,

poster presentation, *13th Int. Symp. "Surfactants in Solution"*, Gainesville, USA, June 11-16, 2000.

ABSTRACT: When a powdered solid is added to a cationic asphalt-in -water emulsion, the surfactant molecules which are dissolved in the aqueous phase adsorb at the solid surface and turn it hydrophobic. The transfer of dissolved surfactant molecules on the solid surface may eventually trigger a desorption from the drop interface. As more powdered solid is added the surfactant inventory in the aqueous phase decreases, and the surface and interface conditions are altered. At some point the drops coalesce and adhere to the solid surface. Based on the adsorption isotherms, and using simple assumptions, a model is build to mimic the heteroflocculation process. The amount of powdered solid required to produce incipient flocculation is linked to the physico-chemical characteristic of the system at a so-called flocculation concentration. This surfactant concentration appears to be slightly lower than the concentration which is at equilibrium with an adsorbed monolayer at the solid surface. Experimental evidence attained with extremely simple equipment is used to validate the model.

CARDENAS A., CASTRO E., MURZI H.,

Multiple Emulsions: Their behavior under Osmotic Gradient,

poster presentation, *13th Int. Symp. "Surfactants in Solution"*, Gainesville, USA, June 11-16, 2000.

ABSTRACT: Multiple emulsions have been extensively studied due to the potential use as liquid membranes for the separation of compounds and in controlled release. An understanding of their behavior is essential in designing multiple emulsions for different purposes. In this study, the time evolution of multiple emulsions under osmotic gradient was considered. Emulsions of the W1/O/W2 type were prepared using the two step method, that is making a primary emulsion W1/O and then pouring it into the external phase W2. Different internal salt concentrations (W1), ratios W1/O (related to membrane thickness) and stirring speed were studied. The initial concentration of salt in the external phase was always zero. The breaking of the emulsion was followed by rheological, conductimetric and microscopic techniques. Results show that as the concentration gradient of the salt is increased, and the W1/O ratio decreased, the breaking of the

multiple emulsion becomes quicker. As the stirring speed increases, the breaking of the multiple emulsion increases, but tends to reach a limiting value. A faster breakage of the emulsion is expected as the concentration gradient is increased, due to a greater osmotic pressure gradient which favors a faster water transport into the droplet. Also, as membrane "thickness" increases, the multiple emulsion droplet becomes more resistant to breakage.

ANTON R. E., PRATO J., URDANETA Y., SALAGER J. L.,

Phase Behavior and Emulsion Properties of Cationic surfactant-oil-water Systems,

poster presentation, *13th Int. Symp. "Surfactants in Solution"*, Gainesville, USA, June 11-16, 2000.

ABSTRACT: The phase behavior of surfactant-oil-water systems containing different cationic surfactants of both the alkyl amine and quaternary ammonium type are reported on a formulation-composition map. The formulation variable is typically the pH for the amine surfactants and the salinity of the aqueous phase for the quaternary surfactants. Both types of systems exhibit a phase behavior in accordance to the general phenomenology found with anionic and nonionic surfactants, including the effect of alkyl chain length and oil nature. Some differences are found however in solubilization ability and temperature effect. The emulsion properties (type, stability and viscosity) are plotted on the same formulation-composition diagram. As with anionic and nonionic surfactant systems, the inversion line exhibits a typical stair shape that delimits six regions so-called A, B, C and with a + or - superscript depending on the surfactant affinity difference. The A region displays the normal and stable emulsions, whereas multiple emulsions are found in the B- and C+ regions. The overall phenomenology found with anionic and nonionic surfactant emulsions may be extended to pH-sensitive and quaternary cationic surfactants in a straightforward way, with only qualitative variations.

TYRODE E., ROJAS O., IGLESIAS E.,

Foamability and Stability of Aqueous Foam generated by Fluorocarbon Surfactants at high Temperature,

poster presentation, *13th Int. Symp. "Surfactants in Solution"*, Gainesville, USA, June 11-16, 2000.

ABSTRACT: The effect of temperature (20-80°C) on foam behavior of fluorosurfactants was studied by means of a modified Bikerman method where dynamic equilibrium is attained. Subsequently the foam is allowed to collapse without further disturbance and the variation of the foam height with time gives account of its stability. Since the system was targeted for experiments at high temperature and pressure, direct observation was not possible. Therefore a novel system was developed. The device is based on the detection of the foam height by a set of infrared emitters and sensors, coupled with a data acquisition system, which is driven on a PC by using Labview software. SDS, HPB, pure cationic and nonionic fluorosurfactant, and their mixtures were tested at different temperatures. In general terms, foaminess and foam stability diminishes with temperature. Compared to low-temperature foamers such as SDS and HPB, the fluorosurfactants exhibit a remarkable stability at high temperature. However, their mixture showed a negative synergic effect at temperature above 40°C. It is conjectured that the cationic fluorosurfactant reduces the cloud point of the nonionic one, separating a surfactant-rich phase that plays an antifoaming role.

