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### **2004 PUBLICATIONS AND COMMUNICATIONS BY LAB. FIRP ASSOCIATES**

**ALLOUCHE J., TYRODE E., SADTLER V., CHOPLIN L., SALAGER J. L.,**  
**Simultaneous Conductivity and Viscosity Measurements as a Technique to Track Emulsion  
Inversion by the PIT Method,**

*Langmuir* **20** (6) 2134-2140 (2004)

*ABSTRACT.* Two kinds of transition can occur when an emulsified water-oil-ethoxylated nonionic surfactant system is cooled under constant stirring. At water-oil ratio close to unity a transitional inversion takes place from W/O to O/W morphology according to the so-called PIT method. At a high water content, a multiple w/O/W emulsion changes to a simple O/W emulsion. The continuous monitoring of both the emulsion conductivity and viscosity allows the identification of several phenomena which take place during the temperature decrease. In all cases, a viscosity maximum is found on each side of the three-phase behavior temperature interval, and correlates with the attainment of extremely fine emulsions, where the best compromise between a low tension and a not-too-unstable emulsion is reached. The studied system contains Polysorbate 85, a light alkane cut oil, and a sodium chloride brine. All transitions are interpreted in the framework of the formulation-composition bidimensional map.

**SALAGER J. L., FORGIARINI A., MARQUEZ L., PEÑA A. A., PIZZINO A.,  
RODRIGUEZ M. P., RONDON M.**

**Using Emulsion Inversion in Industrial Processes,**

*Advances in Colloid & Interface Science*, **108-109**, 259-272 (2004)

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

**ZERPA L. E., QUEIPO N. V., PINTOS S., SALAGER J. L.**

**An optimization methodology of alkaline-surfactant-polymer flooding processes using field scale numerical simulation and multiple surrogates,**

Paper SPE 89387, *Preprints 14th Symposium on Improved Oil Recovery*, Tulsa OK USA, April 17-21, 2004

*ABSTRACT:* After conventional waterflood processes, the residual oil in the reservoir remains as a discontinuous phase in form of oil drops trapped by capillary forces and is likely to be around 70% of the original oil in place (OOIP). The EOR method so-called alkaline-surfactant-polymer (ASP) flooding has been proved to be effective in reducing the oil residual saturation in laboratory experiments and field projects, through reduction of interfacial tension between oil and water phases.

A critical step to make ASP floodings more effective is to find the optimal values of design variables that will maximize a given performance measure (e.g. net present value, cumulative oil recovery), considering a heterogeneous and multiphase petroleum reservoir. Previously reported works using reservoir numerical simulation have been limited to sensitivity analyses at core and field scale levels because the formal optimization problem includes computationally expensive function evaluations (field scale numerical simulation). The proposed methodology estimates the optimal values of a set of design variables (slug size and concentration of the chemical agents) to maximize the cumulative oil recovery from a heterogeneous and multiphase petroleum reservoir subject to ASP flooding. The surrogate-based optimization approach has been shown to be useful in the optimization of computationally expensive simulation-based models in the aerospace, automotive, and oil industries. In this work we have extended this idea along two directions: i) using multiple surrogates for optimization, and ii) incorporating an adaptative weighted average model of the individual surrogates.

The proposed approach involves the coupled execution of a global optimization algorithm and fast surrogates (i.e. based on Polynomial Regression, Kriging, and a Weighted Average Model) constructed from field scale numerical simulation data. The global optimization program implements the DIRECT algorithm, and the reservoir numerical simulations are conducted using the UTCHEM program from the University of Texas at Austin. The effectiveness and efficiency of the proposed methodology is demonstrated using a well-known field scale case study.

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

**Quantitative Spectroscopy Characterization of Emulsions.**

Oral Communication, *Particles 2004 Symposium*. March 6-9, Orlando FL USA (2004)

*ABSTRACT.* Droplets populations are generated from the dynamic equilibrium between the breakup and coalescence phenomena that take place during emulsification process. The estimation of the droplet size and droplet size distribution are important data, not only because they are linked with the manufacturer process, but also they provide information of the properties of the dispersed phase and are an important parameter affecting the emulsion stability. This paper reports measurements of droplet size distribution from multiwavelength transmission data. The spectroscopy technique proposed is on the regularized solution to the inverse problem posed by the multiwavelength turbidity equation. The particle characterization methodology is based on a coupled sampling and dilution strategy combined with spectroscopy methods. The model implemented herein

provides a reliable estimate of droplet populations as a function of the dispersed phase concentrations and several formulation variables.

