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2001 PUBLICATIONS AND COMMUNICATIONS BY LAB FIRP ASSOCIATES

GOETHALS G., FERNANDEZ A., MARTIN P., MIÑANA-PEREZ M., SCORZZA C., VILLA P., GODE A.,

Spacer Arm Influence on Glucido-amphiphilic Compound Properties,

Carbohydrate Polymers, **45** (2), 147-154 (2001).

ABSTRACT: We prepared glucidoamphiphile derivatives from D-glucose, D-galactose and xylitol, in which the glucidic moiety and the hydrophobic alkyl chain are separated by spacer arm E (E = glyceryl, OEt2-?-propyleneglycyl and butyloxy). Their amphiphile characteristics are compared to those of the corresponding analogs 3-O-alkyl-D-glucopyranoses, 6-O-alkyl-D.L-xylitols. We discussed the spacer arm influence on hydrophilic lipophilic balance HLB, critical micellar concentration, water solubility, and phase transition temperatures of thermotropic and lyotropic mesophases.

PEÑA A., SALAGER J. L.,

Effect of Stirring Energy upon the Dynamic Inversion Hysteresis of Emulsions,

Colloids & Surfaces A: Physicochemical Engineering Aspects **181**, 319-323 (2001).

ABSTRACT: The effect of stirring energy upon the characteristics of dynamic emulsion inversion is discussed after an experimental formulation-composition map for emulsions containing an anionic surfactant. It is shown that a vigorous agitation promotes the early inversion of high internal phase ratio emulsions. The hysteresis zone narrows and moves to an intermediate position in the ambivalent region that is attained for lower stirring speeds. A simple model that relates catastrophic inversion patterns to a thermodynamic framework is proposed to explain these features.

SALAGER J. L., BRICEÑO M. I., & BRACHO C. L.,

Heavy Hydrocarbon Emulsions - Making use of the State of the Art in Formulation Engineering,

in *Encyclopedic Handbook of Emulsions*, J. Sjöblom, Ed., Chapter 20 pp. 455-495. Marcel Dekker New York, (2001).

ABSTRACT: Huge heavy crude oil deposits, particularly in Eastern Venezuela, may be economically tapped to almost duplicate the current world petroleum reserves. One of the early and cheaper alternatives was to condition these viscous heavy oils as an emulsified fuel for electricity generation plants. The product that became commercial in 1988 under the trade mark Orimulsion® presents several advantages over more expensive coal. The available state of the art in emulsion science is reviewed before presenting in a pedagogical fashion the formulation engineering basics of this bitumen-in-oil emulsion. Contains 23 figures and 250 references.

ROJAS O. J., NEUMAN R.D., CLAEISSON P.M.,

Desorption of Low-Charge-Density Polyelectrolyte Adlayers in Aqueous Sodium n-Dodecyl Sulfate Solution,

J. Colloid Interface Science **237**, 104-111 (2001).

Lab. FIRP - School of Chemical Engineering - University of The Andes - Mérida Venezuela - Email: firp@ula.ve

ABSTRACT: The association between low-charge-density polyelectrolytes adsorbed onto negatively charge (mica and silica) and an anionic surfactant, sodium dodecyl sulfate (SDS), has been investigated using surface force measurements, ellipsometry, and XPS. All three techniques show that the polyelectrolyte desorbs when the SDS concentration is high enough. The XPS study indicates that desorption starts at SDS concentration of ca 0.1 unit of comc ($8 \times 10^{-4} \text{M}$) and that the desorption proceeds progressively as the SDS concentration is increased. Surface force measurements show that for the polyelectrolyte studied here, having 1% of the segments charged, the desorption proceeds without any swelling of the adsorbed layer. This behavior differs from that observed when polyelectrolytes of greater charge density are used.

ZAMBRANO N., TYRODE E., PEREZ M., SALAGER J. L.,

Effect of Generalized Physico-Chemical Formulation on Emulsion Drop Size,

invited conference, *Particles 2001 Symposium*, Orlando FLA, February 25-27, 2001.