ARAUJO E., BULLON J., CARDENAS A., SANCHEZ J.,

Emulsion Filtration with modified Ceramic Membranes,

6th Int. Conference on Inorganic Membranes, Montpellier France, June 26-30, 2000.

ABSTRACT: The majority of studies concerning the emulsion filtration consists in the separation of phases by the breakdown of emulsions, an application that mainly concerns the wastewater treatment. In this work the separation of stable emulsions was studied in order to obtain concentrated emulsions or to control the droplet size distribution. Many industrial applications in food processing or cosmetics manufacturing are concerned with this type of process. Emulsion filtration through different ceramic membranes was studied with a cross-flow tubular filtration unit. Three different macroporous tubular alumina membranes were used. They had a 0.2, 1.2 and 1.4 micrometer nominal pore diameter respectively. The alumina membranes are normally hydrophilic. However in this study the 1.4 micrometer membrane was submitted to a surface treatment with a polymer of PDMS type (Dow Chemicals) in order to turn it hydrophobic and to change the nature of the interactions between the membrane substance and the emulsion. The filtered emulsions were of the oil-in-water type (O/W). They were prepared using kerosene as the oil phase, with a nonylphenol ethoxylated (EON = 17.5) surfactant which is known to produce extremely stable O/W emulsions. The results of the filtration showed different behavior for the three membranes. During the emulsion filtration with hydrophilic 0.2 micron membrane, the continuous phase was separated by filtration and the emulsion became concentrated. This was attributed to the pore size and the hydrophilic character of the membrane. Owing to the used pressure (800 KPa) the capillary forces were not sufficient to force the oil droplets through the membrane, and the aqueous filtrate was obtained without emulsion break-up in the retentate. For the 1.2 micron hydrophilic membrane, the pressure was sufficient to force some droplets through the membrane, thus obtaining an emulsion in the filtrate. The corresponding permeate and retentate were constituted of stable emulsions which presented different droplet size distributions. Finally, for the hydrophobic 1.4 micron membrane, a higher flow of filtrate was observed whereas a partial oil phase separation took place into the filtrate. This higher flow could be attributed to a slightly larger pore size; however it is believed that the hydrophobic character of the membrane was probable playing a role, as well as causing a partial breakdown of the emulsion.

SALAGER J. L., MARQUEZ L., PEÑA A., RONDON M. J., SILVA F., TYRODE E.,

Current Phenomenological Know-how and Modeling of Emulsion Inversion,

Industrial & Engineering Chemistry Research, **39** (8) 2665-2676 (2000).

ABSTRACT: This paper encompasses classic trends, as well as recent advances, in the understanding of emulsion inversion phenomena. The concept of *SAD* and the so-called formulation-composition map are revisited, in order to introduce recent findings about the effect of variables that are relevant for most practical applications (i.e., stirring energy, viscosity of phases, surfactant concentration and partitioning) upon the standard and dynamic inversion patterns. Thereafter, some advances in the understanding of the mechanism of catastrophic phase inversion, as well as the state of the art in emulsion inversion modelling are briefly referenced and discussed. Whilst the revision is general enough to embrace the efforts of many individuals, emphasis is given to the contributions that were made by and came after Robert S. Schechter's pioneer work.

GRACIAA A., CREUX P., LACHAISE J., SALAGER J. L.,

Zeta Potential at Air-Water Surface related to the Critical Micelle Concentration of mixed aqueous Surfactant Systems,

Industrial & Engineering Chemistry Research, **39** (8) 2677-2681 (2000).

ABSTRACT: The spinning bubble tensiometer technique provides a handy tool to measure the zeta potential at the air-water surface. The method is used to estimate the variation of the zeta potential at the surface of aqueous solutions containing binary mixtures of surfactants (anionic, nonionic, fluorocarbon anionic). The evidence on molecular interactions at the air-water surface is compared with the information deduced from the CMC experimental data.

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

Partitioning of Ethoxylated Octylphenol Surfactants in Microemulsion-oil-water Systems. Influence of Temperature and Relation between Partitioning Coefficient and Physicochemical Formulation,

Langmuir **16** (13) 5534-5539 (2000).