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

**Issues for Emulsifier Characterization: Theoretical and Experimental Studies.**

Poster Communication, *Particles 2004 Symposium*. March 6-9, Orlando FL USA (2004)

**ABSTRACT.** In emulsification processes, the nature and amount of emulsifier plays a key role in the determination of the emulsifier effectiveness, which is related with the emulsion stability and to the distribution of the dispersed phase. To investigate particle nucleation mechanisms in emulsion polymerization, it is necessary to know the distribution of monomer, initiator and emulsifier in the reacting mixture. This research shows the potential of UV spectroscopy as a tool to investigate the behavior of the emulsifier. The emulsifier has been selected such that its chromophoric groups can provide quantitative information on the location of the emulsifier throughout the polymerization reaction. The results provide not only the groundwork necessary for the elucidation of particle nucleation mechanisms during emulsion polymerization but also to further understanding of liquid-liquid emulsions.

**ALVAREZ G., ANTON R., MARFISI S., MARQUEZ L., SALAGER J. L.,**

**Apparent Equilibration Time required for Surfactant-Oil-Water Systems to Emulsify into the Morphology imposed by the Formulation. Part 2: Effect of sec-butanol concentration and initial location.**

*Langmuir* **20** (13) 5179-5181 (2004)

**ABSTRACT** Winsor type I equilibrated surfactant-oil-water (SOW) systems produce O/W emulsions upon stirring. However, if the surfactant is initially dissolved in the oil phase, the attained type after immediate emulsification is usually W/O. If the SOW system is partially equilibrated, it could result in a normal O/W emulsion, as if it were fully equilibrated. The minimum contact time for that to happen, so-called apparent equilibration time  $t_{APE}$ , was previously shown (*Langmuir* **2002**, *18*, 607) to strongly depends on formulation, surfactant molecular weight and oil viscosity. The present report shows that it depends on alcohol concentration and location in the unequilibrated system.

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

**Stability of Emulsions from Multiwavelength Transmission Measurements,**

*Industrial & Engineering Chemistry Research*, **43** (9) 2067-2072 (2004)

**ABSTRACT:** Droplet populations are generated from the dynamic equilibrium between the breakup and coalescence phenomena occurring during the emulsification process. Adequate estimation of the droplet size and droplet size distribution is important, not only because they are related to the manufacturing process but also because the droplet size distribution provides information on the properties of the dispersed phase and the stability of emulsions. This paper reports on a novel spectroscopy method that provides quantitative information for the assessment of the stability of liquid-liquid emulsions. The quantitative criterion is based on measurements of droplet populations as a function of the dispersed phase concentration. This technique is applied to fresh and aged emulsions of saturated hydrocarbons and monomers. The method reported for evaluation of the stability of emulsions is easy to carry out, inexpensive, and highly reproducible.

**CUÉLLAR I., BULLÓN J., FORGARINI A.M., CÁRDENAS A., BRICEÑO M.I.**

**More Efficient Preparation of Parenteral Emulsions or how to improve a Pharmaceutical Recipe by Formulation Engineering.**

Proceedings *5to Simposio Internacional sobre Mezclado Industrial y Procesos*, Junio 1-4, Sevilla, España (2004).

*ABSTRACT.* Parenteral emulsions are special O/W emulsions used to feed patients whose medical condition makes them unable to eat normally. Therefore, parenteral emulsions must comply with several specifications. One is that the maximum droplet size must be below 5 mm in order to avoid the risk of a pulmonary embolism. In this work, we describe the step-by-step procedure followed to simplify a current industrial recipe by applying recently developed principles under the name of formulation engineering. Both hydrodynamic and physicochemical formulation parameters were manipulated to reduce energy input and equipment requirements. The current process consists of two heating steps, three mixing stages and filtering to eliminate droplets larger than 5 mm. The mixing stages require first an agitated tank for the making of a coarse dispersion, then a high-speed mixer and last a two-stage homogenizer. Despite the intensive mixing the emulsion does not comply with droplet size specifications and filtering is necessary. Our procedure requires heating once and then two mixing stages, the first to produce a coarse dispersion and the second to refine droplet size in a conventional agitated tank. Further filtering is not necessary since no droplets larger than 3 mm are produced in the mixing tank. The parenteral emulsions resulting from this simplified and less energy intensive process complies with droplet size requirements and are stable over several months.

