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CELIS M. T., GARCIA-RUBIO L.

Characterization of Emulsions: A Systematic Spectroscopic Study.

J. Dispersion Science & Technology **29**, 20-26 (2008)

ABSTRACT: Emulsification processes results in the generation of droplets populations produced from the dynamic equilibrium between the breakup and coalescence phenomena determined primarily by the formulation and composition variables, mixing characteristics and emulsion preparation. The information contained in the UV-Vis spectrum on the absorption and scattering properties of the emulsions lead to the interpretation of the spectra in terms of the particle size distribution, the particle shape and the chemical composition of the oil and emulsifier. This paper reports analyzes of emulsions on transmission spectrum as function of the oil concentration and physicochemical variables. The quantitative interpretation of the transmission spectrum is performed in the portion where no absorption is present (300-820 nm) leading to reliable estimated of droplet size populations in the range of 1- 20 μm . The possibility of obtaining information from a single multiwavelength measurement makes UV-Vis spectroscopy a powerful tool for characterization of dispersed systems

RONDON M., PEREIRA J., BOURIAT P., GRACIAA A., LACHAISE J., SALAGER J. L.

Breaking of water-in-crude oil emulsions. 2: Influence of asphaltene concentration and diluent nature on demulsifier action.

Energy & Fuels **22**, 702-707 (2008)

ABSTRACT: The stability of water-in-oil emulsions formed during oil slicks or petroleum production operations is insured by natural surfactant molecules (principally asphaltenes) that are present in the crude oil. These persistent emulsions may be broken by adding a suitable demulsifier at the proper concentration to attain a so-called optimum formulation at which the stability of emulsion is minimum. In this report the concentration of asphaltenes is varied by diluting the crude oil with a solvent such as cyclohexane, toluene or mixtures of them. The experimental evidence shows that there exists some critical asphaltene concentration at which the interfacial zone seems to be saturated. Beyond this threshold, the demulsifier concentration necessary to attain the emulsion quickest breaking is constant. Below it, the optimum demulsifier concentration is found to be proportional to the asphaltene concentration. The map of emulsion stability versus asphaltene and demulsifier concentrations exhibits a typical pattern for different demulsifiers and diluents, which contribute to improve the interpretation of the demulsifying action.

RONDON-GONZALEZ M., SADTLER V., MARCHAL P., CHOPLIN L., SALAGER J.
Emulsion Catastrophic Inversion from Abnormal to Normal Morphology. 7. Emulsion evolution produced by Continuous Stirring to generate a very HIPR emulsion.

Industrial and Engineering Chemistry Research **47**, 2314-2319 (2008)

ABSTRACT: When emulsion inversion is produced by continuous stirring, from an abnormal water-in-oil-in-water (w/O/W) system to a normal water-in-oil (W/O) morphology, to create a very high internal phase ratio emulsion (water fraction $f_w > 0.85$), the main mechanism is the continuous inclusion of the initial W external phase as w droplets into the dispersed O drops, which results in an increase of the dispersed (w+O) volume. Once a critical dispersed volume fraction is reached and a local inversion is detected, an additional stirring time, referred as “propagation time”, is required in order to complete the inversion of the system into a W/O morphology, instead of the usual behavior which is an almost instant culmination. This time is related to the energy input necessary to overcome the Laplace pressure involved in the change of the interfacial curvature. The present work shows how this propagation time is affected by the formulation, the composition and the stirring conditions.

MARQUEZ R., BULLON J., MARQUEZ L., CARDENAS A, BRICEÑO M. I., FORGIARINI A.

Rheological changes of parenteral emulsions during phase-inversion emulsification.

J. Dispersion Science and Technology **29**, 621-627 (2008)

ABSTRACT: An efficient emulsification procedure for parenteral soybean oil-in-water, based on current know-how on transitional inversion, was investigated. A fine droplet size lipid emulsion was produced using much lower mechanical energy than the typical industrial process. The aqueous phase was added gradually during mixing and various rates of water addition, as well as surfactant concentration, were evaluated. It was found that as addition rate and surfactant content increased, flow behavior changed significantly at intermediate water content, becoming highly viscoelastic. This behavior was related to the formation of a liquid crystalline phase that, at later mixing stages, turned into small droplets.

