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2014 PUBLICATIONS AND SELECTED COMMUNICATIONS BY LAB. FIRP ASSOCIATES

SALAGER J.L., MANCHEGO L., MARQUEZ L., BULLON J., FORGIARINI A.
Trends to attain a lower interfacial tension in a revisited pure alkylpolyethyleneglycol surfactant-alkane-water ternary system. Basic concepts and straightforward guidelines for improving performance in Enhanced Oil Recovery formulations.
J Surfactants & Detergents **17**:199-213 (2014)
ABSTRACT: Surfactant–oil–water systems exhibit a low interfacial tension minimum when the interactions between the adsorbed surfactant with water exactly coincide with its interactions with oil. This occurrence takes place at the socalled optimum formulation, which was conceptually derived by Winsor in the 1950s and rendered by numerical correlations for enhanced oil recovery in the 1970s. The actual low value of the interfacial tension minimum has been found to increase or decrease with formulation variables and though some hints are available, no general relationship has been reported up to now, probably because too many variables are involved in complex interactions. It is shown in the present article that a linear relationship between low-tension performance and formulation variables can be found for very simple ternary systems containing a pure ethoxylated alcohol, n-alkane and water at variable temperature, i.e., when there are only four degrees of freedom. In such a case the iso-performance contours studied in bi-dimensional spaces are reported to be almost straight lines and as a consequence the path to lower the tension through formulation adjustments is easy to find as being perpendicular as possible to the contours. On the other hand, it is shown that displacing the limit of restrictions like the surfactant precipitation boundary is a priority issue, thus justifying many trends which have been proposed on empirical grounds in the past years. The reported simple guidelines for a simple surfactant–oil– water ternary is likely to considerably facilitate the formulator's work in a real system with a score of formulation variables.
This article was distinguished as the best technical paper published during the preceding year in Journal of Surfactants and Detergents, AOCS 106th Technical Meeting, Orlando May 5, 2015

ONTIVEROS J.F., PIERLOT C., CATTE M., MOLINIER V., SALAGER JL, AUBRY JM
A simple method to asses the Hydrophilic Lipophilic Balance of Food and Cosmetic Surfactants using the Phase Inversion Temperature of C10E4/n-octane/water emulsion.
Colloids & Surfaces A **458**: 32-39 (2014)
ABSTRACT: The modification of the phase inversion temperature (PIT) of C10E4/n-octane/water emulsions wasstudied as a function of increasing amounts of additional second surfactants in order to rank themaccording to their hydrophilic lipophilic balance. Twenty five surfactants, selected from a wide rangeof chemical families, were studied. Well-defined

polyethoxylated alkyl surfactants (CiEj) show a linearvariation of the PIT with their concentration C and can be used as standards to calibrate a scale in termsof dPIT/dC. This parameter leads to a simple classification of surfactants with respect to C10E4. Positiveand negative values correspond to more or less hydrophilic surfactants compared to C10E4, respectively.Several industrial surfactants used in cosmetic and food industries (lecithins, sorbitan derivatives Spansand Tweens, sucrose esters, monoglycerides) were investigated and results are discussed with respectto the HLB scale of Griffin.

ONTIVEROS J.F., FROIDEVAUX R., DHULSTER P., SALAGER J.L., PIERLOT C.
Haem extraction for peptidic hydrolysates of bovine haemoglobin using temperature sensitive C10E4/O/W microemulsion system.
Colloids & Surfaces A **454**: 135-143 (2014)
ABSTRACT: The equilibrium phase behaviour of the tetraethyleneglycol decyl ether (C10E4)/n-octane/1% peptidehydrolysates of bovine haemoglobin systems at fw= 0.5 has been studied. Fish diagrams have been com-pletely built for two hydrolysates with 3 and 15% degree of haemoglobin hydrolysis and they do not differmuch from those having NaCl 0.01 M as aqueous phase. From the knowledge of these diagrams a newmethod is proposed to separate selectively peptide hydrolysates from haem. Most important parametersin extraction, range of temperatures and surfactant concentrations have been established. Five extrac-tions using 5 wt.% C10E4/n-octane/1% hydrolysates (degree of haemoglobin hydrolysis DH = 15%) at 27◦Callowed to eliminate 98% of starting haem, which is concentrated in the middle microemulsion phase,while maintaining 94% of the starting peptide population. In the same conditions, the hydrolysate DH = 3%presents 99.6% of haem elimination and maintains 85.6% peptides in aqueous phase. Well defined feasibil-ity of the selective extractions and process conditions are established to provide depleted haem aqueousphase.