ABSTRACT: The partitioning coefficient of a surfactant between oil and water is related to the free energy of transfer from one phase to the other. The influence of temperature on the partitioning coefficient of octyl phenol ethoxylate oligomers between oil and water is reported. This allow to calculate a numerical expression for both the enthalpy and entropy of transfer of a surfactant molecule, which may be split into contributions of the EO and methylene groups. The variation of the partition coefficient with formulation variables can be used as a yardstick for conceptualising a generalized formulation expression referred to as HLD (hydrophilic-lipophilic deviation) which is close to the previously defined SAD (surfactant affinity difference) concept.

SALAGER J. L.,

Physico-Chemical Formulation Influence on Emulsions and Foams,

Cognis Symposium on Advances in Fermentation Processes, Philadelphia, Sept. 20-22, 2000.

ABSTRACT: Dispersed systems such as emulsions, foams and suspensions are stabilized by the presence of surfactant molecules, which adsorb at surfaces and interfaces. Surfactant molecules are also able to self-associate in a variety of aggregates such as micelles, microemulsions, liquid crystals, bilayers, gels and other more or less organized mesophases, which can contain variable amounts of oil and water. The extremely prolific scientific literature on this subject reports that the occurrence and properties of these systems somehow depend on the nature and concentration of the (often many) different substances, as well as temperature and pressure conditions, which may be gathered under the overall name of formulation variables. However, many phenomena are involved at the same time and they are likely to take place in some competitive way. Thus, it is often extremely difficult to extract any practical know-how from the scientific literature, since most published studies are either too unrealistic to be useful in practice, or too empirical to be worth more than a recipe in a very specific case. Hopefully, things have recently begun to change. Starting with the pioneering R ratio theory proposed by Winsor, and the very simple empirical HLB scale introduced by Griffin half a century ago, the concept of Physico-Chemical Formulation has lately evolved into the more complex but accurate and thermodynamically sound expression so-called Surfactant Affinity Difference (SAD), which numerically renders the effect of all components, as well as temperature and pressure. In very recent years the properties of surfactant-oil-water emulsified systems have been directly linked to the formulation, composition and stirring conditions in a way that allows qualitative predictions to be carried out,

even when complex phenomena, such as emulsion inversion, are involved. Emulsion properties are today likely to be attained on design, and it may be said that we are currently witnessing the onset of emulsion formulation engineering. This is not the case for foams, for which a much less sophisticated understanding, though still considerable, is available. It may be due to the extra complications of these systems, in which opposite phenomena are always competing against one another. However, it could be simply because they have received less attention than emulsions, particularly from the formulation point of view. Many trends are recognized and the molecular adsorption level, which could guide the formulator in his trials to boost foam persistence or to curtail excessive foaminess. As a concluding example of what may be the future know-how on complex dispersed systems such as foaming emulsions, the SAD concept is shown to account for the similarities between an oil-in-water emulsion and a foam, an air-in-water emulsion when the physico-chemical formulation is dominating the external phase film thinning process.

SALAGER J. L.,

Formulación Físico-Química de los Sistemas Dispersados - Del Arte a la Ciencia, o mejor dicho de la Receta a la Ingeniería,

plenary conference, *III Jornadas de Investigación Básica Orientada en Exploración-Producción PDVSA-INTEVEP*, Los Teques, Venezuela, November 13-17, 2000.

ABSTRACT: Se encuentran muchos casos de sistemas dispersados en el área Exploración-Producción: lodos de perforación, cementos, flujo polifásico en medio poroso, recuperación mejorada con surfactantes y polímeros, inyección alcalina, acidificación, control de inyectividad con geles o espumas, deshidratación de crudo, emulsiones combustibles y unos cuantos otros. En la mayoría de estos casos mucho trabajo de investigación y desarrollo queda por hacer para alcanzar una optimización de la tecnología y de los procesos.

En estos sistemas compuestos de por lo menos dos fases inmiscibles, es la presencia de una sustancia surfactante adsorbida en la interfase que produce un cierto grado de persistencia del sistema en el tiempo, lo que es propicio o indeseable según el caso. Aún en un sistema extremadamente simplificado como un ternario surfactante agua-aceite, existe un gran número de variables que impide realizar estudios sistemáticos. En casos reales se pueden solo estudiar una ínfima parte de las formulaciones, de lo cual resulta que hasta hace poco tiempo el empirismo ha reinado en esta materia y la experiencia acumulado ha prevalecido para resolver los problemas prácticos. Formular un lodo o deshidratar un crudo tiene todavía algo de misterioso y de casi mágico que los operadores se rehusan a enfrentar y a satisfacción de los vendedores aditivos.

