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**SELECTED PUBLICATIONS AND COMMUNICATIONS (1994-1997)
BY LAB FIRP ASSOCIATES**

MARQUEZ N., ANTON R.E., USUBILLAGA A., SALAGER J. L.,

Optimization of HPLC Conditions to Analyze widely Distributed Ethoxylated Alkylphenol Surfactants,

J. Liquid Chromatography **17** (5), 1147-1169 (1994)

ABSTRACT: Commercial ethoxylated alkylphenol surfactants are always a mixture of oligomers with different ethylene oxide number (EON). The different oligomers can be separated by various HPLC techniques. Isocratic mode with mixed solvent on silica column allows to separate oligomers up to EON = 10; gradient programming moves the limit up to EON = 15. For higher EON values (up to 25) a NH₂ column has to be used, either with isocratic or gradient mode. Applications to the analysis of microemulsion systems and to the separation of tributyl phenol ethoxylates are discussed. Extreme separation of wide range EON distribution is attained with two columns (Si and NH₂) in series, and a solvent programming

ROJAS O.J., SALAGER J. L.,

Surface activity of Bagasse Lignin Derivatives found in the spent Liquor of Soda Pulp Plants,

Tappi Journal **77** (3), 169-174 (1994)

ABSTRACT: Lignin compounds present in the black liquors from alkaline pulping of bagasse are separated by evaporation to dryness or precipitation by acidifying down to pH 2. The separated lignin compounds exhibits the surface active characteristics of weak acid surfactant mixtures. Their surface tension versus concentration semi-log plot indicates a pattern similar to the break found at the critical micelle concentration of conventional surfactants. The surface activity of the lignin derivatives is strongly pH sensitive, and essentially vanishes in acidic pH conditions

MEDINA A. L.,

Estudio del comportamiento del hierro fijado sobre la caseína bovina fosforilada luego de la hidrólisis producida por las proteasas digestivas,

Archivos Latino-Americanos Nutrición **44** (22) 112-116 (1994)

SALAGER J.L., MARQUEZ N., ANTON R.E., GRACIAA A., LACHAISE J.,

Retrograde Transition in the Phase Behavior of Surfactant-oil-water Systems produced by an Alcohol Scan,

Langmuir **11**, 37-41 (1995)

ABSTRACT: The phase behavior of surfactant-oil-water systems is affected by the so-called formulation variables, i.e., by the nature of the components or their physicochemical characteristics. One of the formulation variables is the alcohol effect, which accounts for the type and concentration of alcohol. In most cases the addition of a lipophilic alcohol contributes to the increase of the amphiphile mixture lipophilicity at the interface, which results in a WI \rightarrow WIII \rightarrow WII transition, similar to the one observed when the water salinity is increased. However, in some cases the Winsor II phase behavior is never reached with the alcohol content increase, and a WI \rightarrow WIII \rightarrow WI so-called retrograde transition is exhibited instead. Such an anomalous case is analyzed here for a system containing a commercial nonionic polyethoxylated surfactant, n heptane, water, and n-pentanol, the concentration of the latter playing the role of the formulation variable. HPLC analysis of the different phases indicates that the surfactant oligomer partitioning between phases is affected by the alcohol content. The retrograde transition due to the increase in alcohol content is shown to come from the strong increase in the partitioning of lipophilic and balanced oligomers into the oil phase, with the remaining surfactant, in particular the interfacial mixture, becoming more hydrophilic.

LACHAISE J., MENDIBOURE B., DICHARRY C., MARION G., BOURREL M., CHENEVIÈRE P., SALAGER J. L.,

A Simulation of Emulsification by Turbulent Stirring,

Colloids Surfaces A: Physicochemical & Engineering Aspects **94**, 189-195 (1995)

ABSTRACT: We present a simulation of the formation of moderately concentrated oil-in-water emulsions generated by turbulent stirring using an ionic surfactant as emulsifier. The simulation is based on a stochastic model in which the mass transfer between the droplets is induced by breakups and coalescences until statistical equilibrium is established. Breakups and coalescences are controlled by probability functions in which the influence of the emulsifier is introduced through efficiency factors. These factors account for the competition between the main conflicting forces acting on the droplets during turbulent stirring. The model has only two adjustable parameters. With a single pair of values, the droplet distribution can be predicted for a variety of emulsification conditions. In this paper, it is shown that the minimum amount of emulsifier required to produce the finest droplet size distribution of various emulsions can be also successfully predicted.