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

**Systematic Study of Spectroscopy on Liquid-Liquid Emulsions.**

Oral Communication. *15<sup>th</sup> Surfactants in Solution Symposium*, June 6-11, Fortaleza Brazil (2004)

*ABSTRACT.* Emulsification processes produce the generation of droplet populations resulting from the dynamic equilibrium between the breakup and coalescence phenomena determined primarily by the nature and amount of emulsifier, mixing characteristics and emulsion preparation. The information contained in the UV-VIS spectrum on the adsorption and scattering properties of the emulsions together with the optical properties of the dispersed phase lead to the interpretation of the spectra in terms of the particule size distribution, the particle shape and the chemical composition of the oil phase and emulsifier. This paper reports the analysis of emulsions on transmission spectrum as a function of the oil phase and emulsifier concentrations in terms of the emulsion droplet size distribution.

**CELIS M. T., FORGIARINI A., CUICAS H., SALAGER J. L.**

**Effect of the Aqueous Phase Viscosity on the Characteristic of the O/W and W/O Emulsions Attained by the PIT Method.**

Poster Communication. *15<sup>th</sup> Surfactants in Solution Symposium*, June 6-11, Fortaleza Brazil (2004)

*ABSTRACT.* The result of any emulsification process, particularly the emulsion drop size, depends on many factors, particularly those related to the stirring protocol. However, some emulsification processes, such as the so-called phase inversion temperature (PIT) method take place with minimum stirring, and there is very little information on what determines

the drop size. The present paper reports the influence of the aqueous phase viscosity on the droplet size distribution and stability of both oil-in-water (O/W) and water-in-oil (W/O) emulsions attained by the PIT method. It is found that an increase in water phase viscosity tends to produce a decrease in W/O emulsion average drop size with a strong tendency to be monodisperse. Contrariwise, an increase in aqueous phase viscosity tends to produce an increase in drop size of O/W emulsions and to turn them highly polydispersed. The results are interpreted with the help of Grace's diagram, which correlates the viscosity ratio and the critical Weber number.

**FENG J., RODRIGUEZ C., IZAWA T., KUNIEDA H., SAKAI T.**

**Effect of Novel Alkanolamides on the Phase Behavior and Surface Properties of Aqueous Surfactant Solutions,**

*J. Dispersion Science & Technology*, **25**, 163-172 (2004)

**ABSTRACT** : The surface tension properties and phase behavior of a new series of alkanolamides, alkanoyl N-methyl ethanolamides (NMEAs) and their mixtures with sodium dodecyl sulfate (SDS) were investigated. NMEAs alone do not form micelles in aqueous solutions but reduce considerably the surface tension until macroscopic phase separation occurs. According to Gibbs isotherms, the surface layer is less compact for the NMEA with the shortest alkanoyl chain. The CMC of SDS solutions is greatly reduced upon addition of a small amount of NMEA and the magnitude of this effect increases with the length of the alkanoyl group. The results indicate the presence of attractive interactions between SDS and NMEA molecules inside micelles. The mixing of SDS with NMEA-16 causes a reduction in the melting temperature of the solid similar to the freezing point depression in a binary system. On the other hand, the eutectic temperature is higher in SDS-conventional dodecanoyl monoethanol amide (DMA) systems in which the mixture is in a solid state at room temperature over a wide range of mixing fractions. Among NMEAs, surface tension decay is faster as the alkanoyl chain length decreases. Only for the dodecanoyl chain could a diffusion-controlled adsorption be identified at low concentration. When small amounts of NMEA are added to SDS aqueous solutions, the surface tension decay is retarded; however, and at long times a lower surface tension is reached. For NMEA/SDS and DMA/SDS systems, an adsorption barrier is likely present. The magnitude of the barrier seems to depend on the SDS/alkanolamide ratio.

**SALAGER J. L., FORGIARINI A., LOPEZ J. C., MARFISI S., ALVAREZ G.,**

**Dynamics of Near-Zero Energy Emulsification,**

*6th World Surfactant Congress CESIO*, Berlin, Germany, June 21-23, 2004. CD Proceedings Session B-S16.