ANTON R.E., ANDEREZ J. M., BRACHO C., VEJAR F., SALAGER J. L.

Practical surfactant mixing rules based on the attainment of microemulsion-oil-water three-phase behavior systems.

In *Interfacial Processes, Phenomena and Molecular Aggregation*. R. Narayanan Ed., *Advances Polymer Science*, vol. **218** : 83-113 (2008) Springer-Verlag, Berlin

ABSTRACT: Surfactant mixtures are generally used to fine tune formulations to an exact property value such as its hydrophilicity. To do so a precise characterization method has to be used. The presented technique consists in the attainment of a microemulsion-oil-water Winsor III three phase behavior in a reference system. It allows to classify surfactants in a hydrophilicity scale with an accuracy equivalent to 0.1 HLB unit. The characterization method is applied in different ways to an unknown surfactant and to mixtures of two base surfactants, and it is used to test the ideality of the mixing rule expression which is equivalent to a linear variation of the characteristic parameter versus the mixture composition. Conditions for linearity of the mixing rule are discussed. The selective partitioning of different species results in non-linear mixing rules whose detection is discussed according to the aspect of the three-phase region in different diagrams. Typical mixing rules for pH sensitive systems containing fatty acids and fatty amines are shown. Anionic-nonionic mixtures are found to exhibit a slight deviation from ideality.

Antagonistic anionic- cationic mixture is shown to be linearized by introducing a virtual catanionic specie.

BRAVO B., SANCHEZ J., CACERES A., CHAVEZ G., YSAMBERTT F., MARQUEZ N., JAIMES M., BRICEÑO M. I., SALAGER J. L.

Partitioning of fatty acids between oil and water.

J. Surfactants & Detergents **11**: 13-19 (2008)

ABSTRACT: Surfactant/oil/water systems in which the surface active substance is a mixture of an undissociated fatty acid (FA) and its sodium salt soap, exhibit the typical phase behavior and the general emulsion phenomenology produced by a formulation scan. The phase behavior transition is induced by changing the FA concentration in the system at a fixed alkaline (NaOH) content in water, which results in a variable lipophilic acid / hydrophilic salt ratio. The partitioning is reported for different FA types (octanoic to myristic) and alcohol co-surfactants between excess oil and water phases of Winsor three-phase optimum formulation system. The concentrations are determined by using a method reported in a previous work to quantify the total acid fraction in each phase.

SALAGER J. L., CHOPLIN L.

Mousses: Formulation et Propriétés (In French)

Techniques de l'Ingénieur, Vol. Génie des Procédés. **J2-200**: 1-14 (2008)

ABSTRACT: Foams: Formation, Formulation and Properties. Importance and characteristics of foams. Stage in a foam life: formation, ripening and collapse. Associated mechanisms. Methods to study foams. Effect of the physicochemical formulation of foam properties. Selection of surfactants and additives to boost foaminess and foam stability. Rheology of foams, characteristics and methods.

ROJAS O., BULLON J., YSAMBERTT F., SALAGER J. L.

Renewable surface-active polymers.

235th American Chemical Society National Meeting, New Orleans LA, April 6-10, 2008

ABSTRACT: We report on the use of lignins as polymeric amphiphiles for the stabilization of emulsions. Lignins' phase behavior in oil/water systems is presented and explained in terms of their mol. affinities under the framework of the Surfactant Affinity Difference (SAD). Emulsions with various oils (including crude oils) were formulated and their properties were rationalized in terms of the phase behavior of the SOW system. Lignin affinities were correlated as a function of the nature of the mol. and other formulation variables, including EACN, pH, and salinity of the aq. phase. It is concluded that lignins are effective emulsion stabilizer; the resulting emulsions behave according to the SAD theory and lignin-based emulsions can be tailored to meet specific emulsion property demands

SALAGER J. L., FORGIARINI A., SCORZZA C., ROJAS O.