YSAMBERTT F., CABRERA W., MARQUEZ N., SALAGER J. L.,

Analysis of Ethoxylated Nonylphenol Surfactants by High Performance Size Exclusion Chromatography (HPSEC),

J. Liquid Chromatography **18**, 1157-1171 (1995)

ABSTRACT: Since Size Exclusion Chromatography does not provide a complete oligomer resolution, it has not been generally considered as a choice method for analyzing ethoxylated surfactant. However, this situation might be changing. In effect, the use of new column technology together with non aqueous carrier solvent, and some operational optimization, can result in fairly good distribution data on the number of ethylene oxide groups per molecule (EON). It is shown that HPSEC provides an excellent EON average estimate over a wider and higher EON range than the the up-to-date HPLC techniques.

IGLESIAS E., ANDEREZ J.M., FORGIARINI A., SALAGER J. L.

A New Method to Estimate Foam Stability,

Colloids Surfaces A: Physicochemical & Engineering Aspects **98**, 167-174 (1995)

ABSTRACT: In classical foam stability studies, foam height variation is monitored versus time. The decay pattern depends, however, upon the foam structure at the start of the decay; in many instances this structure changes significantly during the first few minutes, and it is difficult to select a proper "zero time" of decay. We have found that the decay behavior is very well defined when the original state of the foam is taken as the equilibrium state of the classical Bikerman's experiment, i.e. when the foam formation by bubbling (at the bottom of the column) exactly compensates the foam collapse (at the top). It is found that under such starting conditions, short life foam decay exhibits a linear variation in the foam column height with the logarithm of the elapsed time. A dimensionless H vs. $\log t$ plot exhibits the same features for different systems; thus, both a characteristic height and a characteristic time can be extracted from the experimental data, the latter being readily related to the foam stability. These parameters are used to quantify the effect of additives on the decay of several foam systems containing nonionic and anionic surfactants.

SALAGER J. L., RAMIREZ-GOUVEIA M., BULLON J.,

Properties of Emulsion Mixtures,

Progress Colloid Polymer Science **98**, 173-176 (1995)

ABSTRACT: Emulsions are systems which exhibit some memory of their manufacturing process; thus the same surfactant-oil-water system can result in different emulsions. This paper deals with the mixing of emulsions with the same formulation but different drop size distributions. The two base emulsions are prepared in different vessels according to a standard procedure to attain fine or coarse dispersed systems, with wider or narrower size distribution. Then, they are poured together and blended with a gentle stirring. Experimental evidence indicates that the characteristics of the drop size distribution of the emulsion mixture has a strong influence on the properties of the emulsion mixture, such as its viscosity and its stability. A considerable viscosity reduction can be attained by mixing two emulsions with identical formulation but different size distributions. The features which are found to promote the viscosity reduction are a strong bimodality of the combined distribution, a deep gap between modes, and a certain degree of polydispersity

MIÑANA-PEREZ M. , GRACIAA A. , LACHAISE J. , SALAGER J. L.,

Solubilization of Polar Oils in Microemulsion Systems,

Progress Colloid Polymer Science **98**, 177-179 (1995)

ABSTRACT: A new type of amphiphile that contains both conventional surfactant and lipophilic linker features in a single molecule was designed and tested. In these so-called extended surfactants, a polypropylene oxide chain of variable length is inserted in between the conventional polar and apolar groups. With this type of surfactant, it was possible to produce for the first time a middle phase microemulsion in alcohol-free systems with long chain (C10-C18) synthetic and natural triglyceride oils. High molecular weight hydrocarbons were solubilized as well. The reported solubilization at optimum is found to depend upon both the propylene oxide chain length and the oil structure. The solubilization parameter of polar oils is found to attain quite remarkable values, in the range of several milliliters of oil per gram of extended surfactant, an interesting feature as far as the applications are concerned.

