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**2010 PUBLICATIONS AND COMMUNICATIONS  
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**SCORZZA C., NIEVES J., VEJAR F., BULLON J.**

**Synthesis and physicochemical characterization of anionic surfactants derived from Cashew Nut Shell Oil.**

*J. Surfactants and Detergents* **13**: 27-31 (2010)

**ABSTRACT:** Carboxylate derivatives of cardanol and anacardic acids, which are the main phenolic components of cashew nut shell oil are prepared and tested as anionic surfactants. They lower the surface tension, exhibit a critical micelle concentration, and produce microemulsions in mixtures with dodecyl sulfate. The value of their characteristic parameters in the hydrophilic lipophilic deviation (HLD) scale attained by the unidimensional formulation scan method typify them as hydrophilic surfactants.

**VELASQUEZ J, SCORZZA C, VEJAR F, FORGIARINI A, ANTON RE, SALAGER JL**

**Effect of the temperature and other variables on the optimum formulation of anionic extended surfactants-alkane-brine systems.**

*J. Surfactants and Detergents* **13**: 69-73 (2010)

**ABSTRACT:** Anionic extended surfactants of the alkyl polypropyleneoxide sulfate type are found to obey the linear correlation  $\ln S = k \text{ ACN}$  for optimum formulation (three-phase behavior) of ionic surfactant-oil-water systems, with a k value essentially the same as for n-alkyl sulfates. The addition of n-pentanol produces a shift in optimum formulation without significant change in k. An increase in temperature is found to produce a decrease in surfactant hydrophilicity, which is opposite to the expected behavior of anionic species. This trend, which reminds nonionic surfactant behavior, is probably due to the partial hydration of the very first propyleneoxide units which are located close to the anionic head group.

**ARANDIA M. A., FORGIARINI A. M., SALAGER J.L.**

**Resolving an enhanced oil recovery challenge: Optimum formulation of a surfactant-oil-water system made insensitive to dilution.**

*J. Surfactants Detergents* **13**: 119-126 (2010)

**ABSTRACT:** Upon dilution by the petroleum reservoir connate water, the anionic commercial surfactant blend often used in enhanced oil recovery by low tension, becomes more lipophilic at interface because of the so-called selective partitioning. Hence, the optimum formulation is not maintained when the injected slug moves through the reservoir. An opposite variation is found for ethoxyxylated nonionic surfactant systems. As a consequence of these antagonistic influences, the optimum formulation shift produced by dilution may be eliminated by using an appropriate mixture of anionic and nonionic commercial surfactants, so that the 2 effects exactly cancel out.

**ZERPA L.E., SALAGER J.L., KOH C.A., SLOAN E.D., SUM A.K.**

**Surface chemistry and gas hydrates in flow assurance.**

*Industrial and Engineering Chemistry Research*. **49** In press (2010) DOI: [10.1021/ie100873k](https://doi.org/10.1021/ie100873k)

**ABSTRACT:** A review of surface chemistry concepts is presented, with the principal objective of identifying interfacial phenomena and surface chemistry interactions involved in gas hydrate formation and agglomeration in oil and gas pipelines. There are five types of interfaces where gas hydrates may form and aggregate: gas/liquid, liquid/liquid, gas/solid, liquid/solid, and solid/solid; where the gas is the hydrocarbon gas, liquid is either oil, water or condensate, and solid is either gas hydrate or the pipe wall surface. A review of fundamental interfacial concepts can help create a better understanding of phenomena at these interfaces, and can help industry move from hydrate prevention to risk management. Two areas of surface chemistry have been selected to illustrate the concepts and mechanisms associated with these systems: surfactants and emulsions. Examples from the literature pertaining to gas hydrates are presented for each system

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

**Influence of the mixed propoxy/ethoxy spacer arrangement order and of the ionic head group nature on the adsorption and aggregation of extended surfactants.**

*J Surfactants and Detergents* **13**: 451-458 (2010)

