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***2017 PUBLICATIONS AND SELECTED COMMUNICATIONS
BY LAB. FIRP ASSOCIATES***

SALAGER J.L., FORGIARINI A.M., RONDON M.J.

How to Attain an Ultralow Interfacial Tension and a Three-Phase Behavior with a Surfactant Formulation for Enhanced Oil Recovery: A Review — Part 3. Practical Procedures to Optimize the Laboratory Research according to the Current State of the Art in Surfactant Mixing.

J Surfactants Detergents **20** : 3-19 (2017)

ABSTRACT: The minimum interfacial tension to be reached in enhanced oil recovery by surfactant flooding implies the attainment of a so-called optimum formulation. Part 1 of the present review showed that this formulation may be described as a numerical correlation between the involved variables defining the oil, the water, the surfactant and the temperature. In practice, the crude oil and connate water characteristics are defined for a given petroleum reservoir as well as by its temperature and pressure, so that reaching the optimum formulation requires a specific characteristic parameter of the surfactant used to satisfy the correlation. Since it is unlikely to find a single surfactant that would exactly match the crude/brine/T/P system characteristic of a reservoir, a mixture of at least two surfactant species is in general used. The scan technique method to test the mixing requires about 10 interfacial tension or phase behavior experiments and results in a single data. Hence, the scan experiments have to be repeated many times to find a minimum tension which is low enough. Part 2 of this review showed that there are many formulation variables and, consequently many possibilities to easily choose experimental conditions. Since there is no simple method to select two or more surfactant species, the choice is made from partial experience or intuition, and sometimes at random. The laboratory time and cost to reach an appropriate optimum formulation is often excessive. The present part 3 of the review shows that by cleverly selecting a three-surfactant mixture, the experimental work to attain a very low interfacial tension for a given reservoir case can be considerably reduced. The experimental strategy proposed here makes use of the available information along a proper step by step path toward the optimum.

Highlighted paper by DELGADO et al. (2016)

See somments as a Feature publication in Advances in Engineering, on date 10 January 2017.

<https://advanceseng.com/chemical-engineering/breaking-water-crude-oil-emulsions-estimating-demulsifier-performance-optimum-formulation-attained-instability/>

Breaking of Water-in-Crude Oil Emulsions. 6. Estimating the Demulsifier Performance at Optimum Formulation from Both the Required Dose and the Attained Instability.

COMMENT OF EDITOR: This study proves that demulsifier should be a significantly hydrophilic surfactant, though not too much so as to exhibit a good performance at optimum for both a low required dose and a swift breaking of water-in-oil emulsion. It also shows that mixing quite different species resulting in synergy could produce favorable and quick interactions between the two demulsifier components and asphaltenes with a remarkable performance improvement both in the required dose and in the swift water-in-oil emulsion breaking.

SALAGER J.L. Starting the second decade of the Journal of Surfactants & Detergents.

J Surfactants Detergents **20**: 761-763 (2017)

TEXT: I was not involved in the group of persons who created the Journal of Surfactants and Detergents (JSD), but I participated as an author in the first volume in 1998 to answer a special invitation from the editorial committee. This first contact with JSD is worth a comment.

It happened that in 1993, our FIRP Lab in Venezuela in collaboration with LTEMPM Lab in France had been publishing two articles to introduce the new concept of "lipophilic linker" as an original way to highly solubilize polar oils in microemulsion as a veterinary vehicle. These fundamental work appeared in *Langmuir*, a famous academic and theoretical journal of the area at this time. Five years later the divulgation restrictions from the financial backup contract vanished, and it was time for me to published a third article on the optimization of the lipophilic linker in practice.

It was just when I was preparing this "applied" final paper that I received an invitation from JSD which was presented as the new "intermediate" Journal in Surfactant Science, with an argument from Mike Cox, recently emphasized [1], that it was to bridge the gap between fundamental science and applied topics. This definition matched very well our type of publications in the past 20 years. I had been the regional editor for Latin America of the Journal of Dispersion Science and Technology (JDST) from Marcel Dekker since 1986, and I was going to send our third paper to this journal, but Mike's persuasion was so convincing that I decided to try JSD. Thanks Mike for this prowess, which had me entering the JSD circle.