La situación está cambiando, en buena parte por el esfuerzo de investigación fomentado por la industria petrolera mundial en los últimos 25 años. No solo se ha aprendido a desagregar los diferentes fenómenos interfaciales que influyen las propiedades de los sistemas dispersados, sino que se han estudiado uno a uno, logrando cuantificar relaciones de causa a efecto, en particular entre las variables físico-químicas y las propiedades de los sistemas dispersados.

La comprensión de estos efectos separados no basta a menudo para resolver problemas prácticos en toda su complejidad, ya que en sistemas reales como lodos puede haber hasta 4 fases y numerosas sustancias que conforman una combinación inextricable de emulsión, suspensión sólida y espuma. Sin embargo, ya se está empezando a entender como se combinan los efectos de la formulación, de la composición y del protocolo de agitación o de mezclado utilizado, lo que puede involucrar más de diez variables independientes. Se han recientemente logrado diagnosticar e interpretar diversos fenómenos fuera de equilibrio, que sean de índole cinético espontáneo, que se deban a la programación voluntaria de condiciones, o que presenten histeresis

es decir una memoria de su historia anterior, y por tanto pueden permanecer en equilibrio metastable, o evolucionar catastróficamente.

Si todavía no se sabe bastante para poder pretender llevar a cabo simulaciones globales de procesos, sí se puede desagregar la fenomenología en operaciones elementales, que representan situaciones de equilibrio o evoluciones predecibles, independientes del sistema particular. Ya nació la ingeniería de la formulación, que permite hoy en día traducir el know-how fenomenológico en especificaciones de procesos tales como la fabricación de emulsiones de bitúmen o la deshidratación de crudo. No cabe duda que en los próximos años se hablará de las operaciones unitarias en ingeniería de la formulación como instrumentos básicos en el diseño de procesos y la fabricación de productos, no solo petroleros, sino alimenticios, cosméticos, farmacéuticos, pinturas, recubrimientos y muchos otros.

ANTON R. E.,

Formulación de Sistemas Surfactante-agua-aceite Insensibles a la Temperatura,

poster, *III Jornadas de Investigación Básica Orientada en Exploración-Producción PDVSA-INTEVEP*, Los Teques, Venezuela, November 13-17, 2000.

ABSTRACT: En muchas aplicaciones prácticas que involucran sistemas surfactante-agua-aceite, tales como la recuperación mejorada, la deshidratación de crudo, la fabricación de emulsiones de bitúmen o de asfalto, la inyección de espumas etc., la temperatura es susceptible de variar de un momento a otro o de un sitio a otro. Como consecuencia de esta variación de temperatura, se produce un cambio de formulación, que puede ser particularmente importante para sistemas no iónicos. Tales cambios son perjudiciales porque arrastran cambios en las propiedades del sistema. Es en particular el caso de la llamada formulación óptima en la cual se obtiene el mínimo de tensión interfacial requerido para la recuperación mejorada, y el mínimo de estabilidad necesario a la deshidratación, cuyas condiciones favorables pueden desaparecer al variar la temperatura de unos pocos grados, lo que puede ser difícil o imposible de controlar.

Usando el hecho de que la formulación físico-química varía con la temperatura en sentido contrario para sistemas iónicos y no iónicos, se establece una regla de mezcla para obtener un sistema mixto cuya formulación es insensible a la temperatura. Los datos experimentales se ajustan bastante bien a la regla de mezcla lineal prevista por un modelo de comportamiento colectivo de los diferentes surfactantes de la mezcla. Se encuentra además que se dispone de un grado de libertad adicional para obtener una mezcla a la vez insensible a la temperatura e insensible a la composición, lo que es muy satisfactorio desde el punto de vista de las aplicaciones porque produce una formulación muy “robusta”.

El efecto de la temperatura sobre las emulsiones, en particular las condiciones de inversión, también puede anularse escogiendo una mezcla iónica-no iónica apropiada. Se reportan resultados sobre como mezclar los dos tipos de surfactantes para tanto una emulsión O/W ó W/O estable, como un sistema óptimo microemulsión-agua-aceite, que sean insensibles a la variación de temperatura.

CARDENAS A.

Uso de Membranas en la Industria,

poster, *III Jornadas de Investigación Básica Orientada en Exploración-Producción PDVSA-INTEVEP*, Los Teques, 13-17 nov. 2000.

CARDENAS A. L., BULLON J., SANCHEZ J.,

Membranas: Nuevas Tecnologías de Separación,

poster, *III Jornadas de Investigación Básica Orientada en Exploración-Producción PDVSA-INTEVEP*, Los Teques, 13-17 nov. 2000.

