



**Lab. de Formulación, Interfases,  
Reología y Procesos**

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



**2009 PUBLICATIONS AND COMMUNICATIONS  
BY LAB. FIRP ASSOCIATES**

**SALAGER J. L., ANTON R. E., FORGIARINI A., MARQUEZ L.**

**Formulation of Microemulsions.**

In *Microemulsions: Background, new concepts, applications, perspectives*. C. Stubenrauch, Ed. Chapter 3, pp. 84-121, Blackwell Pub. Oxford UK (2009)

**ABSTRACT:** Basic concepts on microemulsion and formulation. Representation of formulation effects. Physicochemical yardsticks, early concepts (HLB, PIT, R) and generalized formulation (SAD, HLD). Quality of formulation, Winsor's basic premise, alcohol effects, linkers, and extended surfactants. Formulation for special purposes. Mixing rules for surfactants (polyethoxylated nonionics, anionics, anionic-nonionic, anionic-cationic), effect of composition variables and fractionation problems.

**HAEGEL F. H., LOPEZ J. C., SALAGER J. L., ENGELSKIRCHEN S.**

**Microemulsions in Large Scale Applications**

In *Microemulsions: Background, new concepts, applications, perspectives*. C. Stubenrauch, Ed. Chapter 10, pp. 302-344, Blackwell Pub. Oxford UK (2009)

**ABSTRACT: Section 10.2 on Enhanced Oil Recovery.** Poor ultimate oil recovery. Why enhanced oil recovery? Basic Scientific and technical problems for chemical EOR. Principle of ultralow tension attainment. Formulation compatibility with reservoir solids and fluids. Continuous injection process constraints. Current state of the art and future guesstimates.

**ALVAREZ G., POTEAU S., ARGILLIER J.-F., LANGEVIN D., SALAGER J.-L.**

**Heavy oil-water interfacial properties and emulsion stability: Influence of dilution.**

*Energy & Fuels* **23**: 294-299 (2009)

**ABSTRACT:** We have performed a study of dynamic interfacial tension and rheology of interfaces between water and either crude oil diluted in toluene or in a model oil consisting of toluene, in which pentane-extracted asphaltenes were redissolved. We show that the break point of the curve interfacial tension versus the asphaltene concentration is not related to an eventual critical aggregation concentration but rather to the collapse of the asphaltene surface layer. As for other amphiphilic species that adsorb irreversibly at an oil-water interface, the corresponding emulsion stability increases with the amphiphile concentration, even above the collapse point. The behavior of diluted crude oil and model oil are quite similar. However, the surface layers evolve over longer time scales in the case of diluted crude oil, probably because of the contribution of resins that form less polar aggregates with asphaltenes. This results in less stable emulsions, especially before the collapse point.

**SALAGER J.L.**

**Bimodal emulsions. Drop size analysis smart software.**

*Beckman Coulter Particle Characterization Forum*, Miami FL. March 6, 2009.

**ABSTRACT:** Bimodal emulsion are useful in some applications, eg when a low viscosity is required. The data analysis may be carried out easily on a probabilistic-log normal plot in which each of the emulsion distribution is represented by a straight line, whose characteristic may be easily extracted from a linear regression. Empirical formulas to represent the error function and its inverse are proposed.

**PIZZINO A., CATTE M., VAN HECKE E., SALAGER J. L., AUBRY J. M.**

**On-line light backscattering tracking of the transitional phase inversion of emulsions.**

*Colloids Surfaces A* **338**: 148-154 (2009)

**ABSTRACT:** A surfactant/oil/water system (Brij 30/decane/brine) is stirred while continuously changing the temperature in order to induce the swap of the emulsion morphology from O/W to W/O or vice versa. The transitional phase inversion is detected by monitoring both the electrical conductivity and the light backscattering with a Turbiscan (on line) equipment. The optical technique pinpoints the inversion and exhibits several advantages over the conductivity measurement: (i) it does not require any addition of electrolyte in the aqueous phase, (ii) it provides some information on the drop size, and (iii) it works with both O/W and W/O morphologies whereas conductimetry is blind for the latter case.