ABSTRACT: The physico-chemical formulation of the surfactant-oil-water system has a strong influence on the emulsion properties, among them the drop size which is dealt with in this paper. As Winsor III phase behaviour case - often referred to as optimum formulation - is approached from both sides, the interfacial tension decreases, thus favouring the breaking into smaller drops. However, the coalescence rate of neighbouring drops also increases, thus augmenting the drop size. As a consequence of these opposite effects, the emulsion drop size produced in identical composition and mechanical stirring conditions, exhibits a minimum on each side of optimum formulation, whatever the variable selected to carry out the formulation scan. The modification of this trend with increasing stirring and rising internal phase ratio is reported, as well as the case of an emulsion belonging to the so-called abnormal regions with low internal phase ratio. The proper selection of formulation could considerably increase the efficiency of the comminution process.

RAMIREZ M., MIRA I., SALAGER J. L.,

Reduction of Emulsion Viscosity by adjusting a Bimodal Drop Size Distribution,

poster, *Particles 2001 Symposium*, Orlando FLA USA, February 25-27, 2001 *ABSTRACT:* When stirring a high internal phase ratio emulsion in a batch mixing process, the viscosity can first rise because of the decreasing drop size as time elapses, then it can suddenly fall as a consequence of the occurrence a bimodal emulsion. Bimodal emulsions are prepared by mixing two base emulsions in different amounts. The viscosity of the emulsion is found to exhibit a minimum zone whenever the size distributions of the modes of the two base emulsions are well separated, and with a ratio of at least 3 between the small and big drops average. However, the viscosity of the two emulsion mixture depends upon the characteristics of each distribution. The strongest viscosity reduction is found to take place when a polydispersed fine emulsion is mixed with a rather monodispersed coarse one.

ZAMBRANO N., RAMIREZ M., PEREZ M., SALAGER J. L.,

Influence of the Surfactant-Oil-Water Composition on emulsion drop size,

poster, *Particles 2001 Symposium*, Orlando FLA USA, February 25-27, 2001.

ABSTRACT: The composition variables of a surfactant-oil-water, i. e., the surfactant concentration and the water-to-oil ratio, are able to strongly influence the emulsion drop size, at constant stirring conditions. It has been known for a long time that an increase of surfactant concentration is general associated with a drop size reduction. However, this diminution depends upon the stirring conditions and is more significant at low energy stirring. There is thus a trade off between surfactant and stirring effects that are able to reduce the drop size. The water-to-oil ratio effect is complex and sometimes counterintuitive, but it is worth dealing with since it can considerably discount the required energy to attain a certain drop size. As internal phase ratio is increased to approach inversion conditions, the emulsion becomes very viscous, and a small drop size may be attained, which is found to be practically

independent of the stirring energy and phase viscosity. In other words, very fine emulsions can be made, at low energy expense, even with viscous internal phase.

FORGIARINI A., ESQUENA J., GONZALEZ C., SOLANS C.,

Formation of Nano-emulsions by Low-Energy Emulsification Methods at constant Temperature,

Langmuir **17**, 2076-2083 (2001).

ABSTRACT: Formation of nanoemulsions has been studied in the system water/Brij 30/decane at 25°C by three low-energy emulsification methods: (A) stepwise addition of oil to a water-surfactant mixture, (B) stepwise addition of water to a solution of the surfactant in oil, and (C) mixing all the components in the final composition. Nanoemulsions with average droplet size of 50 nm and high kinetic stability have been obtained only at oil weight fractions R lower than 0.3 by emulsification method B. Independent of the oil weight fraction R , emulsions obtained by method B have a lower polydispersity than those obtained by methods A and C. Phase behavior studies have revealed that compositions giving rise to nanoemulsions consist of W_m (O/W microemulsions), L (lamellar liquid crystal) and O (oil) phases at equilibrium. It has been shown that equilibrium properties cannot fully explain nano-emulsion formation. Low values of equilibrium interfacial tensions and phase equilibrium involving a lamellar liquid crystalline phase are probably required but not sufficient to obtain nano-emulsions in this system. The key factor for the nanoemulsion formation has been attributed to the kinetics of the emulsification process. The change in the natural curvature of the surfactant during emulsification process may play a major role in achieving emulsions with small droplet size.