MAJID A.A.A., BRANIFF M., LIU C., DELGADO-LINARES J., CREEK J.L., SLOAN E.D., SUM A., KOH C.A.
Gas hydrate formation from high water content systems containing anti-agglomerant surfactant and salt. Proceedings *8th Int. Conference on Gas Hydrates* (ICGH8-2014) Beijing, China, July 28 - August 1, 2014
ABSTRACT: As oil and gas production and transportation in subsea facilities move to deeper water, the conventional strategy of gas hydrate avoidance using thermodynamic inhibitors (THIs) becomes economically and environmentally more challenging. Furthermore, as production fields mature, the amount of water produced significantly increases (e.g. up to 50-80 vol.% water content), which also leads to the need for alternative solutions to THIs to prevent gas hydrate blockages in pipelines. In this DeepStar sponsored project, we examined the effects of an anti-agglomerant (AA) and salt (NaCl) on water-in-oil emulsion stability with and without the presence of gas hydrates, as well as gas hydrate formation/slurry characteristics using high water volume fractionsystems. Emulsion stability tests were tested using bottle tests and high pressure differential scanning calorimetry. Gas hydrate formation/slurry measurements were performed using a high pressure autoclave cell, with continuous agitation and 12 hour shut-in periods. At high water volume fractions (0.75) a highly viscous foam/emulsion can form when both AA and salt are added into the system, which might not be desirable.

SALAGER J.L., FORGIARINI A.M., BULLON J.
Progress in Designing Emulsion Properties over a Century – Emerging Phenomenological Guidelines from Generalized Formulation and Prospects to Transmute the Knowledge into Know-How.

In *Surfactant Science and Technology: Retrospects and Prospects*. Chap 18. pp 459-487. L.S. Romsted Ed. CRC Press Boca Raton FL (2014)

ABSTRACT: Emulsions have been used for more than a century, but clear guidelines associated with formulation issues have been established only after the effects of physicochemical variables on surfactant-oil-water systems at equilibrium were quantified by the enhanced oil recovery research in the 1970's. In the following 30 years both the phase behavior and the emulsion properties such as type, drop size, stability and viscosity, were phenomenologically related with the generalized formulation concept including the nature of the components as well as temperature. New structures such as non-spherical micelles, microemulsions, liquid crystals, vesicles and other mesophases were studied with recent analytical techniques. At the same time many specific studies have been carried out regarding particular applications of emulsions from foods to personal care products, from agrochemicals to water treatment, from asphalts to fuels, from petroleum recovery to paints, etc. The variety of requirements and uses results in some difficulties concerning the divulgence of scientific information and the organization of the knowledge into a know-how, which has to be improved in the near future.

SILVA I., BORGES B., BLANCO R., RONDON M., SALAGER J.L., PEREIRA J.C.,

Breaking of water-in-crude emulsions. 5. Effects of acid/alkaline additives on performance of chemical demulsifiers.

Energy & Fuels **28** 3587-3593 (2014)

ABSTRACT: The objective is to understand the effects of organic acid and amine additives on the performance of commercial demulsifiers in breaking water-in-crude-oil (W/O) emulsions, according to the proportional regime test developed in previous articles. Both hydrophilic (ethylamine and acetic acid) and hydrophobic (hexanoic acid and hexylamine) species were tested, and all were found to exhibit different effects. The water-soluble species have essentially no effect, despite a change in aqueous phase pH. Hexanoic acid was found to increase the stability of the W/O emulsions, whereas the hexylamine was found to reduce it. Explanations of the effect of these additives on the interfacial formulation are proposed.

MERCADO R. A., SALAGER J.L., SADTLER V., MARCHAL Ph., CHOPLIN L.

Breaking of a cationic amine oil-inpwater emulsion by pH increasing: Rheological monitoring to modelize asphalt emulsion rupture.