**RONDON-GONZALEZ M., SADTLER V., MARCHAL P., CHOPLIN L., SALAGER J.**

**Emulsion Catastrophic Inversion from Abnormal to Normal Morphology. 8. effect of formulation on the inversion produced by continuous stirring.**

*Industrial and Engineering Chemistry Research* **48**, 2913-2919 (2009)

**ABSTRACT:** This paper deals with the influence of the global formulation of a water oil-surfactant system, expressed by the hydrophilic-lipophilic difference (HLD), on the emulsion inversion produced just by the continuous stirring of an abnormal system, without any internal phase addition or any composition change. Evidence confirms that under stirring, a w/O/W multiple emulsion is formed by the continuous inclusion of the external water phase inside the dispersed drops, which results in an increase of the effective dispersed phase volume until a critical value at which the inversion is triggered. Results suggest that the stability of the most internal emulsion determines the kinetics of inclusion and the stirring time required to induce inversion. However, it is the stability of both internal (w/O) and external (O/W) emulsions which determines the dispersed phase fraction at which the inversion is triggered. When different water fractions are used, the change of the critical dispersed phase fraction reveals that this process is affected by the partitioning of the surfactant mixture species between phases and results confirm that the critical dispersed phase fraction is a property related to the interfacial formulation of the system.

**CELIS M. T., GIL A., FORGIARNI A., GARCIA-RUBIO L. H.**

**Characterization of monomer emulsions in terms of droplet size and stability: Effect of emulsifier concentration.**

*J. Dispersion Science & Technology* **30**, 1384-1389 (2009)

**ABSTRACT:** In emulsification processes, the estimation of the droplet size distribution is important data, not only because they are linked with the manufacturer process, but also they are

important parameter affecting the emulsion stability. The aim of this research is to use the Uvvis transmission spectrum as a tool for emulsion characterization (droplet size and stability) as a function of monomer concentration, and the verification of emulsion stability using volume of separated phase's technique. Both techniques are applied to monomer emulsions as a function of emulsifier concentration. Results show correlations between droplet size measurements and stability of emulsions using spectroscopy technique and found to be in agreement with cleared volume method.

**AVENDAÑO J., CELIS M.T., SALAGER J.L., MERCADO R.**

**Adsorción de surfactantes catiónicos sobre arena en función de la carga superficial del sustrato y longitud de la cadena hidrocarbonada del surfactante** [Spanish]

*Ciencia e Ingeniería* **30**, 15-22 (2009)

**ABSTRACT: Cationic surfactants adsorption on sand as a function of the surface charge of the substrate and hydrocarbon tail length of the surfactant** The adsorption of a surfactant molecule in the solid-liquid interface can be represented by a model that includes three fundamental zones, the electrostatic concentration zone, the electrostatic-hydrophobic concentration zone and the hydrophobic concentration zone. The first zone is ruled by the surfactant-substratum interaction (adsorption process begins with a monolayer morphology), the third zone is influenced by the surfactant-surfactant interaction (superficial morphology is basically a totally formed bilayer or a tridimensional aggregate also known as hemimicelle) and the second zone represents a transition between both zones (monolayer stops forming and bilayer or the corresponding aggregate begins to form). This research studies the effects of the hydrocarbon tail length of the surfactant and the pre-treatment of the adsorbent (in order to modify its surface charge) in the adsorption of cationic surfactants on sand. The phenomenon is studied creating adsorption isotherms using the depletion method, and the residual concentration of surfactant in the solution was determined by optical methods. Results show the influence of treatment of the substratum in the adsorption process and also that the relation between the area per molecule of surfactant in the gas-liquid interface and the area per molecule of surfactant in the solid-liquid interface not only decreases as the hydrocarbon tail length of the surfactant increases but it is a quantitative measure of the type of aggregate that is formed in the surface.