**ABSTRACT:** Two families of extended surfactants are prepared with the same head groups (carboxylate, sulfate, disodium phosphate) and different intermediate spacer structures. In one there are an average of 7 propylene oxide groups on the side of the tail and an average of 7 ethylene oxide groups on the side of the head, to produce a sequence of two different polarity segments. In the other case the spacer contains the same average numbers of propylene and ethylene oxide groups but in some homogeneous arrangement. The intermediate spacer structure without ionic head group, and in the cases of the carboxylate and sulfate extended surfactants, has a packing density reduction which is associated to the homogeneously alkoxide arrangement in the spacer. Such arrangement is found to produce about 20 % more surface area at interface, apparently because it results in some plumpness due to the spacer folding to remain close to interface. Both the critical micelle concentration and occupied interfacial area of the extended surfactant increase with the ionization of the anionic group associated to the electrostatic repulsion effect.

**PEREIRA J. C., DELGADO-LINARES J. G., BRIONES A., GUEVARA M., SCORZZA C., SALAGER J.L.**

**Effect of solvent nature and dispersant performance on asphaltene precipitation from diluted solutions of unstable crude oil.**

*Petroleum Science and Technology* In press (2010)

**ABSTRACT :** The asphaltene precipitation kinetics was studied on El Furrial crude oil from western Venezuela, which is known to exhibit serious problems. A Turbiscan backscattering apparatus was used to evaluate the precipitation of asphaltenes with different solvents. The transmittance variation with time is studied as the crude is diluted with heptane, pentane and cyclohexane. Alkane containing systems exhibit a two stage behavior, whereas only one is found when diluting with cyclohexane. Dispersing agents were tested by using the precipitate height as a criterion of effectiveness. Results are reported for ethoxylated nonylphenols, toluene parasulfonic acid, and a commercial dispersant.

**CELIS M.T., FORGIARINI A.M., MARQUEZ L., GARCIA-RUBIO L.H.**

**Characterization of nano-dispersions**

Invited lecture - *Particles 2010*, Orlando FL USA, May 13-19, 2010

**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 method take place with minimum stirring, and produce the nanodispersions 20-500 nm range almost spontaneously, thus it has a considerable potential for practical applications, i.e., these fine emulsions may be used for encapsulation of oil-soluble bioactives, in skin care products and as colloidal drug carriers for pharmaceutical applications. The information contained in the UV-vis spectrum on scattering properties of the fine emulsions together with the optical properties of the dispersed phase lead to the interpretation of the spectra in terms of the droplet size and the distribution of this emulsified systems. This research reports on a technique to monitoring the droplet size distribution of the nanoemulsions using spectroscopy. This particle characterization methodology is based on a sampling and dilution strategy combined with spectroscopy methods. It is shown that the sampling system integrated with a multiwavelength turbidity detector provides reliable information on droplet population. The spectra quantitative interpretation is performed in the spectral range (300 -820 nm) leading to reliable estimated of droplet size populations in the nanosize range. It is shown analyzes of nanoemulsions on transmission spectrum as a function of the oil concentration and the HLB value of the emulsifier, on the droplet size and distribution, and stability of the oil-in-water (O/W) emulsions attained by the phase inversion method.

**SALAGER J.L., FORGIARINI A.M., SCORZZA C., TOLOSA L.I., VELASQUEZ J., ACOSTA E.**

**Extented surfactants – A fine tuned structure to improve interfacial performance.**

Presented in the *101<sup>th</sup> AOCS Annual Meeting*, Phoenix, May 16-19, 2010