My research group contributed to publish in JSD in the next years a few papers dealing with both scientific and practical interest reports, including those concerning our HLD generalized formulation for surfactant-oil-water systems, and a new type of products we had designed for a high solubilization of polar oils called "extended surfactants". My personal contact at University of Oklahoma with John Scamehorn (who was a PhD student colleague of mine at UT Austin in the late 1970s) spreaded to David Sabatini, and Jeffrey Harwell, and to their PhD student Edgar Acosta, as well as industry researcher George Smith from Huntsman, who were all starting in the early 2000's a new line of research following our work on "linkers" and "extended" surfactants. Even if we did not really work on a common project, some exchanges with visits, seminars and discussions took place to make our research work complementary. In 2005 we decided to prepare a review paper on how to "enhance the solubilization in microemulsion" which was selected by the new editor Vaughn Mark Nace as a feature article, and later became one of the most cited paper in JSD. At thos time I published a few other articles in JSD and I participate in AOCS Meetings, including at a technical course on microemulsions at St Louis in 2006, so that I started some acquaintance with AOCS and JSD.

By the end of 2007, I was invited by Jack Wolowiec, AOCS area manager of publications, to be candidate to the Editor-in-Chief new position starting the next year. In 2008, after various email discussions and phone conversations with Robert Moreau (publications chairman at AOCS) and

Dan Solaiman (Chairman of the search committee), I was appointed by the Governing Board as the first non-US Editor-in-Chief (EIC) of an AOCS journal.

In 2008 I first analyzed the transition process of the joint publishing arrangement of AOCS with Springer [2] for extending the targets and the market of JSD, providing an in-line system and a boosting of the visibility. Then I talk to Springer people, particularly Marion Hertel, the Executive Editor in Chemistry, about her recommendations for my new job and the significance of the data in the annual Publisher report from Springer. I also spend a lot of time to carry out a diagnostic about the current situation of JSD using my previous experience as editor of another Journal, editor of a book and author of a lot of publications resulting from academic-industry research-development studies.

The main aspects which were dealt with according to this diagnostic and the corresponding planning to be carried out during my EIC period were :

(1) the scientific level of the articles had to be elevated as much as possible to improve the seriousness of the Journal, in order to motivate the choice of both authors and readers for JSD — this was a critical issue in view of the proliferation of fake peer-review journals particularly from “predatory” publishers from Asia.

(2) the originality of the article content had to be not only maintained, but improved to avoid “junk” papers without really new things, and to enhance JSD recognition, in particular through its citations, among other benefits.

(3) the papers had to be targeted to industry people working in R&D — with a combination of knowledge and know-how, which is not necessarily easy to do, because most of the authors are either from academy or from industry, and only a few involved in both.

(4) the topics had to be consistent with the “surfactants and detergents area” avoiding a too large variety — as in some superexpanded journals publishing 10,000 pages per year.

(5) the personal opinion of top notch specialists with both fundamental and practical expertise had to be invited and promoted, particularly in review papers — to save time for the professional R&D readers, who can have a look only at a very few percents of the literature.

These considerations implied an internationalization of the associate editors list with top level scientists from academy and industry, as well as a more complete coverage of the surfactant science specialities, particularly enhanced oil recovery.

The selection of new associate editors and reviewers having published many articles also allowed the authors to receive more help in the writing of their manuscript.

This was particularly important when the renewed editorial policy concerning originality, started to ask the authors to emphasize as far as possible the content of their original article to unpublished work. For review papers to be solicited to top experts, some original personal opinion was required. In both cases it was asked to the authors to present the two aspects, i.e. knowledge for academy and know-how for industry, and their practical combination.

The selection level of the papers increased, as well as the final quality of the published ones, thanks to systematic detailed recommendations from the EIC and associate editors. Our publications became more cited and their impact started to rise, year after year, and even if the articles became shorter, they were containing more useful information for the AOCS readers.

This situation, by the way, allowed to publish more papers per year, and to attract more authors as well as more readers. The number of articles per year rose remarkably, more than doubling during my EIC period from 2008 to 2014. To accommodate that, Steffen Pauly, our collaborator from Springer, had to make the arrangements to increase the number of pages and then to pass JSD from 4 to 6 issues per year in 2012.

However, this also increased the time the EIC had to dedicate to the job, and in spite of receiving help from AOCS people like Brian Moore and more recently Janet Brown, it became difficult for me to follow with my advancing age and with some research duties required in my laboratory, even with the very efficient and always ready assistance from Pamela Landman, who saved me a lot of time every week for years.

This EIC growing duty was certainly the main reason why my successor George Smith decided to nominate two senior associate editors to back him, one from industry and one from academy, and to increase the number of associate editors. I understand he is also trying some new ideas he is going to talk about in his editorial in a couple of months.

My impression is that JSD has reached in 20 years some fairly good position, which is quite consistent with the original proposal put in practice by Mike Fox and his team of pioneers. My congratulations to all participants in this venture, and my best wishes to George Smith, whom I hope to modestly help as an associate editor a few years more.

