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**2013 PUBLICATIONS AND COMMUNICATIONS
BY LAB. FIRP ASSOCIATES**

DELGADO-LINARES J.G., GUTIERREZ C., SALAZAR F., GUEVARA M., MERCADO R., PEREIRA J.C.

Aplicación de los conceptos clásicos de la física en la práctica ingenieril. La ley de Stokes como herramienta conceptual en el análisis de procesos de deshidratación del petróleo,

Revista Educacion Quimica. **24:** 57-62 (2013) Universidad Autónoma de Mexico

ABSTRACT: Application of classical concepts of physics in engineering practice. Stokes' Law as conceptual tool in analysis of Petroleum Dehydration Processes). Several physical processes have been used in breaking of water-in-crude oil emulsions (petroleum dehydration); heating, water and diluents addition and electrical field application are the most common ones. In all cases, the effect of each operational parameter on the main variables that determine sedimentation rate of water droplets in emulsions can be predicted by Stokes' Law, which constitutes a simple mathematical expression very useful for chemical engineers in design and operation of separation processes of emulsified systems.

PIZZINO A., MOLINIER V., CATTE M., ONTIVEROS JF., SALAGER JL., AUBRY JM.
Relationship between phase behavior and emulsion inversion for a well-defined surfactant (C10E4)/n-octane/water ternary system at different temperatures and water/oil ration.

Industrial & Engineering Chemistry Research **52:** 4527-4538 (2013)

ABSTRACT: The relationship between the phase behavior and the type of emulsion formed under stirring has been studied for a well-defined surfactant/oil/water (SOW) system (ultrapure C10E4/n-octane/water) at three surfactant concentrations (1%, 3%, and 7%). The phase behavior was determined from systems equilibrated at constant temperature. The type of emulsions formed when these pre-equilibrated systems were stirred was established from conductivity measurements, and the so-called "standard inversion frontier" between the two emulsion morphologies (O/W and W/O) was plotted on temperature–water/oil proportion and temperature–surfactant concentration maps (χ and γ cuts, respectively, of the SOW–T prism). Dynamic phase inversions, produced by imposing a temperature variation under continuous stirring, were also observed. In the χ and γ maps, an exact correspondence between phase behavior and emulsion type was not observed, under either standard or dynamic conditions, and some regions of the formulation–composition map clearly shed light on a violation of Bancroft's rule. The strong impact of kinetics (mass transfer of the components), especially at low surfactant concentration, was demonstrated in experiments performed under dynamic inversion conditions. The transitional branch position was found to be significantly affected by the dynamic process, and its extension between the two catastrophic branches was directly associated with the range of three-phase behavior, which, in turn, was quite dependent on surfactant concentration.

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

Ruptura de emulsiones asfálticas catiónicas y no-iónicas mediante adición de arena.

Ciencia e Ingeniería **34**: 111-122 (2013)

ABSTRACT: Cationic and non ionic asphalt emulsion breaking by quartz addition. Cuando una emulsión asfáltica de tipo catiónica, se pone en contacto con un sólido granulado, algunas fuerzas fisicoquímicas tienen lugar, tales como la adsorción sobre la superficie del sólido del surfactante catiónico proveniente de la fase acuosa continua de la emulsión asfáltica. Como consecuencia de estas transferencias moleculares, la superficie del sólido cambia de hidrofílica a lipofílica y el proceso de heterofloculación puede ocurrir dependiendo del área del sólido disponible para la atracción del surfactante. Por otro lado, las emulsiones no iónicas no rompen mediante la adición de la arena, pues no existen fuerzas de atracción electrostática entre el surfactante y el sólido que desestabilicen la emulsión. Todos los sistemas que se estudian están en equilibrio, ellos contienen un surfactante catiónico o un surfactante no iónico, asfalto, arena entre 20 y 53 μm . Dos métodos de ruptura son utilizados.

SALAGER JL, FORGIARINI AM, BULLON J.