**ABSTRACT** : Emulsification is generally carried out by introducing mechanical stirring in a two phase systems. However such methods are not always easy to apply and are often costly, particularly to produce the extremely fine droplets found in the so-called mini or nanoemulsions. The present talk deals with emulsification methods in which stirring has essentially no effect in the breaking mechanisms, which are based on one or several of the following dynamic processes: surfactant mass transfer, spontaneous emulsification, transitional or/and catastrophic phase inversion. They are all produced by interfacial transient events (most often under low-energy homogeneization), either by putting into contact non-equilibrated phases or by changing the formulation, temperature, or the water-

oil ratio of an equilibrated system. A unified approach is presented here on the basis of the generalized formulation concept, and it is shown to be a handy tool to design industrial processes such as polymer coating manufacturing, cutting oil concentrate dispersion or heavy crude oil emulsification.

**YSAMBERTT F., BAUZA R., ROJAS O., BERRIO N., MARQUEZ N., SALAGER J.**  
**Interferencias analíticas asociadas al estudio de la distribución de peso moleculares en fase orgánica de desechos lignícos del pulpado de papel (Spanish)**

*Multiciencias*, 4 (1) 7-15 (2004)

**ABSTRACT:** Se describe un estudio de interferencias presentes en el análisis de la distribución de pesos moleculares (DPM) de ligninas alcalinas de bagazo de caña y de ligninas comerciales. Los análisis se realizaron en columnas Zorbax PSM de 60S, 300S y 1000S, con DMSO como fase móvil y detección UV. Se estudió además la influencia de asociaciones moleculares, y a presencia de picos “fantasmas” a elevados pesos moleculares, con adición de sales de litio en la fase móvil.

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

**Procédés de préparation d’émulsions multiples en une seule étape,**

*11èmes Journées de Formulation – Cosmétologie*, Société Française de Chimie – Société Française de Cosmétiques, Paris, Dec. 8-9, 2004

**ABSTRACT:** Plusieurs stratégies ont été développées sur la base du concept de formulation généralisée développé par Salager *et al.*, permettant la fabrication d’émulsions multiples ayant un contenu de phase interne contrôlé. Ces stratégies utilisent une seule étape de fabrication et deux modes opératoires (batch et semi-batch). Le premier mode opératoire, appelé mode statique consiste en la mise en contact des deux phases (huile et eau), additivées d’agents tensioactifs appropriés, suivie d’un apport d’énergie mécanique spécifique jusqu’à une quantité spécifiée, puis en un apport d’énergie mécanique supplémentaire à composition globale constante.

Ces stratégies reposent sur l’existence d’une fraction critique de phase dispersée, établissant la quantité maximale de phase dispersée qu’une émulsion dite anormale peut contenir sans qu’elle subisse de phénomène d’inversion de phase, quantité maximale préalablement déterminée et fixe pour une formulation donnée. Le contrôle de ces protocoles de préparation d’émulsions multiples s’effectue grâce à un suivi *in situ* de la viscosité ou de la conductivité (simultanément, lorsque la phase externe le permet).

**VILLAREAL A., BRUNETTO M. R., FORGIARINI A. M., SALAGER J. L., FERNANDEZ C.**

**Formulation de nanoémulsions de base à visée dermocosmétique. Applications: Réalisation d’une crème nutritive,**

*11èmes Journées de Formulation – Cosmétologie*, Société Française de Chimie – Société Française de Cosmétiques, Paris, Dec. 8-9, 2004

**ABSTRACT:** L’objectif principal de ce travail était de formuler une nanoémulsion de base à visée dermocosmétique. Une nanoémulsion est un type d’émulsion caractérisée par une taille de gouttelettes très petite (20 à 500 nm) et une faible polydispersité qui lui donne une grande stabilité cinétique, une apparence transparente ou translucide, et favorise le passage transdermique de molécules actives. Pour la réalisation de cette étude, le concept de formulation optimale utilisant le HLB comme variable de formulation dans l’étude du

comportement de phase des systèmes, a été appliqué pour la première fois dans le domaine cosmétique. La méthode d'émulsification par inversion de phase employée pour la formulation des nanoémulsions cosmétiques nécessite de faibles quantités d'énergie, et les variables optimisées furent les suivantes: vitesse d'agitation (350 rpm), vitesse d'introduction de la phase aqueuse (3 mL/min), température (65°C). La nanoémulsion la plus stable a été réalisée avec des surfactifs nonioniques, Span 60/Tween 80 à un HLB de 11,31 et une concentration totale de 8%. Le rapport huile de maïs/paraffine était de 2/10. Dans ces conditions, des nanoémulsions avec des tailles de gouttelettes de 100 nm, un pH de 5,5, et une viscosité de 5 cP ont été obtenues.