**ABSTRACT:** Conventional surfactants exhibit well defined polar and apolar portions. The mixing of different surfactant species, as well as the introduction of additives like cosurfactants and linkers, allows to improve the performance as far as microemulsion solubilization and interfacial tension are concerned. However, such mixed components often fractionate, i.e., they partition between phases and interface in different ways; as a consequence, a hard-to-find optimum interfacial formulation is no longer insured when the surfactant concentration or water-oil ratio change, which is a very common occurrence in practice from laundry to enhanced oil recovery. Fastening together the mixture components in a single molecule that produces the same effect with no fractionation drawback, has been one of the goals of the so-called extended surfactant structure, which contains an intermediate polarity spacer between the head and tail groups. Recent investigations on different types and different applications such as detergency, cosmetics or crude demulsifying, indicate that these surfactants are likely to be particularly performant with problematical oils like high MW paraffin, triglycerides or asphaltenic crudes. Emerging trends are analyzed to correlate the structure to the properties and to guess about the next generation

**VILLAREAL A. M., FERNANDEZ C., FORGIARINI A., MARQUEZ L., NIELLOUD F., SALAGER J.L.**

**Nanoencapsulation de filtres solaires via nanoémulsions.**

*Cahier de Formulation volume 15* “Procédés et formulation au service de la santé” [in French].

Chap. 14. EDP Sciences, Paris. [In press](#) (2010)

**ABSTRACT:** Nanocapsules are mproduced by a sequence of processes involving a phase transition and a chemical reaction. The starting system is an inverse micellar solution of surfactant in an oil phase which, when contacted with water, becomes a lamellar liquid crystal. When more water is added to produce a two-phase system, the liquid crystal stabilizes the formed O/W nanoemulsion. The pH of the aqueous phase is then shifted to promote the a polimerization reaction at the drop surface to generate the capsule wall. An example of this sol-gel process is described, e.g. the encapsulation of sunscreen substances.

**SALAGER J.L., BULLON J., PIZZINO A., RONDON-GONZALEZ M., TOLOSA L.**

[Emulsion formulation engineering for the practitioner.](#)

*Encyclopedia of Surface and Colloid Science*, 1:1, 1-6. P. Somasundaran Ed., Taylor & Francis.

**ABSTRACT:** The formulation and formation of emulsions imply a very large number of variables, hence attaining the sought properties is usually long and tedious because of the large number of experiments to be carried out. The current state-of-the-art on physico-chemical formulation may be thoroughly used to considerably reduce the number of required experiments and to indicate to the formulator the relation between the kind of properties to expect and the generalized formulation expression. After this first order formulation factors selection is carried out, several second order factors are shown to be available to adjust the emulsion properties upward or downward in order to satisfy the specifications, either directly or by mean of a multistep process.

**CELIS MT., FORGIARINI A., MARQUEZ L., GARCIA-RUBIO L.H.,**

[Influence of formulation on characterization of emulsions from transmission spectra.](#)

Paper 129, *5<sup>th</sup> World Congress on Emulsion*, Lyon-France October 12-14, 2010.

**ABSTRACT:** An emulsion is a heterogeneous system containing two liquid phases, one of which is fragmented in the form of droplets. The estimation of the droplet size and droplet size distribution is important data, not only because they are linked with the manufacturer process, but also they give valuable information on the properties of the liquid-liquid systems. The information contained in the UV-Vis spectrum on the scattering properties of the emulsions lead to the interpretation of the spectra in terms of the particle size distribution. The quantitative interpretation of the transmission spectrum is performed in the spectral range (300 -820 nm) leading to reliable estimated of droplet size populations in the range of 1- 20  $\mu\text{m}$  as function of the oil concentration. The aims of this research is to demonstrate the potential of spectroscopy as a tool for characterization of emulsions in terms of droplet size and droplet size distribution, based in measurements of droplet populations as a function of oil concentration. These measurements are applied to emulsions originated of emulsifier/water/ monomer systems as a function of physicochemical variables, such as, nature and emulsifier concentration, and type of monomer. Results show the relation between formulation variables and properties of the emulsions from a single multiwavelength measured. It makes UV-Vis spectroscopy a powerful tool for characterization of dispersed systems.

**DELGADO J.G., NOIK C., DALMAZZONE C., SALAGER J.L.**

[Electrical destabilization of petroleum emulsion.](#)

Paper 206. *5<sup>th</sup> World Congress on Emulsion*, Lyon-France October 12-14, 2010.