How to attain an Ultralow Interfacial Tension and a three-phase behavior with Surfactant Formulation for Enhanced Oil Recovery – A Review: Part 1. Optimum Formulation for simple SOW ternary systems. *J Surfactants Detergents* **16**: 449-472 (2013).

ABSTRACT: Enhanced recovery of crude oil by surfactant flooding requires the attainment of an ultralow interfacial tension. Since Winsor's work in the 1950s it has been known that a minimum interfacial tension and a concomitant three-phase behavior of a surfactant–oil–water system occurs when the interactions of the surfactant and the oil and water phases are exactly equal. It has been known since the 1970s that these conditions are attained when a linear correlation is satisfied between the formulation variables, which are characteristic parameters of the substances as well as the temperature. This first part of our review on how to attain ultralow interfacial tension for enhanced oil recovery shows how formulation scan techniques using these correlations are used to determine an optimum formulation and to characterize unknown surfactants and oils. The physicochemical significance of the original empirical correlation is reported as the surfactant affinity difference or hydrophilic–lipophilic deviation model. We report the range of accurate validity of, and how to test, this simple model with four variables.

ONTIVEROS J.F., PIERLOT C., CATTE M., MOLINIER V., PIZZINO A., SALAGER J.L., AUBRY J.M.

Classification of ester oils according to their Equivalent Alkane Carbon Number (EACN) and asymmetry of fish diagrams of C_{10}E_4 /Ester Oil/Water systems.

J Colloid Interface Science **403**: 67-73 (2013)

ABSTRACT: The phase behavior of well-defined C_{10}E_4 /ester oil/water systems versus temperature was investigated. Fifteen ester oils were studied and their Equivalent Alkane Carbon Numbers (EACNs) were determined from the so-called fish-tail temperature T^* of the fish diagrams obtained with an equal weight amount of oil and water ($fw = 0.5$). The influence of the chemical structure of linear monoester on EACN was quantitatively rationalized in terms of ester bonds position and total carbon number, and explained by the influence of these polar oils on the “effective” packing parameter of the interfacial surfactant, which takes into account its entire physicochemical environment. In order to compare the behaviors of typical mono-, di-, and triester oils, three fish diagrams were entirely plotted with isopropyl myristate, bis (2-ethylhexyl)

adipate, and glycerol trioctanoate. When the number of ester bonds increases, a more pronounced asymmetry of the three-phase body of the fish diagram with respect to T^* is observed. In this case, T^* is much closer to the upper limit temperature T_u than to the lower limit temperature T_l of the three-phase zone. This asymmetry is suggested to be linked to an increased solubility of the surfactant in the oil phase, which decreases the surfactant availability for the interfacial pseudo-phase. As a consequence, the asymmetry depends on the water–oil ratio, and a method is proposed to determine the f_w value at which T^* is located at the mean value of T_u and T_l .

QUINTERO L., PIETRANGELI G., SALAGER J.L., FORGIARINI AM.

Optimization of microemulsion formulations with linker molecules.

Paper SPE 165207. *SPE European Formation Damage Conference*, Noordwijk, The Netherlands June 5-7, 2013

ABSTRACT: Applications of microemulsion technology in the drilling and production industry have increased in recent years. Some of these applications include oil-based drilling fluid displacement to water-based fluid, near-wellbore remediation, well stimulation, enhanced oil recovery, flow-back recovery in shale gas wells, and cement spacers. Microemulsion formulations for these applications need to have high oil solubilization and very low interfacial tension, which is achieved with relatively high concentration of surfactants. High-performance microemulsion systems with lower surfactant concentrations are desired in order to optimize the cost of microemulsion technology applications. The reduction of surfactant concentration and cost could be achieved by introducing linker additives in the formulations. The addition of linker molecules enhances the solubilization property of microemulsions, which increases the hydrophilicity and/or the lipophilicity behavior of surfactants.