As far as my contribution to JSD is concerned, I will try to continue to submit to it some of my best publications with original knowledge and useful know-how.

SALAGER J.L. & FORGIARINI A.M.

Improving Low Tension Formulation Robustness in Enhanced Oil Recovery with properly Optimized Surfactant Mixture.

108th AOCS Annual Meeting, April 30 - May 3, 2017. Orlando FL USA

ABSTRACT: Enhanced oil recovery requires the attainment of ultra low interfacial tension between crude oil and the injected aqueous phase. It is known that the lower the minimum tension, the narrower the range of formulation over which it would take place. Consequently, the general rule is that the lower the tension, the more accurate should be the surfactant formula and the worse is the robustness. This is a very serious problem since the injected formulation is likely to be altered as the surfactant slug progresses through the reservoir. However, there are two ways to avoid this rule. The first one is to use an injected formula as insensitive as possible from the variable likely to be altered like the salinity, temperature, or surfactant mixture characteristics. This can be attained in some cases with complex surfactant mixtures whose components partitioning may be used to counteract the spontaneous change. The second way to improve robustness is to use an artifact in which the spontaneous alteration will result in a transition followed by the opposite retrograde transition, thus producing two optimum formulation zones taking place one after the other. It is shown that such an extended low tension zone may be attained to compensate over some range a spontaneous change in aqueous pH, in brine salinity, and in surfactant originally injected composition.

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

Optimum formulation relationship to predict a solution in micro/macroemulsions applications in Surfactant-oil-water systems.

Keynote Conference. *The European Colloid and Interface Society Symposium EICS*, Universidad Complutense, Madrid, Spain, September 3-8, 2017

ABSTRACT: The 1974 oil embargo motivated a huge research and development effort first in the USA, then in Europe and worldwide, to formulate surfactant-oil-water systems with know-how instruments as pedagogical as Winsor's R ratio, but with commonplace variables and with much more accuracy than by using the HLB number. Shinoda's PIT approach, limited to poly-

ethoxylated surfactants and temperature scans, was extended to the effect of the main formulation variables found in enhanced oil recovery and other practical cases, e.g., oil nature, aqueous salinity, surfactant and cosurfactant types, temperature and pressure.

The basic studies were first carried out with simple systems containing n-alkanes, NaCl aqueous solutions, well defined ionic and nonionic surfactants, alcohols, and variable temperature and pressure. Systematic studies based on Winsor's original ideas were translated into numerical expressions including 5-6 variables to indicate a very general numerical expression of the surfactant affinity difference (SAD) for the oil and water phases, and its dimensionless equivalent so-called Hydrophilic-Lipophilic Deviation (HLD) [1]

$$\text{HLD} = \text{Cps} + k_1 \text{ACN} - k_2 \text{S (or log S)} + k_3 f(\text{A}) + k_4 (\text{T} - \text{Tref})$$

Where Cps is the characteristic parameter of the surfactant, ACN is the oil alkane carbon number, S the NaCl salinity, f(A) the alcohol effect, and T the temperature. k_i are constant coefficients.

An equal affinity of the surfactant for oil and water occurs when HLD=0. It is called an optimum formulation, as a physicochemical situation associated with following general characteristics: a low interfacial tension (in particular ultra low as required in enhanced oil recovery), a three-phase behavior with a bicontinuous microemulsion exhibiting a maximum solubilization of oil and water (as required in formation damage, special cleaning, cosmetics), a minimum macroemulsion stability (as required for crude dehydration and desalting, oil-water separation processes). When HLD is different from 0, its sign indicates the type of macroemulsion produced by stirring, as a corroboration of Bancroft's rule, and its variation from zero is associated with the macroemulsion stability and the trends related to its drop size and viscosity [1]. A continuous change in HLD passing through zero produces an emulsion inversion, and eventually results in a spontaneous emulsification.

The large amount of research and development carried out in the past 30 years in different areas, has allowed to use the HLD concept with finely tuned and more explicit variables, in particular with complex surfactants and oil mixtures. HLD systematic uses avoids the trial and error methods and extremely reduces the time required to find a solution in many applications dealing with petroleum, foods, cosmeceuticals, paints and other micro/macroemulsions cases.

[1] JL Salager et al., Emulsion formulation engineering for the practitioner. In Encyclopedia of Surface and Colloid Science 1: q 1-6. P. Somasundaran Ed., Taylor & Francis, London UK (2011)

SALAGER J.L., ANTON R.E., ARANDIA M.A., FORGIARINI A.M.,

How to Attain Ultralow Interfacial Tension and Three-Phase Behavior with Surfactant Formulation for Enhanced Oil Recovery: A Review. Part 4. Robustness of Optimum Formulation Zone through the Insensitivity to some Variables and the Occurrence of Complex Artifacts.