CARDENAS A., FILLOUS L., ROUVIERE J., SALAGER J. L.,

An Experimental Method to Estimate the Interfacial Mass Transfer through the Interfacial Region of Liquid Membrane Systems,

Ciencia **9** (1), 70-78 (2001).

ABSTRACT: A simple and reliable experimental method is reported to measure the mass transfer resistance through a liquid membrane as found in multiple emulsions for drug controlled release. A straightforward data analysis leads to calculate the mass transfer coefficient corresponding to the crossing of the interfacial region. The method is used to discuss some typical results with both oil and water soluble tracers.

BRICEÑO M. I., SALAGER J. L., BERTRAND J.,

Influence of the Dispersed Phase Content and Viscosity on the Mixing of Concentrated oil-in-water Emulsions in Transition Flow Regime,

4th International Symposium on Mixing in Industrial Processes, Toulouse, France, May 14-16, 2001. e-Proceedings CD paper # 33. pp 286-292.

ABSTRACT: The authors have evaluated the emulsification of oil of varying viscosities for concentrated o/w emulsions ($> 60\%$). Rushton type impellers and baffled mixing vessels were used. The emulsions were prepared in the transition regime ($80 < Re < 200$). It was found that, when the oil content increases, it is the emulsion viscosity that controls droplet size, regardless of the dispersed phase viscosity and the hydrodynamics. The authors have followed an experimental procedure that allows for the full scale-up of the results.

SALAGER J.L., MARQUEZ L., MIRA I., PEREZ M., RAMIREZ M., TYRODE E., ZAMBRANO N., CHOPLIN L.,

Emulsification Efficiency related to the Combination of Mechanical Energy Input and System Formulation and Composition variables,

4th International Symposium on Mixing in Industrial Processes, Toulouse, France, May 14-16, 2001. e-Proceedings CD, paper # 32 pp. 280-285.

ABSTRACT: The reduction of drop size during emulsification may be favoured by changing three types of variables: (1) the physicochemical formulation variables which are linked to the nature of the compounds [water, oil, emulsifier], (2) the composition variables that account for their relative proportions and (3) the variables which characterize the mechanical energy input conditions supplied by the stirring device. After reporting the general trends, the best compromise situations to attain a minimum drop size are located in the three dimensional formulation-composition-stirring space.

SALAGER J. L., ANTON R. E., ANDEREZ J. M., AUBRY J.M.

Formulation des Micro-émulsions par la Méthode HLD (in French),

Techniques de l'Ingénieur, Vol. Génie des Procédés, Rubrique Formulation. Paper # **J2 157**, 1-20 (2001). Web site: www.techniques-ingenieur.fr

ABSTRACT: Some surfactant-oil-water systems result in a microemulsion at equilibrium. Contrariwise to macroemulsions, microemulsions are monophasic, thermodynamically stable systems, which are often transparent or translucent, and exhibit a low viscosity because of a flexible structure. Depending on the formulation, Winsor type I, II, III or IV phase behavior is exhibited. The recently introduced Hydrophilic-Lipophilic Deviation (HLD) is a generalized formulation variable expression which is more powerful than classical concepts such as HLB or PIT, because it takes into account all formulation variables: surfactant type and structure, oil nature, electrolyte type and concentration, alcohol type and concentration, temperature and eventually pressure. The use of HLD is discussed in details and a large amount of data is reported on the characteristic parameters of oil phases and surfactants. Practical examples are discussed. The chapter is aimed at formulators.

BRICEÑO M. I., SALAGER J. L., BERTRAND J.,

Influence of the Water-to-oil Ratio and Dispersed Phase Viscosity on the Mixing of Concentrated Emulsions in Transition Flow Regime,

Trans. Institute Chem. Eng. **79A**, 943-948 (2001).

ABSTRACT: We have evaluated the emulsification of oil of varying viscosities for concentrated o/w emulsions (> 60%). Rushton type impellers and baffled mixing vessels were used. The emulsions were prepared in the transition regime ($80 < Re < 200$). It was found that, when oil content increases, it is the emulsion viscosity that control droplet size, regardless of the dispersed phase viscosity and hydrodynamics. We followed an experimental procedure that allows for the scale-up of the results.