**ABSTRACT:** The present study focused on the level of stability of emulsion formed with one

crude oil containing at least 15% weight of surfactant material as asphaltenes. Asphaltene is the most polar part of molecules issued from oil precipitation, insoluble in aliphatic solvent. Gravity effect on emulsion stability was firstly analysed through classical bottle tests varying the dilution ratio of oil. Addition of cyclo-hexane solvent induces asphaltene aggregation and consequently modifies the interfacial properties. Relations between emulsion stability and interfacial tension are evidenced. Electrical stress is then studied using an electrical stability tester (EST) apparatus and determining the Critical Electrical Field (CEF). Tests performed on water-in-oil emulsion allow to follow the decrease of the critical voltage recorded at a fixed intensity which corresponds to the short-circuiting condition of the apparatus. Synergy is observed between electrical stress effect and action of added surfactant on the water droplet coalescence and consequently on emulsion destabilisation. Finally, direct observation of coalescence mechanism was performed through a microscopic visualisation on a dedicated cell where an electrical field is fixed. The droplets line up following the current intensity line was clearly evidenced before coalescence.

**MARQUEZ L. COMPANY R., ONTIVEROS F., GONZALEZ J.C., NOBOA G., CELIS M.T., FORGIARINI A.**

**Effects of formulation on emulsion drop size in the vicinity of three phase behavior of surfactant-oil-water systems**

Paper 061, *5<sup>th</sup> World Congress on Emulsion*, Lyon-France October 12-14, 2010.

**ABSTRACT:** Near the so-called optimum formulation (HLD = 0), approaching the Winsor III phase behavior, on one hand, the interfacial tension of surfactant-oil-water systems decreases, thus allowing the generation of smaller drops upon stirring; on the other hand, the coalescence rate increases, thus favoring the formation of larger drops. Both opposite effects acting together result in a minimum droplet size. Such a minimum drop size is found on both sides (for O/W and W/O emulsions) of optimum formulation, whatever the variable used to produce the scan. The emulsion stability, and the location of these minima which correspond to the most efficient use of the stirring energy to make small droplets, depends on the formulation (change in HLD) and the alcohol molecule. Under certain formulation-agitation conditions, there is a first minimum for low interfacial tension regions and a second minimum for zones of high stability.

**MARQUEZ R., FORGIARINI A., VEGA K., BRICEÑO M.I., MARQUEZ L., SALAGER J.L.** **Relationship between rheological behavior and the type of formed mesophase when preparing nanoemulsions.**

Paper 153, *5<sup>th</sup> World Congress on Emulsion*, Lyon-France October 12-14, 2010.

**ABSTRACT:** Nanoemulsions are dispersed systems with a droplet size smaller than 100 nm. They are found in a wide range of applications, among them in cosmetics and pharmaceutical products. Their preparation requires the generation of a large interfacial area, which is attained by making use of the current know-how in physicochemical formulation of water/oil/surfactant systems. Water-Paraffin emulsions with Tween 80/Span 20 mixture at HLB = 12 and an initial oil-surfactant ratio of 75/25 were obtained by the Dilution Phase Inversion Method, which consists in adding water to the oil-surfactant mixture and then diluting the mesophase formed in water. The final emulsions contained 5 wt.% of the surfactant mixture, 15 wt.% paraffin oil and 80 wt.% of water. This preparation of nanoemulsions has been related to the formation of a liquid crystal phase during the water addition. Rheological behavior and conductivity of the formed mesophases were measured as well as the corresponding emulsion droplet size. These

properties were monitored during mixing, beginning with the initial mesophase formation, in order to evaluate the time dependency of the emulsification process. Measurements of storage module  $G'$  and loss module  $G''$  of mesophases composed by 10 to 40 % of water were related to the droplet size at the end of the emulsification process and the type of mesophase formed at equilibrium. A relationship was found between the non-equilibrium rheological behavior and the type of mesophase formed at equilibrium and its effect on emulsions droplet size, resulting from the equilibrium dynamics during nanoemulsification.