MIÑANA-PEREZ M., GRACIAA A., LACHAISE J., SALAGER J. L.,

Solubilization of Polar Oils with Extended Surfactants,

Colloids Surfaces A: Physicochemical & Engineering Aspects **100**, 217-224 (1995).

ABSTRACT: Starting with previous results showing that the solubilization of oil and water in a microemulsion can be improved by the introduction of an additive, i.e. a so-called lipophilic linker, a new surfactant type that mimics the additive effect is tested. The so-called extended surfactant has a poly-propylene oxide chain inserted in between the conventional alkyl and ether sulfate groups. These surfactants exhibit a critical micelle concentration and a cloud point that changes with the number of propylene oxide groups per molecule (ranging from 6 to 14). They show three-phase behavior at optimum formulation, with hexadecane, ethyl oleate, and, as reported for the first time, with triglyceride oils, such as soya oil. Outstanding values of the optimum solubilization parameter are reached (in the 10-30 ml g range).

MARQUEZ N., ANTON R.E., GRACIAA A., LACHAISE J., SALAGER J. L.,

Partitioning of Ethoxylated Alkylphenol Surfactants in Microemulsion-oil-water Systems,

Colloids Surfaces A: Physicochemical & Engineering Aspects **100**, 225-231 (1995).

ABSTRACT: Ethoxylated alkyl phenol oligomer partitioning between the microemulsion-water-oil (heptane) phases of a Winsor III system is determined by high performance liquid chromatography for systems containing octyl, nonyl, decyl, dodecyl and dinonyl phenol species. The partition coefficient between the water and oil phases obeys a simple law depending upon the alkyl chain length and the number of ethylene oxide groups per oligomer molecule. The results allow estimation of the energy of transfer of an ethylene oxide group and of a methylene group from oil to water.

ANTON R. E., MOSQUERA F., ODUBER M.,

Anionic-Nonionic Surfactant Mixture to Attain Emulsion Insensitivity to Temperature,

Progress Colloid Polymer Science **98**, 85-88 (1995)

ABSTRACT: It is well known that anionic surfactants becomes more hydrophilic as temperature increases, whereas nonionic surfactants show the opposite trend. By a proper mixing of both types of surfactants it is possible to produce intermediate situations and, eventually, insensitivity to temperature. This mixing principle is applied to both the phase behavior and emulsion properties. The temperature/water-to-oil ratio phase diagram is mapped for different mixtures of an alkyl aryl sulfonate and an ethoxylated alkyl phenol. The experimental evidence indicates that there is a continuous variation from the case 100% of anionic to 100% of nonionic. The three-phase zone behaves as a rotating band which finally flips upside down. The emulsion inversion line undergoes a transition, with an anionic-nonionic intermediate mixture exhibiting an inversion line independent of the temperature. For this anionic-nonionic mixture, the three-phase behavior region is an extremely extended band, and it is associated with an "abnormal" emulsion type all over the temperature and composition range. These emulsions are extremely unstable.

ANTON R. E., GRACIAA A., LACHAISE J., SALAGER J. L.

Phase behavior of pH-dependent systems containing oil-water and fatty acid, fatty amine or both.

4th World Surfactants Congress (Barcelona, Spain, June 3-7, 1996) *Proceedings* Vol. **2**, 244-256. Edited for A.E.P.S.A.T. by Roger de Llúria, Barcelona, Spain, 1996

ABSTRACT: The phase behavior of surfactant-oil-water systems depends upon the hydrophilic-lipophilic interaction at interface. In pH-dependent systems, the surfactant is in general a mixture of two different species: on the one hand the undissociated specie, i.e. acid or amine, which is a

very lipophilic nonionic surfactant, and on the other hand the ionic salt, i.e. carboxylate or ammonium, which is very hydrophilic. A physico-chemical model that includes partitioning between phases and dissociation in the aqueous phase, is proposed and tested on systems containing long chain fatty acids or fatty amines.