Previous studies indicate that addition of a proper linker molecule could significantly increase the solubilization of the oil. The lipophilic linker molecules (e.g. long chain amines, acids, alcohols, phenols) increase the interactions between the surfactant and oil, although with some disorder to avoid formation of highly-organized structures and to decrease the viscosity. This paper provides a comprehensive discussion of work carried out to determine the influence of lipophilic and hydrophilic linkers in microemulsions formulated with anionic/nonionic surfactant blends. The interfacial tension, fluids compatibility, and return permeability evaluation of microemulsion formulations containing lipophilic linkers prove that these additives bring a significant improvement in water injection or crude oil production.

RODRIGUEZ J., SALAGER J.L. , FORGIARINI A.

Evaluation del poder antioxidante de una microemulsión conteniendo quercetina y aceites esenciales mediante un método optimizado de análisis. [in Spanish]

Ciencia e Ingeniería, **34** : 45-50 (2013)

ABSTRACT: **Evaluation of the antioxidant ability of a microemulsion containing quercetin and essential oils through an optimized method of analysis.** This study has determined the antioxidant ability of a microemulsion containing 0.4 wt% quercetin combined with essential oils of rosemary and cidrón (*Rosmarinus officinalis* and *Lippia alba*, respectively), using the method of stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH). Moreover we assessed the influence of various alcohols as a reaction medium when this method is employed monitoring the stability of the radical in the solvent, the kinetics of the reaction, percent of inhibition (% I) of DPPH by antioxidant and the IC50 using spectrophotometry UV-Visible at a wavelength of 517 nm. The method is optimized taking into account the solubility of the vehicle (microemulsion) and the active ingredients (quercetin and essential oils).

SALAGER J.L., FORGIARINI A.M., MARQUEZ L., MANCHEGO L., BULLON J.

How to attain an ultralow interfacial tension and a three-phase behavior with surfactant formulation for Enhanced Oil Recovery – A review. Part 2. Performance improvement trends from Winsor's premise to currently proposed inter- and intra-molecular mixtures.

J Surfactants Detergents 16: 631-663 (2013)

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ABSTRACT: The minimum interfacial tension occurrence along a formulation scan at the so-called optimum formulation is discussed to be related to the interfacial curvature. The attained minimum tension is inversely proportional to the domain size of the bicontinuous microemulsion and to the interfacial layer rigidity, but no accurate prediction is available. The data from a very simple ternary system made of pure products accurately follows the correlation for optimum formulation, and exhibit a linear relationship between the performance index as the logarithm of the minimum tension at optimum, and the formulation variables. This relation is probably too simple when the number of variables is increased as in practical cases.

The review of published data for more realistic systems proposed for enhanced oil recovery over the past 30 years indicates a general guidelines following Winsor's basic studies concerning the surfactant–oil–water interfacial interactions. It is well known that the major performance benefits are achieved by blending amphiphilic species at the interface as intermolecular or intramolecular mixtures, sometimes in extremely complex formulations. The complexity is such that a good knowledge of the possible trends and an experienced practical know-how to avoid trial and error are important for the practitioner in enhanced oil recovery.

DELGADO-LINARES J.G., MAJID A.A.A., SLOAN E.D., KOH C.KA., SUM A.K.

Model water-in-oil emulsions for gas hydrates studies in oil continuous systems.

Energy & Fuels 27 (8) : 4564-4573 (2013)

ABSTRACT: Stable water-in-oil emulsions with water volume fraction ranging from 10 to 70 vol % have been developed with mineral oil 70T, Span 80, sodium di-2-ethylhexylsulfosuccinate (AOT), and water. The mean size of the water droplets ranges from 2 to 3 μm . Tests conducted show that all emulsions are stable against coalescence for at least 1 week at 2 °C and room temperature. Furthermore, it was observed that the viscosity of the emulsion increases with increasing water volume fraction, with shear thinning behavior observed above certain water volume fraction emulsions (30 vol % at room temperature and 20 vol% at 1 °C). Viscosity tests performed at different times after emulsion preparation confirm that the emulsions are stable for 1 week. Differential scanning calorimetry performed on the emulsions shows that, for low water volume fraction emulsions (<50 vol %), the emulsions are stable upon ice and hydrate formation. Micromechanical force (MMF) measurements show that the presence of the surfactant mixture has little to no effect on the cohesion force between cyclopentane hydrate particles, although a change in the morphology of the particle was observed when the surfactant mixture was added into the system. High-pressure autoclave experiments conducted on the model emulsion resulted in a loose hydrate slurry when the surfactant mixture was present in the system. Tests performed in this study show that the proposed model emulsion is stable, having similar characteristics to those observed in crude oil emulsions, and may be suitable for other hydrate studies.