Extended surfactants: a friendly way to solubilize natural oils.

235th American Chemical Society National Meeting, New Orleans LA, April 6-10, 2008

ABSTRACT: The solubilization of polar oils in microemulsions could be considerably enhanced by using so-called extended surfactants which contain a slightly polar but mainly lipophilic spacer arm between the conventional hydrophilic head and lipophilic tail. Provided that the spacer arm is adjusted to play a lipophilic linker role, these molecules are able to cosolubilize 20-

25 times their weight of water and polar oil. The first generation of alkyl polypropyleneoxide sulfate species allowed to deduce the main characteristics of these surfactants, particularly the effect of the spacer arm length on the solubilization of different kinds of oil such as ethyl oleate, natural and synthetic triglycerides and long alkanes. Other head groups such as C6 and C5 sugar, carboxylate and combined heads with several groups, linked with fatty ester tails, exhibit similar properties with more friendly attributes for detergency, biological and health care applications

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

Characterization of dispersed systems using multiwavelength transmission measurements.

Invited lecture. *Particles 2008*, Orlando FL. June 10-13, 2008

ABSTRACT: The stirring of a dispersed system result in the production of droplet/particle populations, generated from the dynamic equilibrium between the breakup and coalescence phenomena during the process, and determined primarily by the formulation and composition variables, mixing characteristics and system preparation. The estimation of the droplet/particle size and droplet/particle 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 stability of the dispersion.. The information contained in the UV-Vis spectrum on the absorption and scattering properties of the emulsions lead to the interpretation of the spectra in terms of the particle size distribution, the particle shape and the chemical composition of the oil and emulsifier. The aims of this research is on analyzes of dispersed systems (i.e. macroemulsions, nanoemulsions, polymers, and suspensions), on transmission spectrum as function of the dispersed phase concentration and physicochemical variables. The quantitative interpretation of the transmission spectrum is performed in the portion where no absorption is present (300-820 nm) leading to reliable estimated of particle size populations in the range of 0.02- 20 μ m. 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 possibility of obtaining information from a single multiwavelength measurement makes UV-Vis spectroscopy a powerful tool for characterization of dispersed systems.

CELIS M. T., FORGIARINI A., BRICEÑO M. I., GARCIA-RUBIO L. H.

Spectroscopy measurements for the determination of polymer particle size distribution. *Colloids and Surfaces A* **331**, 91-96 (2008)

ABSTRACT: Polymer and copolymer emulsion lattices based on styrene and butyl methacrylate monomers are commercially important for many paints, adhesives, and coatings applications. The latex properties depend strongly on the copolymer composition, and particle size distribution, which in turn is function of the preparation of the latex and on the formulation of the emulsion designed for the particular application. This paper describes the implementation of multiwavelength spectroscopy measurements for size and distribution of the latex emulsions. The quantitative interpretation of the transmission spectrum is performed in the portion where no absorption is present (300-820 nm) leading to reliable estimated of particle size populations in the range of 0.02- 20 μ m. Particle size and particle size distribution of polymers and copolymers as function of reaction time and emulsion formulation are found in agreement with Smith and Ewart. The possibility of obtaining information from a single multiwavelength measurement makes UV-Vis spectroscopy a powerful tool for characterization of dispersed systems.

DELGADO J. G., SALAS C., IGLESIAS E., ACOSTA M.

Estudio de la espumabilidad de crudos venezolanos.