MIÑANA-PEREZ M., GRACIAA A., LACHAISE J., SALAGER J. L.

Systems containing mixtures of extended surfactants and conventional nonionics. Phase behavior and solubilization in microemulsions.

4th World Surfactants Congress (Barcelona, Spain, June 3-7, 1996) *Proceedings* Vol. 2, 226-234. Edited for A.E.P.S.A.T. by Roger de Llúria, Barcelona, Spain, 1996

ABSTRACT: The concept of lipophilic linker action recently allowed to develop the so-called extended surfactants in which an intermediate polarity poly-propylene oxide chain is inserted in between the conventional lipophilic and hydrophilic groups. These extended surfactants are found to enhance considerably the interaction on the oil side of the interface up to the point that the formation of microemulsion is now possible with natural and synthetic triglyceride oils, or very long chain hydrocarbons. Extended surfactants of the alkyl poly-propylene-oxide-ethoxy-sulfate type are mixed with conventional ethoxylated alkyl phenol nonionics and the phase behavior and formation of microemulsion is analyzed by changing several formulation variables such as: mixture composition, number of propylene oxide groups, aqueous phase salinity etc..

SALAGER J. L., PEREZ-SANCHEZ M., GARCIA Y.,

Physicochemical Parameters Influencing the Emulsion Drop Size,

Colloid Polymer Science **274**, 81-84 (1996)

ABSTRACT: The stirring-mixing energy is the most obvious factor in the drop size reduction process, but it is not necessarily the most important one. Both the physicochemical formulation and the composition variables are shown to play a determinant role, at constant stirring condition. The generalized formulation versus water/oil ratio diagram allows to map emulsion properties such as emulsion type, stability and viscosity. It is used to discuss the combined effect of the formulation and composition upon the emulsion drop size, through their influences on the interfacial tension, and the emulsion viscosity and stability.

SALAGER J. L.,

Guidelines to Handle the Formulation, Composition and Stirring to Attain Emulsion Properties on Design (type, drop size, viscosity and stability),

in *Surfactants in Solution*, A. Chattopadhyay & K. Mittal, Eds., Surfactant Science Series **64**, Chap. 16, pp. 261-295, M. Dekker New York (1996).

ABSTRACT: In this paper, the basic concepts of formulation, composition and stirring, and their effect on the emulsion formation and properties are reviewed first. Formulation is defined by physico-chemical variables such as the oil alkane carbon number, the water phase salinity, the surfactant characteristic parameters, etc. The equivalence of the different effects is discussed. Then, the generalized formulation concept is introduced, and it is shown how it can be estimated from the actual nature of the components, and how it can be changed to produce a transition. The general phenomenology is then presented on a formulation-composition map: inversion line, O/W, W/O and multiple emulsion zones. Similar maps for the viscosity, stability and drop size data enable the emulsion formulator to pinpoint the best choice for his /her application. Special

features allow even more flexibility, such as the time and space programming of the formulation, composition and stirring. Practical applications are discussed to illustrate the use of these concepts to attain desired emulsion properties.

SALAGER J. L., MENDIBOURE B., DICHARRY C., MARION G., LACHAISE J.,

A Stochastic Simulation of Emulsification by Turbulent Stirring,

CIMENICS 96, March 25-29, 1996, Mérida, Venezuela. Published in *Numerical Methods in Engineering Simulation*, M. Cerrolaza, C. Gajardo & C.A. Brebbia, Eds., pp. 93-105. Computational Mechanics Publications, Southampton UK (1996)

ANTON R. E., RIVAS H., SALAGER J. L.,

Surfactant-oil-water Systems near the Affinity Inversion - Part X : Emulsions Made with Anionic-Nonionic Surfactant Mixtures,

J. Dispersion Science & Technology **17** (6) 553-566 (1996)

ABSTRACT: Anionic and nonionic surfactants exhibit opposite changes in hydrophilicity with a change of temperature. This antagonism can be harnessed by the use of mixtures. The phase behavior and emulsion type are mapped on a temperature water/oil-ratio diagram for different anionic-nonionic mixtures. It is shown that the mixing can result in insensitivity to temperature of different kinds of emulsions.