ROJAS O. J.,

Adsorción de Polímeros Solubles en Superficies Minerales y Fuerzas de Interacción,

poster, *III Jornadas de Investigación Básica Orientada en Exploración-Producción PDVSA-INTEVEP*, Los Teques, 13-17 nov. 2000.

BRICEÑO M. I.,

Mezclado de Emulsiones en Régimen de Transición,

poster, *III Jornadas de Investigación Básica Orientada en Exploración-Producción PDVSA-INTEVEP*, Los Teques, 13-17 nov. 2000.

SALAGER J. L.

Ciencia y Tecnología Universitaria para el Sector Productivo – Un Camino lleno de Obstáculos Que Podemos Eliminar,

Boletín AsoVAC Capítulo Caracas, N° 39, 6-11 (2000)

SALAGER J. L.,

La Investigación Universitaria al Servicio del Sector Productivo ¿Ficción o Realidad.

Conferencia Magistral, 50^{ava} *Convención Annual AsoVAC*, USB Caracas, 22 nov. 2000.

ABSTRACT: Una colaboración estrecha entre las universidades y el sector productivo es ventajosa para ambas partes, ya que junta características y competencias complementarias para producir una sinergia. Hay diversos casos exitosos de tal asociación, como por ejemplo en Suecia, en que el sector universitario participa activamente en sostener el ritmo de innovación de la industria, que lo requiere para mantenerse competitiva a pesar del alto costo de su mano de obra. Sin embargo tal meta no se logra fácilmente, y en el caso de Venezuela, los protagonistas deberían primero diagnosticar la problemática y luego remover los obstáculos que se encuentran en el camino.

La estructura organizacional actual de las universidades no es realmente favorable a tal cooperación, en realidad más bien lo contrario, a pesar de la simpatía manifestada por la gran mayoría de las autoridades académicas. Por ejemplo, prácticamente no se reconoce la experiencia industrial en el baremo de ingreso del personal. Por otra parte no se ofrecen incentivos para realizar investigación “útil”. En la práctica, más bien se penalizan aquellos investigadores que intentan negociar contratos con el sector productivo con trabas administrativas y peajes.

Del lado de la industria, solo las grandes empresas disponen de un personal dedicado a trabajos de investigación y desarrollo, y por tanto capaz de negociar el “modus vivendi” de una cooperación con el sector universitario. Para la gran mayoría de las empresas industriales, en particular las PYMEs, no se dispone ni siquiera de un diagnóstico de lo que se debe cambiar para mejorar la competitividad. Por lo general no hay consciencia de que la innovación es el camino más corto y más seguro en materia de desarrollo e incluso de sobrevivencia.

En los últimos años ha habido intentos aislados para mejorar la situación, como por ejemplo el programa de las Agendas del CONICIT, pero a escala probablemente demasiada modesta para

iniciar un cambio. Ahora, hay señales claras de que el nuevo Ministerio de Ciencia y Tecnología ha tomado consciencia de estos problemas y se está moviendo para aliviarlos con una serie de medidas coordinadas que podrían dar resultados si reciben un financiamiento apropiado.

Pero nada se logrará si el investigador universitario no aprende a darle la vuelta a los peñascos que se encontrara en el camino de una unión entre dos mundos que muchas cosas separan. Hay algunos pocos ejemplos de éxito que permiten vislumbrar lo que podría ser la actuación eficaz y determinante del académico al servicio del sector productivo. No se trata de una ficción, sino de una realidad fundamentada sobre algunos principios simples.

La experticia técnica en el campo es por supuesto imprescindible, y una experiencia industrial previa es a menudo necesaria, aunque no suficiente. La clave del éxito parece radicar en la capacidad del investigador para gerenciar, negociar y organizar, con una sólida base de sentido común y pragmatismo, recordando que lo que el sector productivo necesita no es exactamente conocimiento, sino saber-hacer (“know-how”), y aplicando el dicho de que “el tiempo es dinero”.