Ciencia e Ingeniería **29**, 19-26 (2008)

ABSTRACT: La generación de espuma puede llegar a ser un problema en muchas de las etapas de la producción petrolera. Por ejemplo en los separadores gas-crudo, la aparición de espuma es una circunstancia indeseable. Son muchos los factores que influyen en la formación y estabilidad de la espuma. El presente trabajo estudia la generación de espumas en sistemas solvente-crudo, y se muestra el efecto que tiene la naturaleza del solvente sobre la espumabilidad de la mezcla. Se utilizaron tres crudos venezolanos provenientes de distintos yacimientos. Como solventes se utilizaron querosén y tolueno. Así mismo, se estudió la influencia de la viscosidad del crudo sobre la espumabilidad de las mezclas. Los resultados muestran que la espumabilidad de las mezclas crudo-solvente aumenta si el solvente tiene poco contenido de compuesto aromáticos. De igual forma se encontró que la espumabilidad de los sistemas pasa por un máximo a medida que aumenta la viscosidad del crudo.

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

Interpretación espectral de dispersiones liquido-liquido usando espectroscopia UV-VIS.

[Spanish]

Ciencia e Ingeniería **29**: 27-34 (2008)

ABSTRACT: Las poblaciones de gotas son generadas por el equilibrio dinámico entre los fenómenos de ruptura y coalescencia que se llevan a cabo durante el proceso de emulsión. La estimación del tamaño y la distribución del tamaño de gota proveen información sobre las propiedades de la fase dispersa y son un parámetro importante que afecta la estabilidad de las emulsiones. La información que contiene el espectro de transmisión sobre la dispersión y absorción de las emulsiones da lugar a la interpretación cuantitativa del espectro en términos de tamaño y distribución de tamaño de gota de la dispersión liquido-liquido. El propósito de este trabajo es el de utilizar el espectro de transmisión ultravioleta visible (UV-vis) como una herramienta para caracterizar las emulsiones en términos de tamaño y distribución de tamaño de gota tomando como base las medidas de poblaciones de gotas como una función de la concentración de la fase dispersa. La interpretación espectral es aplicada a emulsiones provenientes de sistemas surfactante/agua/aceite como función de la formulación y de la concentración de la fase dispersa dando lugar el tamaño de gota y distribución de las dispersiones

QUINTERO L., CLARK D. E., JONES T. A., SALAGER J. L., FORGIARINI A.

In situ fluid formation for cleaning oil or synthetic oil based mud.

US Patent Application Publication 2008/0110618A1 (May 15, 2008)

ABSTRACT: Nanoemulsions, macroemulsions, miniemulsions, microemulsion systems with excess oil or water or both (Winsor I, II or III phase behavior) or single phase microemulsions (Winsor IV) improve the removal of filter cakes formed during hydrocarbon reservoir wellbore drilling with OBM. The macroemulsion, nanoemulsion, miniemulsion, microemulsion systems with excess oil or water or both or single phase microemulsions remove oil and solids from the deposited filter cake. In one non-limiting embodiment, the emulsion system (e.g. single phase microemulsion, nanoemulsion, or other emulsions) may be formed *in situ* (downhole) rather than produced or prepared in advance and pumped downhole. Skin damage removal from internal or external filter cake deposition can be reduced.

SALAGER J. L., SCORZZA C., FORGIARINI A., ARANDIA M. A., PIETRANGELI G., MANCHEGO L., VEJAR F.

Amphiphilic Mixtures versus Surfactant Structures with Smooth Polarity Transition across Interface to Improve Solubilization Performance.

7th World Surfactant Congress CESIO, Paris June 23-25, 2008.