SALAGER J.L., FORGIARINI A.M.

Performance improvement trends to attain ultralow interfacial tension with surfactant formulation in EOR.

104th AOCS Annual Meeting & Expo. Montreal, Canada. April 28-May 1, 2013

ABSTRACT: Enhanced oil recovery by surfactant flooding is a candidate to maintain the required oil recovery in the next decades. The low price of petroleum in the 1980-2005 period has considerably reduced the technical work in EOR but more fundamental research has provided a huge amount of information on the relationship between the formulation and the ultralow tension attained at the so-called optimum.

The present review shows that there are many ways to increase the actual performance since Winsor's premises back in the 1950's, but also remarks the trends are often associated with limits which have to be either further displaced or compensated. Formulation optimization is shown to depend on surfactant molecule design with a conflict between molecular size and precipitation, on intermolecular mixtures with a conflict between better interfacial behavior and lost species into the bulk phases, and on intramolecular mixtures which is still an innovative area. Currently proposed best formulas are matching a combination of all these trends with a large variety of alternatives.

SALAGER J.L.

How to improve performance by adjusting formulation in EOR.

Chemical EOR Workshop, IFPEN, Rueil Malmaison, France, May 27-29, 2013

ABSTRACT: Enhanced oil recovery by surfactant flooding was proposed in the 1970's as the method with the highest potential recovery. The basic studies carried out in the past 40 years have shown that a huge number of variables, probably over 10, are involved in the selection of currently proposed efficient formulations to attain a required low interfacial tension in a surfactant-oil-water system. As a consequence the understanding is quite messy and the actual formulations are attained in a fussy way mostly by trial and error, with a lot of confusion as far as explanations and interpretations are concerned. This often makes the formulation for EOR looking like an almost magic research. After 40 years of laboratory fundamental and practical research and some field trials, a review on what can be predicted and what still requires some work can be presented, provided that the many studies are critically interpreted.

This review starts indicating that a proper formulation corresponds to the so-called optimum conditions in a formulation scan in which the tension exhibits a deep minimum as seen in Fig 1. The concept was proposed by Winsor 60 years ago for another application, i.e. solubilization in microemulsions. Winsor introduced the ratio R of the surfactant interactions with oil and water, and reported that when $R = 1$, a so-called optimum formulation is attained with a three phase behavior system with a bicontinuous microemulsion in equilibrium with excess oil and water, concomitant with a minimum interfacial tension, often an ultralow one. Since R depends on all the characteristics of the surfactant-oil-water system like the nature of the components, as well as temperature and pressure, there are many ways to attain an optimum formulation and some of them exhibit a lower tension minimum and thus result in a better performance for enhanced oil recovery. R is a nice concept but cannot be calculated with accuracy, hence a substitute with actual variables had to be introduced. Fundamental work done on real, i.e. typical commercial products, was introduced in the mid 1970's with variables like the surfactant parameters for the head and tail groups, oil alkane carbon number ACN, salinity of the aqueous brine, temperature and pressure. This was supported by a physicochemical concept equivalent to $R=1$, based in the

surfactant affinity difference SAD, i.e. the variation of the standard chemical potential of the surfactant when it passes from oil to water. The empirical correlations were replaced by expressions based on these variables in $SAD = 0$ with some nice matching with simple systems and some inaccuracies for complex ones particularly non-ideal mixtures, involving fractionation, partitioning, and intermolecular interactions and synergies. In the 1980-90's the tendencies were to add more effects. Consequently the correlations involved more and more variables, with additional effects as corrections or adjustments, up to the point where crossed contributions turned out the correlations too complex to keep a simple numerical description of the formulation and its consequences on the tension.