LACHAISE J., MENDIBOURE B., DICHARRY C., MARION G., SALAGER J. L.,

Simulation of the overemulsification phenomenon in turbulent stirring,

Colloids Surfaces A: Physicochemical & Engineering Aspects **110**, 1-10 (1996)

ABSTRACT: An improvement upon the single breakup/coalescence model is presented to account for the overemulsification generated by the turbulent stirring of surfactant-oil water systems. The drop breakup process is revisited to produce small satellite droplets instead of just two equal daughter drops. The proposed multiple breakup/coalescence model has three adjustable parameters. With a single set of these parameters the droplet-size distribution can be predicted for a variety of emulsification conditions. The influence of important variables such as the surfactant concentration and the oil volume fraction is simulated on the model and the data are compared with experimental results.

NUÑEZ G., BRICEÑO M. I., MATA C., RIVAS H.,

Flow Characteristics of Concentrated Emulsions of Very Viscous Oil in Water,

J. Rheology **40** (3) 405-423 (1996)

NIELLOUD F., MARTI-MESTRES G., LAGET J. P., FERNANDEZ C., MAILLOLS H.,

Emulsion Formulation: Study of the Influence of Parameters with Experimental Designs,

Drug Dev. Ind. Pharm. **22** (2) 159-166 (1996)

MEDINA A. L., VEJAR F., RAUCQ D.,

Desalado de los sueros lácteos por electrodiálisis,

Interciencia **21** (4) 224-227 (1996)

MEDINA A.L., MESNIER D., TAINTURIER G. LORIENT D.,

Chemical Phosphorylation of Bovine Casein: Relationships between the Reacting Mixture and the Binding Sites of Phosphoryl Moiety,
Food Chemistry 57 (2) 261-265 (1996)

RIVAS H., GUTIERREZ X., ZIRITT J. L., ANTON R. E., SALAGER J. L.,
Microemulsion and Optimum Formulation Occurrence in pH-dependent Systems as found in Alkaline Enhanced Oil Recovery,
in *Industrial Applications of Microemulsions*, C. Solans & H. Kunieda, Eds., Surfactant Science Series vol. 66, Chap. 15, pp 305-329, M. Dekker, New York (1997)

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- III. Alkaline Flooding Studies
- IV. Optimal Formulation and Microemulsion Formation in pH-Dependent Systems
- V. Interfacial Behavior in Crude Oil/Alkaline Solution Systems
- VI. Field Application

BRICEÑO M. I., RAMIREZ M., BULLON J., SALAGER J. L.

Customizing drop size distribution to change emulsion viscosity
2nd World Congress on Emulsion - CME2, Bordeaux France September 23-26, 1997 Proceedings
Paper 2-1-094

ABSTRACT: The normal trend, i. e., the steady increase in emulsion viscosity as the average drop size decreases, can be drastically altered by customizing the drop size distribution. In a typical batch stirring process the emulsion average drop size decreases with time as well as viscosity increases. However, if the emulsification is carried out with a stirring device that result in a biemulsion, which is actually the combination of two emulsions, an apparent decrease in emulsion viscosity with decreasing average drop size is exhibited. The phenomenon is found to be associated with the occurrence of a polymodal drop size distribution. The biemulsion viscosity is found to depends upon the overall distribution pattern, as well as upon the characteristics of each separated emulsion. A practitioner rule of thumb results from the analysis of the different possible cases.

SALAGER J. L., CASTILLO P., GRACIAA A., LACHAISE J., POIRIER J. E., BOURREL M.

