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Quantifying the concept of physico-chemical formulation in surfactant-oil-water systems – State of the art

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Abstract The properties of surfactant-oil-water systems either at equilibrium or in dispersed state depend upon a large number of formulation variables that include not only the nature of the three components, but also the influence of electrolytes, alcohols and other additives (type and concentration), as well as temperature and pressure.

These variables contribute to an overall affinity balance at interface, a fact that was recognized in Winsor's pioneering work as an attempt to interpret the experimental results rendered by the use of Bancroft's rule or Griffin's HLB. Then, Shinoda introduced the Phase Inversion Temperature (PIT), a characterization parameter that relies on an easily attainable experimental situation, whereas Beerbower and Hill proposed the Cohesive-Energy-Ratio (CER) approach as an attempt to develop a theoretical concept that could be easily linked with experimental results. In the 1970s, the Enhanced Oil Recovery research drive resulted in an extensive amount of experimental work dedicated to the

development of multivariate empirical correlations for the attainment of three-phase behavior, a very well defined physico-chemical situation. The correlations contain a numerical contribution of the effect of each formulation variable that was later identified as an energy contribution to the surfactant affinity difference (SAD), a generalized formulation variable. The straightforward use of the correlations motivated experimentalists to extend its validity to very different systems, far beyond the original oil recovery scope. On the other hand, the surfactant partition coefficient between oil and water, an early measurement of the physico-chemical match, has been recently reinstated to a prominent place thanks to enhanced analytical methods; this approach is shown to lead to the same kind of quantitative description as the SAD, with a partial contribution of each group to the overall balance.

Key words Surfactant – HLB – PIT – formulation – microemulsion

Introduction

Surfactant-oil-water systems occur in hundreds of domestic applications such as personal care products, pharma-

ceuticals, foods and beverages, laundry and washing compounds, paints application, and so forth, as well as industrial processes such as waste water treatment, enhanced oil recovery, detergency and cleaning, paper making, ore separation, etc.

These systems are often formulated to provide many different properties such as tensioactivity, wettability, dispersion stabilization, solubilization in microemulsion, fancy rheological behavior, visual enhancement with liquid crystal or latex dispersion, etc. As a consequence, the number of components in a commercial product is often astonishingly high, for instance in the 40–50 range. No wonder that the formulation has been considered an art, in which a successful “magic recipe” is worth a lot of development time and money.

This paper is aimed at showing that the Art of formulation has evolved into a Science, and that much know-how is now available to reduce the uncertainties of the formulator alchemy.

What is the physico-chemical formulation?

The formulation deals with the nature of the components, while the proportions or respective amounts are considered as composition variables. In the simplest ternary system case, there will be three components, i.e., the surfactant (S), the oil (O) and the water (W), each with its chemical potential yardstick that quantitatively defines its physico-chemical state at a given temperature and pressure.

The physico-chemical formulation variables are thus at least five in a true ternary: three standard chemical potentials, temperature and pressure; in an actual SOW system there are many more formulation variables, since all components are often very complex mixtures, either in order to produce a synergy or to adjust some property. The aqueous phase always contains electrolytes that can be different in nature and concentration, while the oil phase can be as simple as a pure alkane or as complex as a crude oil. On the other hand, so-called additives, e.g., co-surfactants, co-solvents, hydrotropes, or protective colloids are introduced into the system for some reason.

HLB and PIT

The first approach was to implicitly reduce the number of variables to be taken into account down to only one or two. Obviously, this short cut has a chance to work only if the selected variables are the most important ones, and/or if the other formulation variables are either constant or have a negligible effect on the particular problem. Although this simplification can lead to serious inaccuracies, it is the simplest way to reduce the dimension of the formulation problem.

This was the premise taken in the two first empirical yardsticks: 1) Griffin’s Hydrophile–Lipophile Balance or

HLB introduced in 1949, and 2) Shinoda’s Phase Inversion Temperature or PIT proposed in 1964 [3].

The HLB number depends essentially upon the surfactant, although the original experimental determination based on an emulsion stability maximum was taking into account the oil phase nature. However, these experiments are very tedious and inaccurate and are no longer into use. Today, the HLB is a surfactant characteristic parameter that is calculated directly from the relative weight of the hydrophile and lipophile part of the surfactant. For instance, the HLB number of polyethoxylated nonionic surfactants is estimated by:

$$\text{HLB} = \frac{100}{5} \times \frac{\text{molecular weight of polyethylene oxide chain}}{\text{total molecular weight}} \quad (1)$$

As a consequence, the HLB number cannot render the effect of the water phase salinity, or the influence of the temperature, or other variables which are known to affect the physico-chemical situation in SOW systems. This means that the inaccuracy can be as serious as several HLB units in some cases. Another drawback is that surfactants with the same HLB number can exhibit quite different behavior, in particular if they contain mixed products that exhibit a fractionation phenomenon.