**GONZALEZ A.M., BARRIOS F., RODRIGUEZ A., SALAGER J.L.**

**Espumabilidad y estabilidad de la espuma generada por el licor negro tratado por el reactivo de Fenton** (Spanish)

*Ciencia e Ingeniería* **30**, 41-46 (2009)

**ABSTRACT: Foamability and foam stability of black licors treated with Fenton's reagent.**

This report deals with the foaming capacity of black liquor (BL), and presents an evaluation of the foamability and foam persistence produced by using the Ross-Miles method. The BL is an effluent from the pulp and paper industry containing a high proportion of lignin as well as inorganic compounds, which should not be discharged into the environment. The BL used to produce foams was treated with a Fenton reagent (FR) containing an iron concentration ranging from 2.5 to 10 mM and a H<sub>2</sub>O<sub>2</sub> concentration of 500 mM. When the foams produced from BL, with and without FR treatment, were compared, it was found that the addition of FR increased both foam stability and foamability. Conductivity, pH, superficial tension, and phenol concentration were measured both before and after foaming at the top and bottom of the foam column. It was found that the FR treatment decreased the BL phenol concentration, which is an

interesting feature that helps in the reduction of pollutants. The BL samples that were FR treated and foamed exhibited a lower phenol concentration. Therefore, the combination of FR treatment with a foaming process can be used to decrease the concentration of phenolic derivatives and to reduce pollution.

**SALAGER J. L., FORGIARINI A., MARQUEZ L., TOLOSA L., VEJAR F.**

**Microemulsiones para la recuperación mejorada de crudo y para la limpieza de pozos.** [Spanish] *Ciencia e Ingeniería* **30**, 79-92 (2009)

**ABSTRACT: Microemulsions for enhanced oil recovery and well cleaning.** Microemulsions are monophasic systems in which water and oil are made compatible by an amphiphilic mixture that usually contains surfactant and alcohol. Unlike macroemulsions, microemulsions are thermodynamically stable and exhibit a low viscosity; they produce an ultralow interfacial tension with water and oil. They are used at low surfactant concentration in a three-phase microemulsion-water-oil slug process to mobilize oil. The low tension and low stability of formed emulsions allow for a very significant improvement in oil recovery. On the other hand, at a sufficiently high surfactant concentration, they are used as single phase well cleaner to increase permeability for injection and production, as well as in formation damage treatment. Recent studies indicate that the optimum formulation principle applies to both cases, in the former as the injected slug, and in the later when the injected pill mixes with the formation fluids containing emulsions or suspensions.

**SALAGER J.L., SCORZZA C., VELASQUEZ J., ARANDIA M.A., FORGIARINI A.M.**

**Inter and intramolecular amphiphilic mixtures as an optimum compromise to enhance solubilization in microemulsion. From Winsor model to recent advances with extended surfactants.**

*100th American oil Chemists' Society Annual Meeting*, Orlando FL May 3-6, 2009

**ABSTRACT:** The solubilization in microemulsion is maximum in a formulation scan when the interactions of the amphiphilic substances adsorbed at interface for the oil and water phases are exactly equilibrated. Improved solubilization performance could be attained by increasing both interactions. This could be reached first by increasing the size of both surfactant groups. However at some point a limit is attained when the surfactant precipitates. A second way to improve the solubilization performance is to use a mixture of amphiphiles, typically a hydrophilic and a lipophilic amphiphiles combination. This technique has also a limit because the more they are unbalanced, the more the mixture components tend to partition into the bulk phases instead of co-adsorbing at interface. The partitioning could be reduced by attaching the parts together, i.e. by forming an intramolecular mixture. This was the basic motivation to build up the so-called extended surfactant structures. Recent advances in the study of such structures are reported, showing that the optimization of their solubilization performance may be carried out by accumulating favorable features such as increasing balanced interactions and mixing slightly different species.

**BOURIAT P., RONDON M., LACHAISE J., SALAGER J.L.**

**Correlation between Interfacial Tension Bump and Optimal Crude Oil Dehydration**

*Energy & Fuels* **23** (8) 3998-4002 (2009)

**ABSTRACT.** In the presence of a large excess of asphaltenes in oil phase, an interfacial tension anomaly (a small bump of the order of 1 mN/m), is found to correspond to the optimum formulation where the fastest water-in-oil emulsion breaking is observed. This correspondence,

also observed elsewhere for other systems indicates that strong interaction should occur between asphaltenes and demulsifiers. Therefore, the optimum formulation would correspond to a situation where there is enough demulsifier to remove the asphaltenic interfacial gel by orogenic displacement, but not too much to cause adsorption of large asphaltenic/demulsifier complexes which would slow down emulsion drainage.