SALAGER S. E., TYRODE E., CELIS M. T., SALAGER J. L.,

Influence of the Stirrer initial Position on Emulsion Morphology. Making use of the Local Water-to-Oil Ratio Concept for Formulation Engineering Purpose,

Industrial & Engineering Chemistry Research **40**, 4808-4814 (2001).

ABSTRACT: The initial location of the stirrer in the emulsification vessel can induce the resulting emulsion type. The interpretation in term of mixing phenomena leads to the use of the local water-to-oil ratio (WOR) concept in the formulation-composition map. The know-how associated to this phenomenology allows to interpret in a straightforward way the kind of complex procedures commonly employed in emulsion manufacturing, particularly those associated with inversion and multiple emulsion attainment.

SALAGER J. L., ANTON R. E., BRICEÑO M. I., CHOPLIN L., MARQUEZ L.,

The Emergence of Formulation Engineering in Emulsion Making - Transferring Know-how from Research Lab. to Plant,

oral presentation, *Formula III*, October 13-16, 2001. La Grande Motte, France.

ABSTRACT: All variables capable of altering the physico-chemical formulation, including temperature, have been gathered in a generalized concept linked to the phase behavior of surfactant-oil-water

systems. Early concepts like Winsor's R ratio or Shinoda's PIT have evolved into the more complex but more complete HLD, i.e., the deviation from a reference so-called optimum formulation for three-phase behavior. This considerable reduction of the number of degrees of freedom has allowed dealing with other important variables in emulsion making, i.e., water-to-oil ratio (composition) and stirring. The general phenomenology representing the emulsion properties (type, stability, rheology, drop size) can be qualitatively mapped now in a three-dimensional map, where each region exhibits definite features, e.g., O/W type, small drop size, and low stability. Travelling in the map from one region to another corresponds to modifications in formulation, composition and stirring along a path which describes the protocol of change in an industrial process dealing with emulsion making, inversion or reworking. Each path can be associated to the emulsion transformation that results from it, i. e. inversion, rupture, stabilization, etc. A dozen of different path cases emerge from a systematic categorizing. They are defined as unit operations in emulsion formulation engineering, because they correspond to one or a combination of very specific processes, such as mixing, diluting, heating, quenching etc. Because of the so-called memory effect, emulsions can "travel" along a path whereas retaining some property, e.g. drop size, while on the contrary other is altered, e.g. stability. These more complex transformations can be described by assembling unit operations in time and space. This allows interpreting the design of complex industrial processes such as crude oil dehydration, or the manufacturing of paint, cosmetics, or heavy hydrocarbon emulsions.

CATTE M., VAN HECKE E., POPRAWSKI J., SALAGER J. L., AUBRY J. M.,

Phase Equilibria of Oil-Water-ethoxylated Surfactant Systems. An Original Way for Predicting Triglyceride-based Emulsion Properties,

poster, *Formula III*, October 13-16, 2001. La Grande Motte, France.

ABSTRACT: The generalized formulation concept of HLD (hydrophilic lipophilic deviation) makes microemulsions and emulsions formulation less empirical. This concept based on phase behavior and Winsor types observation is well known when oil is mineral. In this work, a similar approach is applied to 11 triglycerides-based oils (9 vegetable oils and 2 pure triglycerides) and 2 ethoxylated surfactants (nonylphenol and tridecanol). For each water/oil/surfactant system, formulation scans varying the ethylene oxide groups number (EON) are performed at 50°C, 55°C et 60°C. In such systems, triglycerides-based oils do not behave exactly like mineral oils. However, each of these systems at equilibrium can be characterized by $EON_{0,5}$ defined as the EON of the surfactant that would equally partition into the aqueous and the oily phases. According to these $EON_{0,5}$, it is possible to compare the oils as well as the surfactants. As an example, whatever the kind of surfactant and the temperature, $EON_{0,5}$ obtained with linseed oil is 1 unit higher than $EON_{0,5}$ obtained with palm oil. This is probably related to the high content of linolenic acid (C18:3) in linseed oil, whereas palm oil is richer in palmitic acid (C16:0). Actually, $EON_{0,5}$ should simulate the situation where HLD is close to zero, that is favourable for microemulsion formation. As an extent and according to the generalized formulation concept, when emulsions are desired, surfactants having EON far from $EON_{0,5}$ would be preferred. This last hypothesis is now being experimentally confirmed.