Nevertheless, the HLB scale is still very widely used, probably because of its extreme simplicity and because it gives a “guesstimate” that many would consider good enough. However, it is believed that many experimental discrepancies and probably a considerable lost of research and development time can be credited to HLB inaccuracy.

The PIT was originally the temperature at which a non-ionic surfactant switched its dominant affinity from the aqueous phase to the oil phase, in a so-called phase transition process. Later on, it was related to the emulsion inversion, to be finally renamed HLB-temperature a few years ago to mean that it was the temperature at which the hydrophilic and lipophilic tendencies of the surfactant were balanced. This concept is linked with the dehydration of the polyethoxylated chain with increasing temperature that reaches a point where the surfactant is no longer soluble in water and a surfactant phase separates from the original aqueous solution (in absence of oil phase), and results in a turbidity occurrence at the so-called cloud-point. It has been known for quite a while that the presence of a small amount of dissolved hydrocarbon can change the cloud point, but this effect is not actually manageable enough for measurement purposes. On the contrary the PIT measurement results in much more reliable data, which take into account two formulation

variables, i.e., the surfactant type and the oil phase nature. Of course variables such as the water salinity or the alcohol addition are not taken into account and can alter the PIT estimate.

Although the PIT is limited to ethoxylated nonionic surfactant systems and to the usual liquid water range of temperature which can be handled safely, it has a very important precursor position when related to the recent advances. In effect, the PIT experimental procedure was indeed the first unidimensional formulation scan in which the temperature is changed continuously with all other formulation variables held constant, until an experimentally detectable situation arises.

In the light of current knowledge, it can be said that this was a farsighted view and a precursor technique. Today, the PIT can be viewed as the optimum temperature in the multivariant SAD (Surfactant Affinity Difference) concept to be discussed later on. *A posteriori*, this explains why the PIT of surfactant mixtures follows a linear mixing rule with respect to the PITs of the base surfactants, a fact that could have surprised some thermodynamic specialists of the time. It is now known that this may be a quite approximated rule because of the fractionation phenomena that are likely to occur near the PIT.

Winsor *R* ratio

The second kind of approach presented by Winsor [4] in 1954 was theoretical in essence. The relationship between the different components was not measured through some experimental occurrence but it was estimated according to a balance of interaction energies between the surfactant molecules (located at interface) and the oil and water bulk phase molecules, per unit surface area.

The original Winsor interaction energies ratio was written

$$R = \frac{A_{CO}}{A_{CW}} \quad (2)$$

later on, a more complete definition was preferred:

$$R = \frac{A_{CO} - A_{OO} - A_{LL}}{A_{CW} - A_{WW} - A_{HH}}, \quad (3)$$

where the interaction subscripts C, O, W, L and H, respectively refer to the surfactant as a whole, the oil, the water, the surfactant lipophilic and hydrophilic group.

A change in the *R* ratio from $R < 1$ to $R > 1$ or vice versa was associated to essentially all phase behavior transitions and corresponding phenomena occurrence, a bulk of know-how that has been reviewed extensively [5].

Winsor's clever rationalization was some 20 or 30 years ahead of his time. It introduced a very important feature, i.e., the concept of a unique, global, and overall formulation parameter, e.g., the *R* ratio, to render the effect of all the distinct formulation variables actually manipulated by the formulator. In other terms, he stated that a physico-chemical situation in a SOW system could be handled with a single parameter instead of the score of known formulation variables. This was extremely important for the advancement of subsequent research, since it made it clear that the observed phenomena should not be related to the specific numerical values of the formulation variables (a premise which was unmanageable because of the large number of variables), but instead to some overall physico-chemical condition to be satisfied by and depending upon these variables.

Winsor failed to find a quantitative numerical expression for this *R* parameter as a function of the individual formulation variables, probably because the liquid state theory was not advanced enough to estimate accurately the molecular interactions; in any case, it would have lacked the high speed computer required to carry out such calculations, which by the way, are probably not yet sufficient. As a matter of fact, the level of approximation used in the current model is still relatively crude [6].

On the other hand, it can be said that Winsor missed a point that could have made its concept easier to link with experimental measurements. Winsor was dealing with energies, and as it is known from the first law of thermodynamics, the energies do sum up. It can be conjectured that had Winsor taken the algebraic sum of the interaction energies rather than their ratio, the translation of the generalized formulation concept into a numerical equation would have evolved earlier. Yet, Winsor's *R* ratio allowed him to make his point and to relate the generalized formulation, i.e., the *R* value, to the phase behavior of SOW systems [4–5].

Winsor's research work indicated that in a true SOW ternary there were only so-called I, II, and III, three types of diagrams, and that the type of diagram, and thus of multiphase region, depended only upon the interaction energies ratio *R*.