**RODRIGUEZ M.P., XUEREB C., BERTRAND J., SALAGER J.L.**

**Influence of process variables on the mechanism of emulsification by inversion,**

*8th World Congress in Chemical Engineering, Montreal, Canada August 23-27, 2009*

**ABSTRACT:** Phase inversion of an abnormal emulsion is a low energy process used to produce a fine emulsion with viscous oils. Provided that the formulation conditions are appropriate, the continuous addition of a phase into another under continuous stirring, would result in the formation of a so-called abnormal emulsion which would invert at some point into a normal and stable one. The mechanism of inversion may involve or not the formation of a transient multiple emulsion, an occurrence which is of paramount importance in practice. The present paper reports the influence of process variables such as the addition rate, stirring, and vessel volume, as well as formulation on the type of inversion mechanism.

**SALAGER J.L., RODRIGUEZ M.P.**

**Integrated process to transport heavy crude oil as an O/W emulsion: Recent Advances.**

*8th World Congress in Chemical Engineering, Montreal, Canada August 23-27, 2009*

**ABSTRACT:** The long distance transport of emulsified heavy crude oils has been shown to be a feasible alternative in the 1980's with the orimulsion project in western Venezuela, and may be an alternative in cold climate as in the peruvian Andes mountain range or in Canada plains. Most studies have been focussing on the O/W emulsion transport stage, though the overall process involves three stages, i.e. the emulsification, the O/W emulsion flow through a pipeline and the demulsification, which cannot be considered as independent issues. An integrated approach may be designed by fine-tuning formulation changes that provide property adjustments in each stage and allow to optimize the process as a whole.

**SALAGER J.L., VILLAREAL A., MARQUEZ L., FERNANDEZ C.**

**Nanoencapsulación en el sector higiene-salud.**

*Escuela franco-venezolana de nanotecnología, ENANO 2009, Caracas 2-6 de noviembre 2009*

**ABSTRACT:** La encapsulación es un tipo de acondicionamiento en el cual un producto activo se ubica en una partícula hecha de un material sólido por lo menos en su periferia y en general de forma esférica. La estructura sólida de la cápsula tiene tres propósitos, que pueden ser alternativos o simultáneos, los cuales se aplican a cualquier de las tres estructuras indicadas en la figura, y a cualquier tamaño, con calificativos como microcápsula (1-100  $\mu\text{m}$ ) o nanocápsula (50-1000 nm) : (1) inmovilizar o fijar el material activo, (2) proteger el producto activo o los auxiliares de formulación de una interacción desfavorable o degradante con el medio exterior, finalmente la distribución de la materia activa en el interior de una cápsula permite soltarla hacia el exterior en forma de un suministro controlado por difusión desde el corazón de la capsula y permeación a través de la pared. Las aplicaciones son extremadamente numerosas, y en los últimos 40 años han salido del orden de 10.000 artículos y 8.000 patentes en diversos campos como el químico y petroquímico, pigmentos para imprenta y pinturas, medio de almacenamiento de información, papel copia sensible a la presión, adhesivos, catalizadores, productos

fitosanitarios, alimentos y biotecnología, reacciones en microreactores, tratamientos enzimáticos, fermentaciones diversas etc

**PIZZINO A., MOLINIER V., CATTE M., SALAGER J.L., AUBRY J.M.**

**Bidimensional analysis of the phase behavior of a well-defined Surfactant (C10E4) / Oil (noctane) / Water – Temperature system.**

*J. Physical Chemistry B* **113**: 16142-16150 (2009)