MARQUEZ L., GRACIAA A., LACHAISE J., SALAGER J. L.,

Hysteresis Behavior in Formulation-induced Emulsion Inversion,

poster, *Formula III*, October 13-16, 2001. La Grande Motte, France.

ABSTRACT: As a consequence of the association between emulsion type and physicochemical formulation, any formulation variable can trigger an emulsion inversion. Generally, a change, or an inversion, of the emulsion morphology takes place at the so-called optimum formulation. When composition, formulation or temperature are continuously varied, non equilibrium processes can occur, and, if the system is stirred, these processes may delay the emulsion inversion. Such delays introduce

an hysteresis region in the composition-formulation diagram. In catastrophic inversion, due to a change in composition, hysteresis regions have already been identified. However until now, no delay has been found in the transitional inversion, probably because emulsions whose formulation is close to optimum formulation are very unstable and thus could adapt themselves very quickly to the dominant morphology. Because the presence of delay is known to modify the emulsion properties, as in paints or cosmetics manufacture, any exception to this rule is worth investigating. In the present study, we show that under some conditions, hysteresis regions can also be found in a transitional inversion driven by a temperature change in a nonionic system containing Tween mixtures. These results show that the emulsion morphology of the studied SOW systems exhibits a high resistance to the physicochemical constraints.

NARDELLO-RATAJ V., POPRAWSKI J., CHAILLOUX N., SALAGER J. L., AUBRY J. M.,
Classification and Emulsification of Aliphatic and Olefinic Cosmetic Oils through the "optimum formulation" Concept,

poster, *Formula III*, October 13-16, 2001. La Grande Motte France.

ABSTRACT: Several aliphatic and olefinic oils used in cosmetics, e. g., paraffin, squalane, squalene and other, were characterized by using the HLD (Hydrophilic-Lipophilic Deviation) concept. Optimum formulations for Winsor III type occurrence were determined by the unidimensional scan technique and detected by measuring the highest solubilization or the lowest interfacial tension with water. The systems used contained ethoxylated nonionic surfactants and isopropanol.

NIELLOUD F., FORTUNE F., FERNANDEZ C., DRAUSSIN S., MARTI-MESTRES G.,
Retchtschaffner Design applied to the Formulation of Oil-in-Water Submicron Emulsion in the Dermatological Field,

poster, *Formula III*, October 13-16, 2001. La Grande Motte France.

ABSTRACT: The formation of oil-in-water submicron emulsions stabilized by nonionic surfactant (glyceryl stearate and cetareth-12, cetareth-20) and containing a variety of dermatological acceptable oils (liquid paraffin, dibutyl adipate, dioctylcyclohexane) has been studied with the help of experimental design. The choice of the initial formula is based on our knowledge of the phenomenon. A "Retchtschaffner experimental design" was used to evaluate the joint influence of several variables. Only 16 experiments were necessary to estimate the effect of 5 factors (mode of formulation, nature and concentration of oil, concentration of surfactant, surfactant/cosurfactant ratio) and their first order interactions. Both the phase inversion temperature and classical emulsification methods are used. After formulation emulsions are kept at 25°C and two experimental responses were measured: particle size after 7 days and stability after 50 days. A 0-5 scale was used to evaluate the emulsion stability ranging from completely broken to still transparent miniemulsion.

PIERLOT C., POPRAWSKI J., CATTE M., SALAGER J. L., AUBRY J. M.,
Determination of the coefficients of the HLD Theory for Emulsions by Experimental Design with 7 factors at 3 levels,

poster, *Formula III*, October 13-16, 2001. La Grande Motte France.

ABSTRACT: An experimental design with 7 factors at 3 levels was carried out to corroborate the HLD expression which links the occurrence of optimum formulation for Winsor III type phase behavior and formulation variables (oil, salinity, salt type, alcohol type and content, temperature, surfactant type and concentration). The optimum formulation is detected by scanning the EON (ethylene oxide number) of the nonionic surfactant mixture. The results confirm the first order variation of the HLD model and point out the importance of the oil phase nature, alcohol type and concentration, as well as temperature.