After that, it was clear that the formulation effect could be described, at least in the ternary approximation, through a single, although complex, parameter that can be referred to as the generalized formulation whatever its actual form, *R*, or as in other concepts to be discussed later on. This was quite a breakthrough since it reduced considerably the number of independent variables to be handled, and it made it possible to compare or compensate effects of the different formulation variables, and to find alternate physico-chemical situations without carrying out millions of experiments.

If it is understandable that Winsor's work was overlooked in his time and over the next 20 years, because it had no direct application beyond the pedagogical message, it is unfortunate that this concept had not permeated yet in industrial practice after the enhanced oil recovery research effort of the 1970s showed its importance in the resolution of actual problems [5, 7].

Cohesive energy ratio

In an attempt to attain a formulation concept with both the theoretical content of Winsor's R and the down the bench numerical data feature of the HLB, Beerbower and collaborators [8] introduced the Cohesive Energy Ratio (CER) approach in 1971. From the conceptual point of view it was very similar to Winsor's R , but this time it was the ratio between the adhesion energy of the surfactant "layer" with the oil phase, and the adhesion energy of the surfactant "layer" to the water phase. To express this ratio, first recall that the cohesion energy between molecules of a pure component system is calculated as:

$$\delta^2 = \frac{\Delta H_{\text{vap}}}{v_L}, \quad (4)$$

where ΔH_{vap} is the enthalpy of vaporization, and v_L the molar volume in the liquid state, both measurable quantities. δ is the so-called solubility parameter, that is a direct measurement of the intermolecular cohesion forces. When a mixed system is dealt with, the adhesion forces between the two kinds of molecules are calculated according to London's geometric mean relationship as follows.

If

$$\delta_{AA}^2 = \frac{\Delta H_{A\text{-vap}}}{v_{A\cdot L}}$$

and

$$\delta_{BB}^2 = \frac{\Delta H_{B\text{-vap}}}{v_{B\cdot L}} \quad \text{then} \quad \delta_{AB}^2 = \delta_{AA} \delta_{BB}. \quad (5)$$

Solubility parameters have been measured and tabulated for hundreds of substances, and they are often used in relation with the regular solution model to estimate the activity coefficient in a mixture and the eventual separation into two phases. The adhesion between the surfactant and the oil phase was estimated by calculating a δ_{AB}^2 term where A represented the oil phase and B stood for the lipophilic part of the surfactant that was assumed to be similar to that of a hydrocarbon with the same chain length. Unfortunately, the corresponding adhesion energy on the water side of the interface was not easily calculated, in particular because of the lack of experimental data for the hydrophilic group of some surfactants.

As a consequence of this drawback, as well for the lack of accuracy of the geometric mean assumption in this case, the final numerical value of the cohesive energy ratio was as inaccurate as the HLB number and even worse in some cases, and the CER was no real help in practice.

Numerical correlations for optimum formulation

In 1973, the oil embargo triggered an intense research effort to develop enhanced recovery processes aimed at bringing to the surface the oil that remained trapped in the reservoir porous medium, after the conventional secondary recovery was carried out. Among the proposed methods were the so-called low-tension, micellar or surfactant flooding processes, in which a surfactant solution of appropriate formulation was injected in the reservoir to produce an ultra low interfacial tension between the crude and the water, so that the capillary forces could be easily overwhelmed by a water flooding [7]. The huge amount of research carried out in industrial and academic centers showed that an ultra low tension minimum could be attained when the formulation matched the Winsor III case, at which $R = 1$. The occurrence of a so-called optimum formulation (as it was labeled because it coincided with the ultralow tension occurrence) was thus linked with a precise physico-chemical situation in which the affinity of the surfactant for the oil phase exactly equilibrated its affinity for the water phase. Since these affinities could possibly change with any of the formulation variables, it was necessary to know how this could happen from the practical point of view, i.e., with numerical data related to bench variables such as the water salinity, the temperature or the oil phase nature.

Exhaustive experimental studies carried out for both anionic and nonionic surfactant systems showed that the optimum formulation was attained whenever a certain condition between the formulation variables, so-called correlation for optimum formulation, was satisfied.

Salager et al. found that for anionic surfactants the correlation can be expressed as [9]:

$$\ln S - K \text{ACN} - f(A) + \sigma - a_T \Delta T = 0. \quad (6)$$

For nonionic surfactants Bourrel et al. [10] found a similar correlation:

$$\alpha - \text{EON} + b S - k \text{ACN} - \phi(A) + c_T \Delta T = 0, \quad (7)$$

where S is the salinity in wt. % of NaCl, ACN or Alkane Carbon Number is a characteristic parameter of the oil phase, $f(A)$ and $\phi(A)$ are function of the alcohol type and concentration, σ , and α are parameters characteristic of the surfactant structure, and EON is the average number of ethylene oxide group per molecule of nonionic surfactant.