J Surfactants Detergents **20**: 987-1018 (2017)

ABSTRACT: In enhanced oil recovery, not only the low-tension performance, but also the robustness at optimum formulation is an important issue. The fourth part of our review series is dedicated to robustness, defined as the width of the zone exhibiting three-phase behavior around the optimum formulation, whatever the scanned variable. It is first corroborated from a screening of the available data in the literature that the tension minimum is inversely proportional to the square of the three-phase range in the HLD scale. However, since there is still an inaccuracy of about a factor 10 in the tension minimum, some significant improvement can be attained in some cases by increasing the three-phase behavior width in two ways. The first some formulation

variable such as temperature, surfactant mixture composition or concentration, and water-to-oil ratio. The second way is to produce an artifact through which the optimum formulation is produced twice in a scan. If the distance between the two events in the scan is reduced down to be zero, their corresponding three-phase behavior zones merge and result in a wider WIII region with a low tension. Several cases of such events are reported: alkaline scans, anionic-nonionic and anionic-cationic mixture changes, linear change in composition in three-surfactant mixture, partial precipitation from a surfactant mixture in a salinity scan, and excessive partitioning of polyethoxylated nonionics. More complex transitions with three effects in a single scan or three concomitantly scanned variables show even more possibilities in practice.

PIERLOT C., ONTIVEROS J.F., ROYER M., CATTE M., SALAGER J.L.

Emulsification of viscous alkyd resin by catastrophic phase inversion with nonionic surfactant.

Colloids & Surfaces A, accepted (2017)

ABSTRACT: The addition of water to hydrophobic alkyd resin containing a hydrophilic nonionic surfactant (polyethoxylated-20-oleyl alcohol) was used to produce the emulsion morphology change from W/O to O/W in a small thermostated reactor (50 mL). The so-called catastrophic phase inversion of the water/alkyd resin system was detected by monitoring both, the viscosity by torque measurement and the electrical conductivity, until an equal weight fraction of water and resin is attained ($fw = 0.5$). The two methods provide similar values of the phase inversion point (PIP). Although the determination of the PIP exhibits a small inaccuracy, it is clear that different torque profiles and PIP are observed depending on the resin neutralization level, the surfactant concentration and the water addition rate. For the non-neutralized resin, both, PIP and emulsion drop size, decrease with surfactant concentration increase. The completely neutralized resin could be emulsified using a minimum of 2 wt % of surfactant in the final emulsion. In such a case the water fraction at which inversion occurs ($fw_{Inv} = 0.36$) is independent of the surfactant concentration and a small resin drop diameter (< 200 nm) can be obtained. A more precise study of the reached drop size of the emulsion versus resin neutralization (0, 25, 50, 75, 100 and 125%) indicates that a minimum diameter is obtained around 90–100% neutralization, with no effect of overneutralization. For non-neutralized resin a maximum fw_{Inv} (0.25) can be obtained by reducing water addition rate allowing the production of 0.5 μm droplets in a longer process.

ONTIVEROS J.F., PIERLOT C., CATTE M., SALAGER J.L., AUBRY J.M.

Determining the Preferred Alkane Carbon Number (PACN) of nonionic surfactants using the PIT-slope method. *Colloids & Surfaces A*, accepted (2017)

ABSTRACT: In this paper the Phase Inversion Temperature (PIT) of the $\text{C}_{10}\text{E}_4/\text{n-Octane}/0.01\text{M NaCl}_{(aq)}$ emulsion was used as a reference to determine the changes introduced by adding small amounts of a second surfactant S_2 . The so-called PIT-slope method allowed the calculation of the $dPIT/dx_2$ value, i.e. the linear variation of PIT with the molar fraction x_2 of second surfactant S_2 . For nonionics polyethoxylated surfactants C_iE_j , $dPIT/dx_2$ showed a linear dependency respect to the Preferred Alkane Carbon Number (PACN), one of the parameters of the HLD equation based on phase behavior. We calculated here the PACN from PIT and x_2 data for C_iE_j and other nonionic surfactants derived from isosorbide or glycerol. When possible, the experimental PACN is determined from n-alkane scans at 25°C, and used to validate the proposed estimation method. The effects of changing the oil nature and water salinity on $dPIT/dx_2$ are discussed in terms of the HLD equation and validates the hypothesis that allows calculate the PACN.