Parecen haber cuatro características organizacionales que incrementan la eficiencia de un grupo investigativo universitario y su capacidad de cooperación con el sector productivo. (1) La primera es la mayor simplicidad, se podría decir mayor “virtualidad”, en la organización administrativa del grupo, con el fin de reducir las trabas burocráticas y evitar un sistema jerárquico piramidal que colide con el individualismo típico del investigador universitario. Cuando más simple y más flexible la estructura organizacional del grupo de trabajo, más fácil adaptarla a las circunstancias y al mercado. (2) La segunda es la asociación sistemática de la responsabilidad y de la autoridad, en particular en lo que se refiere al uso de los recursos en cada proyecto que se realice. Eso elimina la necesidad de una jerarquía rígida. Un mismo investigador puede ser responsable y jefe administrativo de un proyecto, y simple colaborador de segunda línea en otro. (3) La tercera es la creación de un atractor científico-administrativo que haga que un investigador tenga un fuerte “interés” en asociarse con el grupo, porque allí encuentra reconocimiento, protección, respaldo, oportunidades de proyectos y de financiamiento. Un atractor se compone de un conjunto de experticias que suministra el aval y garantiza la productividad, y de un servicio de apoyo técnico-administrativo eficiente que se ocupa de las tareas catalogadas de fastidiosas por el investigador. Este atractor es por supuesto indispensable para compensar la entropía nata de cualquier agrupación humana, en particular en la “anarquía organizada” del mundo universitario latino. Sin atractor no hay mucha probabilidad que se forme un grupo con más de un experto. El atractor tiene también un papel importante en la formación de una red que transpasa el recinto universitario y las fronteras, con el fin de acumular competencias valiosas y variadas. (4) En realidad, es el atractor que permite cumplir con el cuarto requisito para un grupo universitario que pretende colaborar con el sector industrial, a saber lograr una masa crítica de investigadores que garantice una variedad suficiente de competencias para resolver un problema real en un tiempo realista. Cabe notar que esta masa crítica puede estar compuesta de elementos ubicados en un mismo laboratorio, en una misma universidad o en lugares lejanos enlazados vía internet. En una red “federativa” de diferentes grupos investigativos, la masa crítica variará con la naturaleza de cada proyecto que se lleve a cabo en forma concertada.

Alcanzar estas condiciones favorables no requieren milagros de parte del investigador universitario, sino sentido común, paciencia y determinación. Hay evidencia de que las condiciones están evolucionando favorablemente, y que el recién creado Ministerio de Ciencia y Tecnología quiere acelerar el proceso. Es quizás el momento oportuno para que el investigador

universitario decida dedicar por lo menos una parte de su tiempo a realizar investigación útil, en el sentido de que tenga un impacto sobre algún sector de la sociedad, sin importar que su trabajo sea fundamental o aplicado, y sin importar su campo de especialización. Que tal comenzar por preguntarse ¿A que trabajo original, pero también impactante, puedo dedicar mi tiempo? Como decía Einstein, lo importante es hacerse la buena pregunta.

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

Studies of the Relation between Phase Behavior and Emulsification Methods with Nanoemulsion Formation,

Progress Colloid Polymer Science **115**, 36-39 (2000).

ABSTRACT: The main aim of this work was to study the relationship between the type of phases present during the emulsification process, the order of addition of components and the droplet size of the resulting emulsions. In this study, a pseudoternary water/poly(oxyethylene) nonionic surfactant/decane system was chosen as a model system to form oil-in-water emulsions at constant temperature in order to know the equilibrium phases and also those involved in the emulsification process. The low-energy emulsification methods studies were: A) addition of oil to an aqueous surfactant dispersion. B) addition of water to a surfactant solution in oil and C) mixing preequilibrated samples of the components. Emulsion droplet size distributions were obtained by means of laser diffraction and scattering methods as well as by optical microscopy. The emulsions obtained with methods A and C were more polydisperse than those obtained by method B. Furthermore, with method B very small droplet size emulsions, nanoemulsions, could be obtained. The results have been interpreted according to the changes in the natural curvature of the surfactants during the emulsification process.

RODRIGUEZ C., SHIGETA K., KUNIEDA H.,

Cubic-Phase based Concentrated Emulsions,

J. Colloid Interface Science **223**, 197-204 (2000)

ABSTRACT: The effect of different types of added oil on the formation of a discontinuous micellar-type cubic phase was investigated in water-polyoxyethylene dodecyl ether (C₁₂EO₂₅) systems by phase study and small angle-X-ray scattering. The thermal stability of the cubic phase increases upon addition of oil, especially short-chain hydrocarbons. However, in the heptane system, the maximum melting temperature of the cubic phase is lower than that for decane due to the formation of a different liquid crystal phase. The effect of polyols on C₁₂EO₂₅ cubic phases was also investigated. It was found that the thermal stability of the cubic phase decreases with polyol concentration. The destabilizing effect becomes large as the polyol molecule penetrates further into the surfactant palisade layer. Although the solubilization of oil in the cubic phase is very low, a large amount of excess oil can be incorporated and a transparent cubic-phase-based concentrated emulsion is formed. The transparency is attributed to the very small difference in the refractive indices between the cubic and excess-oil phases.