CD Proceedings paper O-A17

ABSTRACT: According to Winsor's theory, solubilization in microemulsion is best when the amphiphilic layer at interface exhibit an equal interaction with oil and water phases. The solubilization generally tends to rise as both interactions increase per unit interfacial area. Increasing the adsorption density is the first efficient way to increase solubilization. A further improvement may be attained by enlarging both the hydrophilic and lipophilic groups of the surfactant, which is essentially a way to extend the reach of the surfactant molecule in both bulk phases. However, there is also a limit to such increase because most surfactants with lipophilic chain containing more than 16-18 carbon atoms are no longer soluble in water, whatever the head group. An indirect extension of the tail interaction with the oil phase could be provided by an additive, so-called lipophilic linker, which is essentially a slightly polar oil that is preferentially segregated close to the interface. Similarly, a so-called hydrophilic linker, i.e. a slightly lipophilic hydrotrope, could impart a better interaction on the water side of the interface. The presence of these linker molecules actually tends to produce a smoother polarity transition across interface, which is associated with a lower interfacial tension and a higher solubilization. However, it is more secure to generate the transition by using a single molecule that contains a continuous change in polarity, such as the so-called extended surfactants. In the first generation of extended surfactants an alkoxy spacer arm of the polypropyleneoxide type was inserted in the middle of a dodecyl ether sulfate molecule. According to the found properties, this spacer arm provides an extension of the lipophilic group. Nevertheless, the precipitation penalty due to the tail extra-length is avoided. Other extended surfactants have been synthesized on this model, with head groups such as sulfate, ethoxy-sulfate, carboxylate, ethoxy-carboxylate, C6 glucoside, xylitol and double head combinations, and with conventional tail from dodecyl to octadecyl. The number of polypropylene oxide units (ranging from 5 to 15) is a main parameter in the adjustment of the properties. Extended surfactants are found to exhibit outstanding solubilization and low tension with high molecular weight hydrocarbons and polar oils such a triglycerides, for which the performances of conventional surfactant are poor. Their ability to mix with conventional surfactant while keeping their specific solubilization capacity place the extended surfactants in a position of choice for many potential applications ranging from pharmaceutical and cosmetic formulas, or soak-only detergency to petroleum well remediation.

CELIS M. T., MANCHEGO L., CONTRERAS M., FORGIARINI A., VEJAR F., MARQUEZ L., BRICEÑO M. I., SALAGER J. L.

Efecto del polímero carboximetil celulosa sobre la inversion de emulsiones.

Ciencia e Ingeniería **29**, 115-122 (2008)

ABSTRACT: La inversión de fase es el proceso en donde una emulsión aceite-en- agua (O/W) es transformada a una emulsión agua-en-aceite (W/O). Este cambio se produce según dos mecanismos: el primero que se basa en la variación de la formulación del sistema es conocido como inversión transicional y el segundo es producido por un cambio de la relación agua/aceite y

se llama inversión catastrófica. Esta última depende, entre otros factores, de la energía de agitación, velocidad de adición y de la viscosidad de la fase aceite. Este trabajo muestra el efecto de la variación de la viscosidad de la fase acuosa mediante la adición de un polímero aniónico (carboximetil celulosa de sodio) y de la velocidad de agitación sobre el comportamiento de fase y la frontera de inversión estándar. Los resultados muestran que al añadir la carboximetil celulosa se produce no solo un aumento de la viscosidad de la fase acuosa sino también un cambio de la formulación que resulta en el sistema al equilibrio en un incremento notorio en el ancho de la zona trifásica hasta alcanzar la viscosidad de 0,5 Pa.s. y una amplitud no significativa de esta zona entre 0,5-1Pa.s. También 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 para viscosidades menores de 0,5 Pa.s. y permanece invariante para viscosidades mayores

ONTIVEROS J., MEDINA H., BULLON J., CARDENAS A.

Extracción de zinc y cobre mediante membranas líquidas emulsionadas en diferentes condiciones fisicoquímicas de la fase externa.