In this business the most important issue is of course the performance, i.e. the tension minimum γ^* along a formulation scan. Comparisons have to be done between two systems each corresponding to a minimum tension γ^* , i.e. two optimum formulations along two scans, as seen in figure 1. This implies the variation of (at least) two formulation variables, which means that there is no way to relate the performance modification directly with a single variable change, and this is quite a complexity, both from the experimental point of view and for the interpretation, and of course for the predictions.

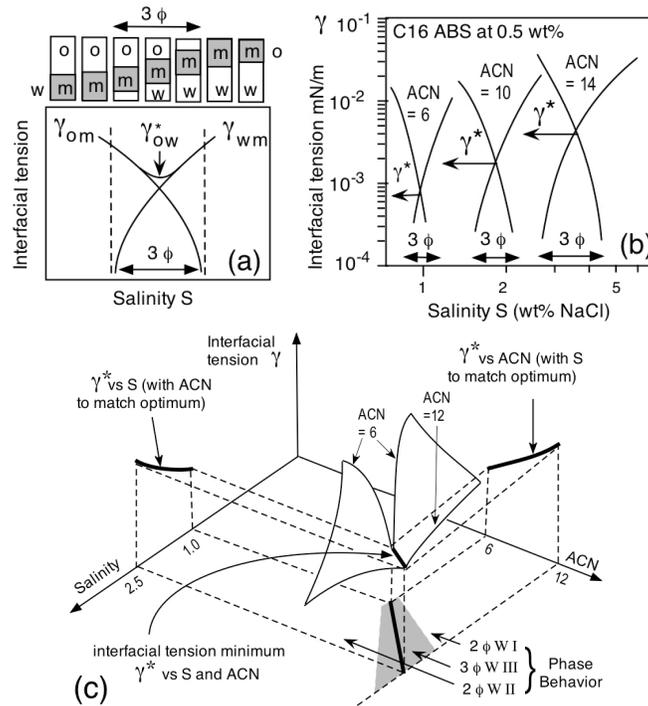


Fig 1. (a) Minimum tension γ^* in a formulation scan; (b) comparison of minimums in scan with dual formulation changes; (c) tension variations versus two variables, particularly minimum tension γ^* .

In practice empirical studies carried out in the 1980-1990's were often ignored and people are often not comparing two optimum formulations, thus wasting a lot of research and development time without getting any useful result. A few studies have been carried out the right way, showing tendencies but not exhibiting very clear trends, often because there are too many variables to carry out any trial and error approach in a reasonable time. The situation is like trying to run before starting to learn to walk. It is thus essentially impossible to try to work in practice from scratch in a space with 10-15 variables. The understanding has to be built up in

more simple systems, e.g. with 2-3 variables, which may be considered as "ideal" and probably not sufficient to explain all cases, but appropriate to start to understand. Some fundamental studies were carried out with an ultrapure surfactant-oil-water ternary and are a good start to interpret the surfactant-oil-water performance behavior even if the species are not the ones used in EOR.

We have recently reworked on these ultrapure system studies with a number of variable reduced to what can be plotted in 2D-3D graphs. The three independent variable case allows to find extremely simple trends which were completely undiscovered so far. From these data the performance, i.e. the minimum tension value at optimum γ^* , was essentially linearly linked with any formulation variable, at other variables constant, with the exception of one which is adjusted to match the correlation for optimum, as seen in figure 2. This allows to propose a generalized representation of the performance versus formulation variables and to generate some guidelines on the way the studies to improve performance should be handled. The results indicate that in the simple ternary there is no performance maximum, but essentially straight line iso-performance contours. This means that the changes to improve a performance should be selected along some direction until a limit is found, in most cases precipitation, phase separation, unwanted strong adsorption or excessive lost by partitioning. The consequence is that the displacement of the boundaries in the formulation feasible space is a quite significant feature (i.e., the second most important one) to improve performance.