POPRAWSKI J., MARTI M. J., SALAGER J. L., AUBRY J. M.,

Application of the HLD Concept: from Microemulsions to Macroemulsions of Pine Oil with a Nonionic Surfactant,

poster, *Formula III*, October 13-16, 2001. La Grande Motte France.

ABSTRACT: The phase behavior of ethoxylated tridecanol surfactants/water/pine oil was studied according to the unidimensional formulation scan technique. The oil phase was either pine oil or its main components (terpineols), which were characterized within the HLD framework. Stable oil-in-water emulsions were prepared by using the bidimensional formulation-composition map.

FORGIARINI A., ESQUENA J., GONZÁLEZ C., SOLANS C.,

Influence of the Phase Behavior on Nanoemulsion Formation and Stability,

oral presentation, *Formula III*, Oct. 13-16, 2001. La Grande Motte France.

ABSTRACT: Nanoemulsions are transparent or translucent emulsions with extremely small droplet size (in the range 20-500 nm) and high kinetic stability. Due to these properties, nanoemulsions resemble microemulsions although the latter are thermodynamically stable. An advantage of nanoemulsions over microemulsions for practical applications is that nanoemulsions require lower surfactant concentration for their formation.

RODRIGUEZ C., KUNIEDA H., NOGUCHI Y., NAKAYA T.,

Surface Tension Properties of Novel Phosphocholine-based Fluorinated Surfactants

J. Colloid Interface Science **242**, 255-258 (2001)

ABSTRACT: Surface and interface tension properties of novel fluorinated surfactants containing a phosphocholine group were studied using the Wilhelmy and spinning drop methods. Using a conventional cationic fluorinated surfactant, we found that the values coming from the Wilhelmy plate method are not always accurate due to the effect of the wetting angle. The novel fluorinated surfactants show high surface activity not only in water but also in organic solvents such as m-xylene and methanol. They seem to be more effective in reducing surface tension at low pH values. The novel fluorinated surfactants are also effective in reducing the interfacial tension between water and hydrocarbon oil.

RODRIGUEZ C., NAITO N., KUNIEDA H.,

Structure of vesicles in homogeneous short-chain polyoxyethylene cholesterol ether systems,

Colloids Surfaces A: Physicochemical Engineering Aspects **181**, 237-246 (2001)

ABSTRACT: Mixtures of the homogeneous nonionic surfactant trioxyethylene cholesterol ether ChEO3 and water were examined by microscopy, small angle X-ray scattering, differential scanning calorimetry, electron-spin resonance and fluorescence spectroscopy. A lamellar liquid-crystalline phase with peculiar characteristics is found above 75% of surfactant concentration. This phase seems to consist of a rather rigid and ordered bilayer when compared with typical $L\alpha$ -phases although the degree of crystallinity is less than that of $L\alpha$ -phases in nonionic systems with the same EO chain. The peculiarities of this phase are attributed to the rigid and bulky hydrophobic group of surfactant. The dispersion of this lamellar phase in water leads to the formation of very stable vesicles with a wide range of morphologies at rather low surfactant concentrations.

PIERLOT C., POPRAWSKI J., CATTE M., SALAGER J. L., AUBRY J. M.,

Applications des plans d'expériences à la détermination d'un modèle pour la formulation d'émulsions optimales,

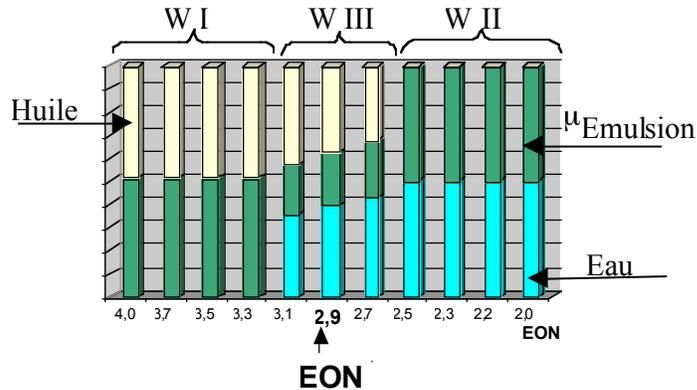
oral presentation, *Chimiométrie 2001*, CNAM Paris-France, December 4-5, 2001.