Ciencia e Ingeniería **29**, 157-164 (2008)

ABSTRACT : Se extrajo zinc de una solución acuosa mediante la tecnología de membranas líquidas emulsionadas. Se analizó el efecto de la acidez de la fase interna, la concentración de surfactante (Span 20) y la concentración del transportador (DEHPA) en la separación del metal de la fase acuosa. La extracción obtenida para la formulación sin ningún aditivo en la fase acuosa externa y partiendo de una solución de concentración inicial 500 ppm de zinc es de 33,4 % para diez minutos de operación. La adición de soluciones amortiguadoras, ya sean ácidas o básicas, aumenta la extracción a 75,8 %, 75,7 % y 86,7 % cuando se emplea ácido cítrico/citrato de sodio, amoniaco/cloruro de amonio y amoniaco puro respectivamente. La variación en la concentración del transportador, el surfactante y la acidez de la fase acuosa interna tienen efectos similares: un aumento gradual de la extracción conforme aumentan dichas concentraciones hasta un punto en el cual la extracción disminuye. Las concentraciones óptimas son de 0,75% de Span 20, 4% v/v de DEHPA y 1,5 M de ácido sulfúrico. Utilizando esta formulación en la preparación de la emulsión se encontró que la extracción de zinc es 36%. Un aumento de velocidad de agitación desde 100 rpm hasta 250 rpm permite elevar la extracción de 94%. Esta formulación, bajo las mismas condiciones de agitación permite extraer cobre en un 57,3%.

ISEA F. BLÉ C., MEDINA A. L, AGUIRRE P., BIANCHI G., KAUSHIK S.

Estudio de digestibilidad aparente de la harina de lombriz (*Eisenia andrei*) en la alimentación de trucha iris (*Oncorhynchus mykiss*).

Rev. Chilena Nutrición **35**, 62-68 (2008)

ABSTRACT: The primary objective of this investigation was to determine the apparent digestibility coefficient (ADC) of earth worm flour (EW) and compare it with other raw feeding materials already evaluated like wheat bran (BW) and soy cake (CS) in the feeding of rainbow trout (*Oncorhynchus mykiss*). Fifteen trouts of an average weight of 100 g were placed in duplicate tanks provided with an automated fecal material collecting system. CS and EW flour showed a protein ADC of 90.1 % and 90.0 % respectively, when comparing them with BW (57.2 %). Energy ADC was superior in CS (48.3 %). Digestible energy was superior in EW (17.1 KJ/g) followed by CS (14.9 KJ/g) and AT (2.4 KJ/g). We conclude that the EW flour has an excellent protein and energy digestibility.

VIELMA R. A., ROSALES D., ROSALES Y., MEDINA A. L., VILLARREAL J.

Perfil electroforético y calidad microbiológica de la harina de lombriz (*Eisenia fetida*).

Rev. Chilena Nutrición **35**, 225-234 (2008)

ABSTRACT: A electrophoretic and microbiological study [more probable number (NMP), total (CT) and fecal coliforms (CF), aerobic-mesophils bacteria (BAM), molds and yeasts] in worm's flour of *Eisenia fetida* was carried out. In the electrophoretic profiles using gels of standard concentration, different protein fractions with molecular weights between 39.6 and 43.5 kDa were separated. When gels with growing gradient of concentration were used, proteins with higher molecular weights (124.4 and 106.8 kDa) were separated with more detail. The protein characterization using different electrophoretic systems used in this study allows the analysis of different protein fractions that could have a nutritional importance. The counts of BAM, CT, CF, molds and yeasts in this flour were low, indicating an innocuous product. With the use of non-conventional resource, an interesting field of investigation begins involving food enrichment, representing an alternative at the industrial level.

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

Nanoencapsulation de filtres solaires via nanoémulsions (in French)

13^{èmes} Journées de Formulation de la Société Française de Chimie "Procédés et formulations au service de la santé". Nancy France. December 4-5, 2008

ABSTRACT: Les nanocapsules sont produites par une séquence d'opérations alliant transition de phase et réaction chimique. Le système de départ est une solution micellaire inverse de surfactif dans une phase huile qui, lors de sa mise en contact avec une phase aqueuse, évolue en un cristal liquide lamellaire. Quand on ajoute une proportion d'eau supplémentaire de façon à ce que le comportement de phase devienne diphasique, le cristal liquide stabilise la nanoémulsion H/E formée. Le pH de la phase aqueuse est alors changé pour favoriser une réaction de polymérisation à la surface des gouttes pour former les nanocapsules. On discute un exemple de ce procédé sol-gel pour encapsuler une solution de filtre solaire.