In practice the precipitation limit due to the hydrophobic part of the surfactant is pushed away by introducing branching in the tail which make it more water soluble or by making it slightly polar by introducing polypropylene oxide chain. Mixing different surfactants (and sometimes co-surfactants) most of the time result in better solubility, although it produces selective fractioning. However it is sometimes a tricky issue associated either with welcomed synergy or with inconvenience like phase separation. When mostly used variables are added in actual systems, in particular with mixtures of surfactants, co-surfactants, electrolytes and oils, the interactions and synergy occurrences allow to change the basic straight line iso-performance contours into bended contours presenting minimums or maximums. The appropriate corresponding effects are susceptible to produce a performance maximum in the feasible zone, thus displacing the best performance case inside the practical limits.

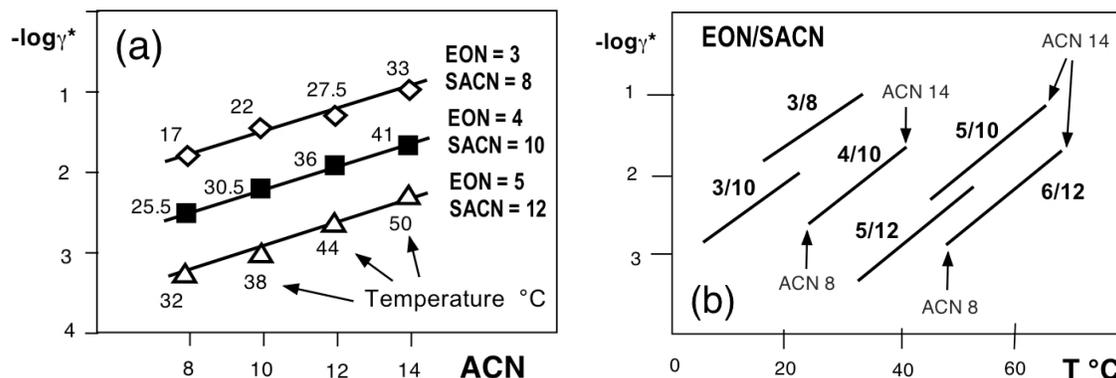


Fig 2. (a) Variation of performance ($-\log \gamma^*$) vs ACN at temperature adjusted for optimum formulation ($\text{SAD}=0$) and (b) vs temperature at ACN adjusted for optimum formulation. Both are data for surfactants of the n-alcohol ethoxylates type (EON= ethylene oxide number; SACN = surfactant n-alkyl carbon number in tail)

The current state of the art indicates how a formulation can be adjusted to improve performance by the combination of several guidelines which will be presented in this review: (1) general

trends with simple systems showing the appropriate dual changes of formulation; (2) displacement of the restriction limits further away by physico-chemical effects; (3) bending of the iso-performance contours through non-linear effects, to promote interactions and synergies through surfactant structure modification or intermolecular and intramolecular mixtures, resulting in performance improvement inside the feasible zone. The formulator able to understand these guidelines will avoid the often used time-consuming random trial and error, will reduce considerably the number of essays, and will be able to find the optimum formulation that corresponds to the best performance in a system with predetermined restrictions.

AVENDAÑO J., PANNACCI N., HERZHAFT B., GATEAU P., COUSSOT P.

Enhanced displacement of a liquid pushed by a viscoelastic fluid.