ABSTRACT. L'intérêt principal de la théorie du HLD (Hydrophilic Lipophilic Deviation) développée par Salager (1) est de prévoir la nature de l'émulsion obtenue en fonction des tensio-actifs, du sel, de l'huile, de l'alcool et de la température utilisés. A titre d'exemple, des valeurs négatives du HLD conduiront à des émulsions de type Winsor I (phase huileuse en équilibre avec la microémulsion), des valeurs positives seront synonymes de Winsor II (microémulsion + eau) et les trois phases seront présentes si HLD est égal à zéro (eqn 1, Fig. 1). Dans ce dernier cas, la formulation sera dite optimale.

$$HLD = \alpha - EON + b.S - K.ACN - \phi)A(+ c_T \Delta T \quad (1)$$

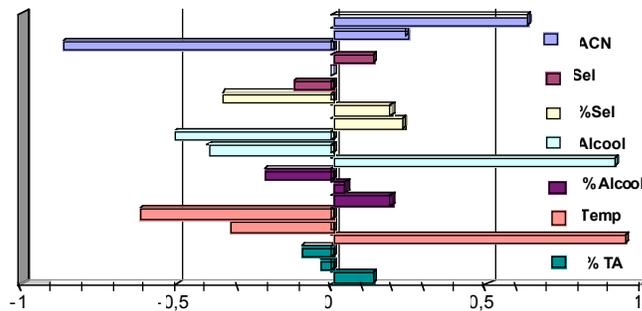
Figure 1. Determination de EON*

Afin de déterminer les coefficients du modèle mathématique de l'équation (1), 16 expériences ont été réalisées avec 7 facteurs (huile, sel, % sel, alcool, % alcool et % tensio-actif) à 3 niveaux. La réponse était le nombre d'oxyde d'éthylène du tensio-actif (EON*) qui permet d'obtenir une valeur nulle pour le HLD (Fig. 1).



Le traitement de cette réponse permet de confirmer le modèle du premier degré du polynôme (1) et montre l'influence importante de la nature de l'huile, de l'alcool et de la température. (Fig. 2). Les valeurs numériques de ces coefficients sont semblables à celles obtenues par régression multilinéaire sur 64 expériences.

Figure 2. Effets des facteurs sur la valeur de EON*



[1] J.L. Salager, Formulation concepts for the emulsion maker, in *Pharmaceutical Emulsions and Suspensions*, F. Nielloud and G. Marti-Mestres Eds, M. Dekker, 2000.

RODRIGUEZ C., UDDIN Md. H., FURUKAWA H., HARASHIMA A., KUNIEDA H.,
Polymer-Surfactant Interactions: Effect of Mixing Lipophilic and Hydrophilic Silicone Surfactant Systems,

Trends in Colloid Interface Science XV, P. G. Koutsoukos Ed., *Progress Colloid Polymer Sci.*, **118**, 53-56 (2001).

ABSTRACT: The phase behavior of a hydrophilic A-B-type silicone surfactant, (CH₃)₃SiO-[(CH₃)₂SiO]_{3.8}-(CH₃)₂SiCH₂CH₂CH₂-O-(CH₂CH₂O)_{51.6}H, Si_{5.8}C₃EO_{51.6}, was investigated by phase study and small-angle X-ray scattering. It forms a micellar cubic phase and a hexagonal phase in aqueous mixtures. The structure of the cubic phase seems to be face-centered type. When lipophilic surfactant (Si₁₄C₃EO_{7.8} or Si₂₅C₃EO_{7.8}) is added to Si_{5.8}C₃EO_{51.6}/water systems, a transition

from hexagonal phase to lamellar phase takes place, owing to a change in the hydrophile-lipophile balance of the system. The change in the surface area per surfactant molecule is larger as the polydimethylsiloxane chain is longer, even if the EO number remains constant. This fact is attributed to the coiling of the long lipophilic chain in order to reduce the entropy loss.