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

Mécanismes d'inversion de phase catastrophique lors de l'émulsification d'huiles visqueuses.

Poster. *13^{èmes} Journées de Formulation de la Société Française de Chimie "Procédés et formulations au service de la santé"*. Nancy France 04-05/12/2008

PARUTA E., SADTLER V., MARCHAL P., CHOPLIN L., MARFISI S., SALAGER J. L.

Influence de la formulation optimale et de la fraction de phase dispersée sur le comportement rhéologique des émulsions gels. Poster. *13^{èmes} Journées de Formulation de la Société Française de Chimie "Procédés et formulations au service de la santé"*. Nancy France 04-05/12/2008

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

Determinación del punto de precipitación de los asfaltenos en crudos venezolanos,

Ciencia e Ingeniería **29**: 225-232 (2008)

ABSTRACT: Se determina el punto de floculación de los asfaltenos utilizando diferentes técnicas experimentales reportadas en la literatura, para varios crudos venezolanos. Estos crudos fueron escogidos por la poca información que sobre sus puntos de precipitación se reporta en la literatura. Entre los métodos usados se encuentran: el método de la mancha sobre papel, el

método de medición de conductimetría y las pruebas reológicas. Los resultados muestran que existe una buena concordancia entre los puntos de precipitación determinados con cada uno de los tres métodos empleados.

URBINA-VILLALBA G., FORGIARINI A.M.,

Influence of Brownian motion on the Ostwald ripening process. ECIS Conference and COST D43 Workshop, Cracow, Poland. August 31 - September 5, 2008

ABSTRACT: It is a common practice to characterize the process of Ostwald Ripening (OR) by a linear variation of the cube of the average radius of a dispersion as a function of time (r^3 vs. t). The LSW theory [1,2], also predicts a characteristic LSW-distribution which is only observed in very stable systems after long periods of time [3]. Such distribution has a characteristic cut-off at $1.5 r$, and is skewed to the left (towards lower particle radii), while most experimental distributions appear to be skewed to the right with no cut-off radius. In this regard some authors had pointed out the effect of the rheological properties of the interface on the ripening process, and had also considered a mechanism in which the surfactant layer acts as a membrane, slowing down surfactant diffusion to the external phase [4]. In the first case, OR-simulations produce a right-skewed tail in the distribution, while in the second case, the analytical treatment suggest a more bell-shaped, symmetrical distribution. Curiously, the effect of particle movement on OR has not been considered, although it is by far the most strong assumption of the LSW theory. In this work we present the results of incorporating the algorithm of De Smet [5] for Ostwald Ripening simulations to our Emulsion Stability Simulations code. In this preliminary calculations, the effect of Brownian dynamics in the evolution of a dodecane/water emulsion is studied [6]. It was found that right-skewed distributions can be obtained as a result of the coalescence of drops. Furthermore, the typical r^3 vs. t holds in dilute systems, despite the fact that a polydisperse distribution of drops is produced.

[1] I.M. Lifshitz, and V.V. Slezov, *J Physical Chemistry of Solids*, **1961**, 19, 35.

[2] C. Wagner, *Zeitschrift fur Elektrochemie*, **1961**, 65, 581.

[3] V. Schmitt, C. Cattalet, F. Leal-Calderon, *Langmuir*, **2004**, 20, 46.

[4] A.S. Kabalnov, K.N. Makarov, A.V. Pertsov, E.D. Schukin, *J Colloids and Interface Science*, **1990**, 138, 98.

[5] Y. De Smet, L. Deriemaeker, and R. Finsy, *Langmuir*, **1997**, 13, 6884.

[6] T. Sakai, K. Kamogawa, K. Nishiyama, H. Sakai, and M. Abe, *Langmuir*, **2002**, 18, 1985.

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