**ABSTRACT:** The equilibrium phase behavior of the well-defined system tetraethyleneglycol decyl ether (C10E4) / *n*-octane / water (SOW) at variable temperature (T) was revisited by careful analysis of the three bidimensional cuts, namely the gamma  $\gamma$  (at constant water-oil ratio), khi  $\chi$  (at constant surfactant concentration) and delta  $\Delta$  (at constant temperature) plots. A straightforward methodology is reported to determine the frontiers of the triphasic (Winsor III) domain on any cut of the SOW-T phase prism. It comes from the systematic analysis of another cut, here  $\gamma$  at different water-oil ratios and  $\chi$  at different surfactant concentrations from the knowledge of D cuts at different temperatures. The method has been validated through comparison with experimental results. It enables to show, for the first time, the evolution of a SOW system three-phase body contours with (i) water-oil ratio, (ii) surfactant concentration and (iii) temperature. It exhibits a strong impact of the surfactant affinity for the pure oil and water phases on the shape of the phase diagrams. The systematic study of the effect of the surfactant concentration on the aspect of the  $\chi$  plot sheds light on an unusual shape found at low surfactant concentration.

**DELGADO J. G., MERCADO R.,**

**Balances de masa y energía simplificados, aplicados a un proceso de craqueo catalítico del petróleo [in Spanish]**

*Educación Química* **4**, 455-459 (2009)

**ABSTRACT: Mass and Energy Simplified Balances Applied to a Petroleum Catalytic Cracking Process.** The most important economic activity in Venezuela is the Petroleum's Industry. Likewise, Venezuela constitutes a high technology refining processes country, and therefore, it has facilities that should be assisted and optimized by human resources with solid technical basis. Fluid Catalytic Cracking was taken as a study case. The main processes and unit operations involved were identified, as well as feeds and products streams. By applying mass and energy conservation principles, it was possible to determine caloric requirements and products distribution.

**FORGIARINI A., PIETRANGELI G., ARANDIA M. A., GUEDEZ V., CELIS M. T., SALAGER J. L., MARQUEZ L.**

**Influencia del tipo de alcohol sobre la formación de nanoemulsiones de aceite de soya-en-agua.**

*Ciencia e Ingeniería* **30** In Press (2009)

**ABSTRACT:** Las emulsiones son mezclas de dos líquidos inmiscibles, uno de ellos disperso en forma de gotas en el otro líquido que forma la fase continua. Cuando el tamaño de gota de las emulsiones está comprendido entre 20 y 500 nm, suelen denominarse nano-, mini-emulsiones o emulsiones submicrométricas. Se han propuesto diversos métodos para preparar nanoemulsiones entre los cuales se encuentran los métodos de inversión transicional (a composición fija) denominado método de temperatura de inversión de fases (PIT), comúnmente usados en sistemas

formulados con surfactantes no-iónicos del tipo etoxilado. En general, y en particular con otros tipos de surfactantes, la inversión transicional puede ser efectuada con un cambio de cualquier otra variable de formulación como la salinidad de la fase acuosa, la hidrofiliicidad de la mezcla surfactante o el efecto del co-surfactante (efecto del alcohol). La influencia del alcohol en la formulación de microemulsiones, sistemas termodinámicamente estables, ha sido extensamente descrita, sin embargo, el efecto de los alcoholes en la formación de las nanoemulsiones no ha sido considerada en estudios sistemáticos. El objetivo de este estudio es mostrar la influencia del tipo y cantidad de alcohol sobre el tamaño de gota de emulsiones de aceite de soja-en-agua obtenidas con mezclas de surfactantes no-iónicos utilizando un método de baja energía. Las emulsiones fueron producidas mediante dilución con agua de sistemas agua/surfactante/aceite de soja, es decir, por el cambio de la relación agua/aceite a temperatura constante. El tamaño de gota y estabilidad de las nanoemulsiones se han relacionado con el tipo de alcohol y la existencia de mesofases de cristal líquido durante el proceso de emulsión.