Colloids & Surfaces A **458**: 63-68 (2014)

ABSTRACT: When a caustic soda solution is slowly added up to a cationic oil-in-water emulsion, prepared withdodecylamine as surfactant, the chemical equilibrium is altered. As a consequence, a progressive viscos-ity diminution is observed until complete emulsion destabilization. Original cationic emulsions are stablethanks to the droplet electrical double layer formed by the ionized surfactant adsorption on the liquidinterface at very low pH values. However, the alkali addition changes the chemical equilibrium in dif-ferent ways, such as reducing the hydronium ion concentration, allowing for dodecylamine deionizationand increasing the ionic species concentration. These changes and the fact that the emulsion's dropletsize and distribution remain constant (noticed by granulometric measurements) during the process, let us assuming that viscosity decreases as a consequence of the overall positive layer charge diminution.However, emulsion destabilization can be explained in terms of some formulation parameters such likeSAD or HLD. Our system evolves from a very negative to a positive HLD value passing

through the opti-mal formulation when destabilization is observed. An interfacial formulation analysis is presented and ahypothetically extrapolation to asphalt emulsions is briefly analyzed.

PIERLOT C., ONTIVEROS J.F., CATTE M., MOLINIER V., SALAGER JL, AUBRY JM
Evaluation of the hydrophilic lipophilic balance of food and cosmetic surfactants using the phase inversion temperature of C10E4/n-octane/water emulsions.
1st Asian Conference on Oleo Science, September 8-10, 2014, Sapporo, Hokkaido, Japan
ABSTRACT: The modification of the phase inversion temperature (PIT) of $C_{10}E_4$/n-octane/water emulsions was studied as a function of increasing amounts of additional second surfactants in order to rank them according to their hydrophilic lipophilic balance. Twenty five surfactants, selected from a wide range of chemical families, were studied. Well-defined polyethoxylated alkyl surfactants (C_iE_j) show a linear variation of the PIT with their concentration C and can be used as standards to calibrate a scale in terms of dPIT/dC. This parameter leads to a simple classification of surfactants with respect to $C_{10}E_4$ (Figure). Positive and negative values correspond to more or less hydrophilic surfactants compared to $C_{10}E_4$, respectively. Several industrial surfactants used in cosmetic and food industries (lecithins, sorbitan derivatives Spans and Tweens, sucrose esters, monoglycerides) were investigated.

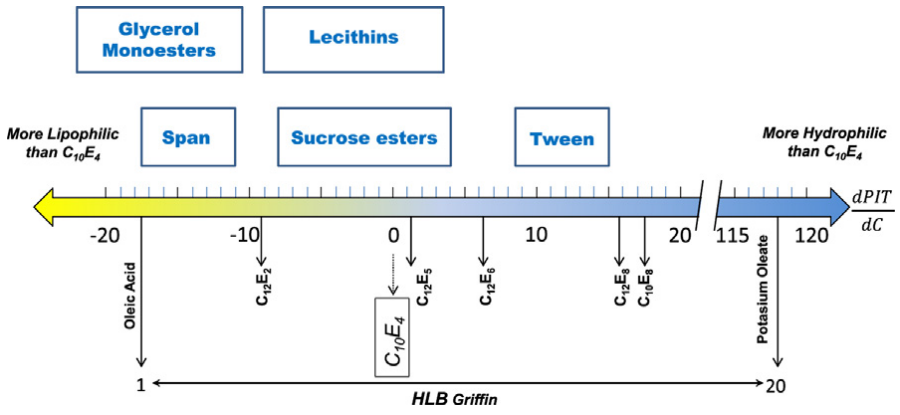

Figure. Surfactants classification using the dPIT/dC method.

MIAO S., CALLOW N., DASHTBOZORG S.S., SALAGER J.L., JU L.K.
Ethylation of Di-rhamnolipids: A green route to produce sugar fatty acid nonionic surfactants.
J Surfactants & Detergents **17:** 1069-1080 (2014)
ABSTRACT: Sugar fatty acid nonionic surfactants have attracted great attention due to their good biodegradability,vbiocompatibility, and bio-based characteristics. Regioselective sugar acylation is difficult to control for chemical reactions. The immiscible nature between hydrophilic sugars and hydrophobic fatty acids also negatively affects the reaction efficiency. In the present study, a group of sugar fatty acid nonionic surfactants, ethyl di-rhamnolipids, was synthesized. Di-rhamnolipids were isolated from a Pseudomonas aeruginosa fermentation broth containing a rhamnolipid mixture with about 64 % di-rhamnolipids, and then purified by silica gel chromatography. Di-rhamnolipids were successfully ethylated at 0 °C for 24 h, confirmed by HPLC–MS and 1H-NMR analyses. Preliminary emulsification test indicated that ethyl di-rhamnolipids were a potential class of useful sugar fatty acid nonionic surfactants. The synthesis process was mild, did not require regioselective sugar acylation, and offered a new way of developing novel sugar fatty acid nonionic surfactants.