J Colloid Interface Science **410**: 172-180 (2013)

ABSTRACT: We consider the displacement, in a rectangular channel, of a Newtonian oil pushed by different types of liquids (Newtonian, shear-thinning, viscoelastic) of slightly higher apparent viscosity. In the absence of viscoelastic effects the interface between the two fluids becomes sharper at larger velocities, so that the thickness of the lateral film left behind increases with the flow rate. On the contrary, with a viscoelastic fluid, the shape of the interface is almost independent of the velocity so that the thickness of the lateral film is approximately constant. Moreover this thickness decreases when the ratio of normal to tangential stresses increases, suggesting that this effect can be attributed to normal stress differences. A heuristic theoretical approach tends to confirm this statement

AVENDAÑO J., PANNACCI N., HERZHAFT B., GAREAU P., COUSSOT P.

Entrance and exit effects for a viscoelastic liquid displacing a simple liquid through a contraction.

J of Non-Newtonian Fluid Mechanics **199**: 51-60 (2013)

ABSTRACT: We studied the displacement of the interface between a viscoelastic fluid pushing a simple liquid through a rectangular contraction by following the front interface deformation in time. The progressive deformation of the interface until apparent stabilization is followed, which makes it possible to identify a transient and a stationary regime. For low Weissenberg number the shape of the interface is essentially similar to that between two simple liquids. For sufficiently large Weissenberg number the shape of the interface is different: it is narrower before the entrance and wider just after the exit. The characteristics of this shape are qualitatively analogous to those of the interface between the vortices and the convected regions for the flow of a single viscoelastic fluid through a contraction–expansion. This suggests that the entrance effect is due to extensional effects and the exit effect is due to normal stress effects.

PIERLOT C., ONTIVEROS J.F., TAKAHASHI H., CATTE M., MOLINIER V.,

SALAGER J.L., AUBRY J.M. Classification of esters oils using C10 E4 /Oil/Water systems.

Australia-Japan Symposium, Nagoya, September 19-21, 201

ABSTRACT: Esters oil are frequently used in the cosmetic industry as isopropyl myristate and isopropyl palmitate. The aim of the present work is characterize several esters (Figure 1) by determination of the equivalent alcane (EACN) which would have the same oil compartment when emulsified. The physicochemical formulation plays a major role in the phase behavior of surfactant/oil/water systems and therefore on the properties of emulsions. Salager introduced the concept of hydrophilic lipophilic deviation HLD a dimensionless expression of the variation of chemical potential $\mu^{*w}-\mu^{*o}$ required to transfer a surfactant molecule of the oil phase to the aqueous phase.

For non ionic surfactant, at the optimum formulation the HLD law becomes simplified as :

$$0 = \alpha - k \cdot \text{ACN} + c_T (T^* - T_{\text{ref}})$$

where α , k , and c_T are characteristic parameters of the surfactant, “ACN” is the number of carbon atoms for the n-alkane, and T_{ref} is the difference between the temperature of the system and the reference temperature (25°C). T^* can be determined on the Fish diagram at the intersection of Winsor I, II, II and IV areas. Using $C_{10}E_4$ surfactant, we have determined the fish diagram for several esters and determined the Equivalent Alkane Carbon Number (EACN) using calibration curve. The effect of number of ester’s groups, the position of the functional group and the number of carbon atoms in the “alcohol” and “acid” chain is rationalized. Conductivity and rheolo-gical experiments will be investigated to see the correlation between T^* and the phase inversion temperature.

Reference : J.F. Ontiveros, C. Pierlot, M. Catte, V. Molinier, A. Pizzino, J.L. Salager, J.M. Aubry, *J. Colloid Interf Sci* 403: 67-76 (2013)

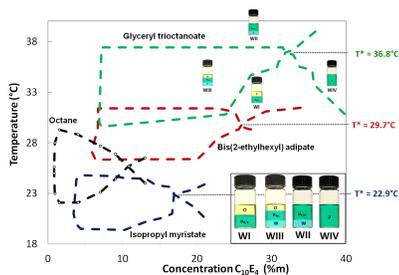


Fig. 1. Fish diagrams for isopropyl myristate, bis(2 ethylhexyl) adipate and glyceryl trioctanoate $C_{10}E_4$ /Octane/Water system.