KUNIEDA H., TANIMOTO M., SHIGETA K., RODRIGUEZ C.,

Highly Concentrated cubic-phase Emulsions: Basic Study on D-Phase Emulsification using isotropic Gels,

J. Oleo Science **50** (8) 633-639 (2001)

ABSTRACT: In a hydrophilic octaethylene glycol dodecyl ether (C12EO8)-water system, a micellar cubic phase is formed below 20°C. Upon addition of decane, the maximum temperature of micellar cubic phase I1 is increased, and moreover, the hexagonal liquid crystal region changes to the I1 phase. Beyond the solubilization limit of decane in the I1 phase, highly viscous and gel-like O/I1 emulsions are formed in the two-phase region of I1+O. In the case of a surfactant mixture (C12EO 4.8) containing C12EO8 + C12EO3, a single I1 phase region is not present in a pseudo ternary phase diagram of water/C12EO4.8/decane system, but an I1+O region appears in the oil-rich region. C12EO4.8 forms lamellar liquid crystal in the aqueous system but C12EO3 in the mixture is dissolved in oil and the mixing fraction of C12EO8 in the surfactant aggregate increases as oil is added. Finally a two-phase region of I1+O appears. It is considered that the O/I1 emulsion gel or gel based on the cubic phase corresponds to the gel appeared in the so-called D-phase emulsification process. Upon addition of alkyl polyol such as glucerol or 1,3 butanediol, the transparency of the emulsion in the I1+O region increases because the difference in refractive index between the cubic phase and excess oil is decreased. The maximum temperature of the I1 phase decreases with increasing polyol content. Consequently, the addition of alkyl polyol is not crucial to form O/I1 gels in an oil-rich region.

PEÑA A. A., MILLER C. A.,

Kinetics of compositional ripening in emulsions stabilized with nonionic surfactants,

J. Colloid Interface Science **244**, 154-163 (2001)

ABSTRACT: The rates of solubilization of single n-decane/squalane drops were measured in solutions of the pure nonionic surfactant C12E8 containing different amounts of solubilized decane at 22°C. Solubilization of squalane was negligible for these conditions. The results showed that mass transfer rates of decane were controlled by interfacial phenomena, not by diffusion in the micellar solution, when transfer was either from drop to solution or vice versa. Good agreement with experimental data was obtained by using a model which assumed that the decane/squalane drops were ideal solutions. This model based on interface-controlled mass transfer was extended to describe the behavior of mixed emulsions stabilized with nonionic surfactants. Predictions of time variation of drop sizes for a particular mixed emulsion studied by B. P. Binks *et al.* [*Langmuir* **14**, 5402 (1998)] were in better agreement with the experimental data than those of the authors' model based on diffusion control.

FORGIARINI A., ESQUENA J., GONZÁLEZ C., SOLANS C.,

Formation and stability of nanoemulsions in mixed nonionic surfactant systems.

Progress Colloid Polymer Sci. **118**, 184-189 (2001)

ABSTRACT: The formation of nanoemulsions has been studied in water/mixed nonionic surfactant/oil systems using two emulsification methods. In one method, the composition was kept constant and the temperature was changed (phase-inversion temperature, PIT Method), while in the other method, water was added dropwise to a solution of the mixed surfactants in oil at constant temperature (method B). The droplet size and stability were determined as a function of surfactant mixing ratio, W_1 at 25°C. The

droplet size of nanoemulsions obtained by the PIT method is practically independent of W_1 and falls in the range 60-80 nm. In contrast, the droplet size of nanoemulsions prepared by method B, is highly dependent on W_1 and varies between 60 and 300 nm. At W_1 values where the PIT or the hydrophile-lipophile balance temperature (T_{HLB}) of the system is close to 25°C, the droplet sizes of the nanoemulsions are similar for both emulsification methods. There are three equilibrium phases of the latter compositions: an aqueous micellar solution or oil-in-water microemulsion (W_m), a lamellar liquid-crystalline phase and an oil phase (O). In addition, these nanoemulsions showed higher kinetic stability than those with lower W_1 values (higher T_{HLB}) and consisting of two liquid phases (W_m+O).