**MERCADO R., SADTLER V., MARCHAL P., CHOPLIN L., SALAGER J.L.**

**Rheological study of the breaking of a cationic oil-in-water emulsion on Fontainebleau sandstone.**

Paper 167. 5<sup>th</sup> World Congress on Emulsion, Lyon-France October 12-14, 2010.

**ABSTRACT:** To optimize and control the road making processes, the physicochemical phenomena that occur during the breaking of a cationic oil-in-water emulsion by the addition of a negative-charged-surface solid are followed by rheological measurements. A model emulsion, with average droplet size of 15-20 microns, is prepared by dispersion of paraffin oil in cetylpyridinium chloride (CPC) aqueous solution. The results show that the oil fraction decreases after each addition of Fontainebleau's sandstone aliquots. As the droplets size and distribution remain constant during the process, we conclude that the emulsion heteroflocculation is the result of oil droplet adsorption on the sand surface, followed by the coalescence of the oil droplets around the sand particles.

**FORGIARINI A., CELIS M.T, MARQUEZ L., SALAGER J.L.,**

**Properties of emulsions obtained with extended surfactants.**

Paper 147. 5<sup>th</sup> World Congress on Emulsion, Lyon-France October 12-14, 2010.

**ABSTRACT:** New extended nonionic surfactants, C12(PO)14(EO)<sub>n</sub> where  $n = 7, 12$  and  $20$  were investigated as stabilizers for *n*-alkanes/water and soybean-oil/water emulsions. These are nontoxic substances current investigations on different applications such as detergency, cosmetics or crude demulsifying, indicate that extended surfactants could be used to formulate micro or emulsion containing problematical oils like high MW paraffin, triglycerides or asphaltenic crudes. In this work was found that the droplet size of O/W emulsions depends on the ACN of *n*-paraffin as well as the hydrophilicity of the extended molecule, i.e when the extended surfactant was more hydrophilic, the minimum drop size was obtained for smaller values of ACN of *n*-alkanes. Extended surfactant formed soybean oil-in-water emulsion with small droplet sizes and high kinetic stability. Multiwavelength spectroscopy technique was applied for determination of the average diameter of the droplets.

**GAFANHAO M., IGLESIAS E., DELGADO J.G.**

**Determinación del punto de precipitación de los asfaltenos en crudos venezolanos** [in Spanish] *Ciencia e Ingeniería* **31** In press (2010)

**ABSTRACT: Determination of precipitation point of asphaltenes in venezuelan crudes oils.**

The flocculation point of asphaltenes in Furial and Carabobo crudes are compared, by measurements with the spot method, and by conductimetry and rheometry, which give very consistent results, although the spot method is the simplest one to carry out. The flocculation is attained with the Furial crude with 80% *n*-heptane, whereas it is with 77% for Carabobo crude.

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

**Volumetría de determinación espectrofotométrica de un surfactante catiónico tipo diamina, mediante la formación de un complejo coloreado.** [in Spanish]

*Ciencia e Ingeniería* **31** In press (2010)

**ABSTRACT: A Spectrophotometric Method to Determine a Cationic Surfactant of the Alkyl Propylen Diamine Type, via the Formation of a Colored Complex.** A simple, quick and accurate method is reported to quantitatively determine the concentration of a cationic surfactant of the alkyl propylen diamine type, which does not exhibit a chromophoric group and thus cannot be directly detected by photometry. Methyl orange is used as a chromogenic reagent to produce a derivative containing two methyl orange molecules per alkylamine molecule, that absorbs in the UV-Vis range. The absorbance variation versus the amine/methyl orange ratio allows the determination of the end point. Detection limits for alkyl amine range from  $2 \times 10^{-5}$  M to  $3 \times 10^{-4}$  M.

**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 (2010)

**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

**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) [in Spanish]

**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.

*Updated November 30, 2010*