**CELIS M. T., CALDERON J., MANCHEGO L., AVENDAÑO J., SALAGER J. L.**

**Inversión de emulsiones incluyendo acrilatos en la formulación (in Spanish)**

*Ciencia e Ingeniería* **30** in Press (2009)

**ABSTRACT:** El efecto de la viscosidad de la fase acuosa sobre el comportamiento de fase y la línea de inversión estándar han sido estudiados en sistemas al equilibrio, así como la inversión catastrófica en régimen dinámico, en la dirección anormal normal ( $C+ \rightarrow A+$  y  $B- \rightarrow A-$ ), para los sistemas formados por dodecil benceno sulfonato de sodio (DBSS)-dodecil sulfato de sodio (DSS)-agua-querosén-pentanol. El cambio de la viscosidad de la fase acuosa se produce por la adición de poliacrilato (textilan 567) a las soluciones acuosas, a las cuales se les ajusta el pH por adición de hidróxido de amonio. Los resultados indican que la adición de poliacrilato altera la formulación, la cual da lugar a la variación en el comportamiento de fase y en la inversión estándar. Un aumento de la viscosidad de la fase acuosa produce un desplazamiento de la rama catastrófica (zona B-/A-) de la línea de inversión estándar, lo que reduce la zona de emulsiones O/W. Adicionalmente, el aumento de la viscosidad de la fase acuosa en un proceso de inversión dinámica, ocasiona el desplazamiento de la línea de inversión B-/A- hacia porcentajes de agua superiores, y el de la frontera C+/A+ hacia porcentajes menores de agua

**MARFISI S., ALVAREZ G., PARUTA E., MORENO P., ANTON R., SALAGER J. L.**

**Deshidratador electrostático de Laboratorio para probar formulaciones desemulsionantes. Mecanismo de electrocoalescencia [in Spanish]**

*Ciencia e Ingeniería* **30**: 229-236 (2009)

**ABSTRACT: Laboratory Electrostatic Dehydrator for Testing Demulsifier Formulations.**

An electrostatic dehydrator laboratory equipment was designed and built to test in a systematic way demulsifier formulations used to break up water-in-crude emulsions at the well head in order to reach the commercial 1 % BSW specifications in petroleum trade. The piece of equipment may be used to test chemical treatment formulations in refinery operations like the desalting of heavy oil cuts. The apparatus principle is to promote a downward flow of water as a coalesced film on the electrode surface, therefore resulting in a quick separation of the water, in a time much shorter than in the droplet settling mechanism in the conventional bottle test.

**URBINA-VILLALBA G., FORGIARINI A., RAHN K., LOZSAN A.**

**Influence of flocculation and coalescence on the evolution of the average radius of an O/W emulsion. Is a linear slope of  $R^3$  vs.  $t$  an unmistakable signature of Ostwald ripening?**

*Physical Chemistry Chemical Physics* **11**: 11184–11195 (2009)

**ABSTRACT:** The LSW theory of Ostwald ripening, predicts a linear variation of the cube of the average radius of a dispersion as a function of time ( $R^3$  vs.  $t$ ) [I. M. Lifshitz, V. V. Slyozov, J. Phys. Chem. Solids, 1961, 19, 35–50; C. Wagner, Z. Elektrochem., 1961, 65, 581–591]. It also envisages a left-skewed drop-size distribution with a cut-off radius of  $1.5 \cdot R$ . Consequently, non-linear changes of  $R^3$  vs.  $t$  are usually ascribed to either a transient period of time (previous to the attainment of the asymptotic limit of ripening) or other destabilisation processes. Up to now the effect of Brownian motion on Ostwald ripening (OR) has not been considered, although it is by far the strongest limitation of the LSW theory. In this work we show the results of incorporating the algorithm of De Smet et al. for Ostwald ripening simulations [Y. De Smet, L. Deriemaeker, R. Finsy, Langmuir, 1997, 13, 6884–6888] to our emulsion stability simulations (ESS) code. In particular, the short-time evolution of a dilute dodecane/water nanoemulsion in the absence of stabilisers is studied. At high ionic strength, the simulations suggest that  $R^3$  can change linearly with time during the transient period of Ostwald ripening, due to the flocculation and the coalescence of the drops. This behavior is confirmed by the experiments for  $t < 100$  s. At low ionic strength a concave downward curve is observed, both theoretically and experimentally.

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