**GONZALEZ A. M., SALAGER J. L., BRUNETTO M. R., GALLIGNAMI M.,
BURGUERA J. L., BURGUERA M., PETIT de PEÑA Y.,**

Determination of Molecular Weight Distribution of Lignin derivatives by aqueous phase High Performance Size Exclusion Chromatography (HPSEC),

J. High Resolution Chrommatography **23** (12) 693-696 (2000)

ABSTRACT: Several lignin derivative products are analysed by aqueous phase High Performance Size Exclusion Chromatography (HPSEC): Calibration and sample analysis are carried with a Superosa 12HR column (30 cm x 10 mm I.D.) purchased from Pharmacia. The mobile phase is a sodium hydroxide solution, that eventually contains other electrolytes such as NaCl, LiCl and Na₄P₂O₇. Sodium polystyrene sulfonate standards are used for calibrating purposes. Optimum mobile phase to analyze sample with average molecular weight around 4500, 8000 and 12000 Daltons is found to contain 0.1 M sodium hydroxide.

FERNANDEZ C., MARTI-MESTRES G., RAMOS J., MAILLOLS H.,

LC Analysis of Benzophenone-3: II Application to Determination of *in vitro* and *in vivo* Skin Penetration from Solvents, Coarse and Submicron Emulsions,

J. Pharmaceutical Biomedical Analysis **24**, 155-165 (2000)

ABSTRACT: The aim of this study was to determine the skin penetration of benzophenone-3 *in vitro* and *in vivo* in order to investigate a possible influence of formulation. Six different vehicles, three solvents and three different emulsion types were evaluated *in vitro* and *in vivo*. Each vehicle was applied to the skin model at 2 mg cm⁻². First, histological studies on ear pigskin and human skin were evaluated. *In vitro* measurements were performed with static diffusion cells using pigskin at 1, 2, 4, and 8-h. *In vivo*, benzophenone-3 concentration in stratum corneum was evaluated by the stripping method after 30-min application on forearm volunteers. It was shown that ear pigskin and human skin appear similar and in both experiments significant differences between vehicles were noticed. The six vehicles could be ranked in the same order of benzophenone-3 skin concentration. At 8-h, the highest concentration of benzophenone-3 in skin was obtained with propylene glycol, and O/W submicron emulsion. On the contrary, the two oily solvents, W/O emulsion and O/W coarse emulsion restrain the concentration of this UV-filter in the skin. At each time, permeability *in vitro* and *in vivo* were well correlated. Low concentrations were measured in the receptor fluid suggesting that percutaneous absorption of this UV-filter across the skin would be minimal. The *in vitro* and *in vivo* skin penetration capacity of benzophenone-3 from six vehicles was confirmed and quantified. A satisfactory relationship between binary *in vitro* and *in vivo* was established.

RODRIGUEZ C., KUNIEDA H.,

Effect of Electrolytes on Discontinuous Cubic Phases,

Langmuir **16**, 8263-8269 (2000)

ABSTRACT: We investigated the effect of adding a lyotropic salt (NaCl) and a hydrotropic salt (NaSCN) on the discontinuous cubic phase formed in highly hydrophilic nonionic (C₁₂EO₂₅) and ionic (DTAC) surfactant systems by phase study and small-angle X-ray scattering (SAXS) measurements. In C₁₂EO₂₅ systems, only a small decrease in the thermal stability of the cubic phase was observed upon addition of NaCl or NaSCN. It was also found that NaCl induces a slight reduction on the effective surface area per surfactant molecule (a_s), whereas in the case of NaSCN, a_s increases. These results are attributed to changes in the hydration of the poly(oxyethylene) (EO) chain. On the other hand, in DTAC systems, the addition of both NaCl and NaSCN leads to a transition from the discontinuous cubic phase to the hexagonal phase, related to a more pronounced shrinkage of a_s and to the micellar growth within the cubic phase. Changes in micellar structure resemble that occurring in diluted systems upon addition of salt. The stability of the cubic phase increases when long hydrocarbon-chain oils are added to DTAC/brine systems, because of the formation of swollen micelles with a more positive

curvature and a moderate axial ratio. In oil-present systems, a_s shrinks when the counterion is changed from chloride to bromide. The influence of the degree of counterion dissociation on the phase behavior is discussed.