**BRAVO B., CHAVEZ G., YSAMBERTT F., GRACIAA A., LACHAISE J., ANTON R., SALAGER J. L., MARQUEZ N.**

**Thermodynamic Parameters of the Chromatographic equilibrium distribution Process of Amphiphilic Compounds by HPLC. Part I. Fatty Acids.**

*Ciencia*, **12** (4) 315-322 (2004)

**ABSTRACT:** The retention behavior of fatty acids on a reverse phase HPLC column is reported. Retention increases as the acetonitrile/methanol mobile phase becomes richer in acetonitrile. For a given solvent mixture, retention increases (linearly) with the acid chain length. Retention factor ( $k$ ) is dimensionless and independent on any geometrical parameter of the column or HPLC system. It could be considered as a thermodynamic characteristic of the absorbent—eluent system. HPLC experiments carried out at different temperatures allow to plot the variation of  $\ln k$  vs  $1/T$ , and to calculate the  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  of transfer of one molecule from the mobile phase to the stationary phase. According to Van't Hoff expression, the retention decreases as temperature increases. Both  $\Delta H^\circ$  and  $\Delta S^\circ$  are found to be negative, a result that corroborates that the adsorption of the n-alkyl chains onto the stationary phase is favorable from the energetic point of view, and that it increases the molecular order.

**FERNANDEZ A., USUBILLAGA A., SALAGER J. L.,**

**Síntesis de un nuevo surfactante extendido con cabeza polar carbohidrato,**

*Ciencia* **12** (3) 229-236 (2004)

**ABSTRACT:** Se requieren surfactantes con un bajo nivel de toxicidad para ser usados en productos alimenticios, farmacéuticos o cosméticos. En el presente estudio se describe la síntesis de un nuevo surfactante extendido que tiene una cabeza polar de glucopiranosas, cola lipofílica de n-dodecanol y una extensión o brazo espaciador de polipropilenglicol que enlaza estos dos elementos. La estructura, tanto de los intermediarios como del producto final, fue establecida mediante análisis de resonancia magnética nuclear ( $^1\text{H}$  y  $^{13}\text{C}$ ). Se discuten los posibles usos de este tipo de surfactante en la industria farmacéutica.

**BRICEÑO M.I., COBOS S.**

**Escalamiento del proceso de mezclado de emulsiones O/W concentradas (Spanish)**

*Ciencia e Ingeniería*, **23** (3), 125-133 (2004).

**ABSTRACT: Concentrated O/W emulsion mixing process scale-up.** In this work the scale-up procedure for the mixing process of concentrated O/W emulsions is presented. The goal was to prepare emulsions of increasing concentration (50 to 80% oil) but for similar hydrodynamic conditions in such a way that the effect of physico-chemical variables could be isolated and evaluated. This is not a straightforward procedure due to the steep increase

of viscosity and rheological complexity of these emulsions as concentration increases. Within this framework of analysis, rheological behavior was first evaluated as a function of oil concentration and droplet size. From this evaluation, empirical correlations were obtained for predicting emulsion viscosity as a function of volume fraction for a given droplet size. Then, following a conventional scale-up procedure and the results of the rheological study, the mixing volume of required for every concentration of oil was calculated. This mixing volume tends to increase with oil content, but in doing so, the flow regime (transition) and specific power were of the same magnitude for all systems evaluated. The experimental results show that the scale-up procedure was adequate.

**URDANETA R., BORREGALES C., BULLON J., CARDENAS A.**

**Effect of milk homogenization in yield and properties of soft ripening cheese.**

*Revista Técn. Ing. Univ. Zulia* **27** (2) 75-82 (2004)

**ABSTRACT:** The influence of homogenization on the milk droplet size distribution, the soft ripening cheese yield and organoleptic properties were studied. Different fat contents of milk were used: 2.5, 2.8 and 3.2 %. Cheeses were made with pasteurized and homogenized milk (HM) and pasteurized non homogenized milk (NHM). The milk was homogenized with a needle valve at 0.93 MPa/10 min and 1.2 MPa/15 min. Cheeses were submitted to a ripening process of 16 days. A panel of tasters made the taste analysis. The hardness was tested with a penetrometer. The HM cheeses had the best organoleptic properties with the 3.2% HM cheese considered the best of them all. The best yield was obtained with the HM milk; it was a 30 to 40% better than with NHM. The softest cheeses were those made with HM as shown by the penetration index (highest index 22 mm).

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