Breaking of an Asphalt Emulsion on a Mineral Aggregate: Phenomenology, Modeling and Optimization
2nd World Congress on Emulsion - CME2, Bordeaux France September 23-26, 1997 Proceedings
Paper 3-3-096

ABSTRACT: When a cationic asphalt emulsion is contacted with a granulated solid, physicochemical driving forces result in the adsorption onto the solid surface of the surfactant contained in the continuous aqueous phase of the emulsion. As a consequence of these molecular transfers a change from hydrophilic to hydrophobic of the solid surface wettability is observed, as well as emulsion breaking provided sufficient solid surface is available. Systems are studied at equilibrium. They contain different cationic surfactants, asphalt and quartzite powder. Adsorption isotherms at the solid surface and liquid interface are reported, as well as various measurements of the solid surface hydrophobation, versus surfactant concentration. A simple optimization model is proposed to determine the best surfactant concentration and emulsion/solid

ratio.

SALAGER J. L., PEREZ-SANCHEZ M., RAMIERZ-GOUVEIA M., BRICEÑO M./I., GARCIA Y.

Combining formulation, composition and stirring to attain a required emulsion drop size — State of the Art.

2nd World Congress on Emulsion - CME2, Bordeaux France September 23-26, 1997 Proceedings Paper 1-2-093

ABSTRACT: Emulsion drop size is often a specification of manufacturing processes, and they are in general several alternate way to attain a certain size, not all at the same expense or technical difficulty. Physicochemical formulation variables, including temperature, can modify both the interfacial tension and the coalescence rate, that have a direct effect upon emulsions size. A minimum drop size can be found as a compromise of opposite trends near optimum formulation, both in the O/W and W/O cases. Formulation programming can result in situations that are not directly available with equilibrated systems. The composition effect is often indirect, through a change in viscosity (by modifying the internal phase ratio) or surfactant adsorption. In most case it is also directly linked with the stirring efficiency that drastically depends upon viscosity, flow pattern in the emulsification device and shear regime. Unsteady state effects such as inversion hysteresis and quenching allow to retain the memory of some situations. A comprehensive State of the Art of coupling effects is presented.

ANTON R. E., GARCES N., SALAGER J. L.

A correlation for three-phase behavior of cationic surfactant-oil-water systems.

J. Dispersion Science & Technology 18, 539-555 (1997)

ABSTRACT: The phase behavior of cationic surfactant/oil/water/alcohol systems was systematically scanned to correlate the attainment of three-phase microemulsion-oil-water systems with the following formulation variables: water phase salinity as sodium chloride concentration, oil alkane carbon number (ACN) or equivalent ACN when the oil phase is not an alkane, surfactant alkyl chain length, surfactant hydrophilic group (both amine salts at acid pH and quaternary ammonium compounds at neutral pH), alcohol and temperature effects. The numerical correlation is mathematically similar to the one found for anionic surfactant systems. Differences in coefficient and parameter values allow comparisons between both types of ionic surfactant systems. The linear expression corroborates the theoretical interpretation proposed in other publications

MARQUEZ N., SUBERO N., ANTON R. E., GRACIAA A., LACHAISE J., SALAGER J.,
Effect of the Alkylate Isomerism upon the Surfactant Separation in HPLC Column and Partitioning between Water and Oil,

Separation Science & Technology 32 (6) 1087-1098 (1997)

MARTI-MESTRES G., FERNANDEZ C., PARSOTAM N., NIELLOUD F., MESTRES J. P. MAILLOLS H.,

Stability of UV Filters in different Vehicles: Solvents and Emulsions,

Drug Dev. Ind. Pharm. 23 (7) 647-655 (1997)

YSAMBERTT F., ANTON R.E., SALAGER J. L.,

Retrograde Transition in the Phase Behavior of Surfactant-oil-water Systems produced by an Oil EACN Scan,
Colloids Surfaces A: Physicochemical & Engineering Aspect **125**, 131-136 (1997)