ROJAS O. J., ERNSTSSON M., NEUMAN R.D., CLAEISSON P.M.,

X-ray Photoelectron Spectroscopy in the Study of Polyelectrolyte Adsorption on Mica and Cellulose,

J. Physical Chemistry B **104**, 10032-10042 (2000).

ABSTRACT: X-ray photoelectron spectroscopy was used to estimate the absolute amount of cationic polyelectrolytes that adsorbs on mica cellulose surfaces in aqueous media. The calculation takes advantage of the knowledge of the mica crystal composition at the basal plane and its ion-exchange properties in aqueous solution. The XPS was operated under monochromatic and unmonochromatic mode and good agreement was observed in the resulting adsorbed amount. The evaluation of the amount of cationic polyelectrolyte adsorbed on cellulose was achieved using calibration curves obtained from adsorption data for the same polyelectrolytes on bare mica surfaces. The adsorption isotherm for polyelectrolytes of low charge density adsorbed on cellulose reveals that their affinity toward cellulose is weaker compared to that observed for highly charged surfaces such as mica. The effect of the polyelectrolyte charge density on the adsorbed amount and the number density of charged segments adsorbed on cellulose were also investigated. From these results it can be concluded that nonelectrostatic interactions are the main contributors to the adsorption of polyelectrolytes on cellulose, but it cannot be ruled out that electrostatic effects also take part in the adsorption mechanism. Finally, it is demonstrated that it is not correct to use the adsorbed amount of polyelectrolytes to determine the surface charge on cellulose surfaces.

LARA M. A., RODRIGUEZ A., GONZALEZ A. M., BULLON J., HOLMQUIST O., ROJAS O.,

Biodegradación de Ligninas de Licores Negros,

VII Congreso Técnico Papelero Venezolano, Maracay, 1-2 dic. 2000.

RODRIGUEZ C., MACHNITSCH F. ROJAS O.,

PAC como Barredor de Basura Aniónica,

VII Congreso Técnico Papelero Venezolano, Maracay, 1-2 dic. 2000.

SALAZAR F., ROJAS O.,

Adsorción de Poliacrilamidas sobre Substratos Papeleros,

VII Congreso Técnico Papelero Venezolano, Maracay, 1-2 dic. 2000.

ROJAS O. J., CLAEISSON P. M., NEUMAN R. D.,

Adsorción de Polielectrolitos de Baja Densidad de Carga sobre Superficies Sólidas y Fuerzas de Interacción Superficial,

Revista Investigación y Ciencia, **21** (2) 36-42 (2000).

SHIGETA K., RODRIGUEZ C., KUNIEDA H.,

Solubilization of Oil in Discontinuous Cubic Liquid Crystal in Poly(oxyethylene)_n Oleyl Ether Systems,

J. Dispersion Science & Technology **21** (7) 1023-1042 (2000).

ABSTRACT: The structural change of the discontinuous cubic (I1) phase upon addition of oil (heptane, decane, hexadecane) is investigated by small-angle X-ray scattering. In polyoxyethylene oleyl ether (C18:1EO_n) system having long polyoxyethylene chain (n=19, 30, 50.8) the I1 phase is formed in a wide concentration range. Only in C18:1EO19 systems, the structure of the I1 phase changes from body-centered to face-centered cubic lattice upon addition of oil. According to the analysis of the change in effective cross-sectional area, the solubilization of hexadecane increases the repulsion between polyoxyethylene chains, while solubilization of heptane makes it decrease. The solubilization of decane keeps the repulsion constant. Since the repulsion hampers the curvature change due to the solubilization, the solubilization capacity is in the order heptane > decane > hexadecane. The oil penetration into the palisade layer are also discussed in term of the change in the effective volume of the lipophilic part of the surfactant molecule.

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

Formation and stability of nanoemulsions in mixed nonionic surfactant systems.

Paper THU O-6, *14th Conference European Colloid Interface Society (ECIS 2000)* Patras, Greece. September 17-22, 2000

ABSTRACT: Emulsions with extremely small droplet sizes (ranging from 10 to 500 nm) have attracted a great deal of attention from both basic and applied viewpoints. These emulsions, referred to as nanoemulsions, miniemulsions, ultrafine emulsions, etc., may possess high kinetics stability and a transparent or translucent visual aspect. The main aim of this work was to study the influence of the emulsification method and phase behaviour in the formation of oil-in-water nanoemulsions. A system composed of water, two nonionic ethoxylated surfactants, with different alkyl chain length and degree of ethoxylation, and an aliphatic hydrocarbon was chosen as model system. Phase behaviour was determined by means of equilibrium phase diagrams with constant surfactant mixing weight ratio at 25°C. Emulsions were prepared according to several low-energy emulsification methods: A) stepwise addition of oil to a water-surfactant mixture, B) stepwise addition of water to a solution of the surfactants in oil, and C) fast cooling of sample from the HLB temperature to a lower temperature (the so-called phase inversion temperature, PIT, method). Emulsion droplet sizes were determined by dynamic light scattering and optical microscopy. Emulsification method B and C gave emulsions with the smallest sized and narrowest size distributions. The size and stability of nanoemulsions have been related to the nature of the phases present in the system.