ΔT is the temperature deviation measured from a certain reference (25 °C), k , K , a_T and c_T are empirical constants that depends upon the type of system.

Surfactant affinity difference (SAD)

Let us call SAD the “Surfactant Affinity Difference”, that is, the difference between the negative of the standard chemical potential of the surfactant in the oil phase and the corresponding term for the water phase.

$$\text{SAD} = -\mu_0^* - (-\mu_w^*) = \mu_w^* - \mu_0^* . \quad (8)$$

The equivalence of the right-hand term of the correlation with SAD/RT was proposed several years after the finding of the empirical correlations, as a physico-chemical interpretation of their meaning [11]. Now, it is clear that SAD is a form of the generalized formulation parameter, hopefully expressed in terms of measurable and manipulable variables. It is worth noting that the correlations do not contain any cross-term, but on the contrary, are linear forms of independent terms, as in thermodynamics' first law. Each term can be viewed as an energetic contribution to the overall interaction balance.

The original purpose of these correlations was to relate numerically the effect of the different formulation variables in order to attain or to maintain an optimum formulation at SAD = 0 by changing two or more variables in a compensated way. In addition to the cited original works, several other studies contributed to extend the range of application of these correlations to other oils, other electrolytes and other surfactants, and some reviews are available [5, 11].

The by-product of these studies was that an optimum formulation can be taken as a reference state, that can be accurately pinpointed by experiment. As a consequence, an off-optimum formulation can be defined as a deviation from optimum formulation. Thus, it is possible to compare systems in a same physico-chemical state (same deviation from optimum formulation) although they have no single formulation variable with a common value. This deviation concept was successfully applied to describe the relationship between the formulation and the emulsion properties.

It should be mentioned that the same kind of reasoning was carried out by other investigators, with quite similar results from the conceptual point of view, even though they did not attain the numerical quantification level of the SAD expression.

Krugliakov [12] recently presented to western audience his concept of Hydrophile–Lipophile Ratio (HLR), which is the ratio of the energy of adsorption of the surfactant molecule from the water phase to its energy of adsorption from the oil phase; this was first published in

the Russian literature 20 years ago. This is essentially the same overall presentation as Winsor's, but with an energy term whose variation can be traced back to the formulation variables, at least in some approximate way. In any case, it seems that the HLR suffers from the same drawback as Winsor's R ratio, i.e., it is a ratio of energy terms instead of an algebraic difference.

Free energy of transfer and partition coefficient between excess phases of a Winsor III system

In his 1957 analysis of the physical-chemistry of emulsifying agents, Davies [13] presented two different suggestions. First, he proposed to split the HLB into group contributions, probably with an implicit energy summation underneath this idea; and on the other hand, he related the distribution of the surfactant between oil and water to the HLB.

The free energy of transfer of a molecule of surfactant from water to oil is:

$$\Delta G_{(w \rightarrow o)} = RT \ln(C_w/C_o), \quad (9)$$

where the C_w and C_o are the surfactant concentrations in water and oil, respectively. Davies related the partition coefficient to HLB and to the rate of coalescence of the two types of emulsions, according to his theory that the emulsion type was determined by the ratio of these rates. In his analysis, he took care to point out that the partitioning should be considered in absence of any micellar structure. This was quite a problem as far as the analytical technique was concerned. In effect, the CMC of nonionic surfactant is so low that the concentrations to be dealt with were beyond the range of separation-detection equipment available in the 1960s.

The measurement of surfactant distribution in oil–water systems with extremely low surfactant concentration is not the only experimental path. There is another elegant way that works at high surfactant concentration, i.e., the analysis of surfactant in excess water and excess oil in three-phase systems which are at optimum formulation. This technique was used by Graciaa and collaborators [14] to interpret and predict the partitioning of ethoxylated nonionic oligomer mixtures and to compute the actual interfacial composition with a pseudophase model. Since the partitioning was measured at optimum formulation, there was as many partitioning data as optimum formulation. In other words, the partitioning depended not only upon the surfactant HLB, but also upon all formulation variables.

In a recent investigation aimed at screening different cases of optimum formulation SOW systems, Marquez [15] showed that the partition coefficient of a surfactant

species is an excellent indicator of the concept of generalized formulation. In the assumption that the activity coefficient is unity, which is legitimized by the low surfactant concentration found in the excess phases of Winsor type III systems, then the equilibrium between the water and oil phases can be written in terms of the chemical potentials of the surfactant:

$$\begin{aligned}\mu_w &= \mu_o = \mu_w^* + RT \ln C_w / C_{w,ref} \\ &= \mu_o^* + RT \ln C_o / C_{o,ref},\end{aligned}\quad (10)$$

where the standard chemical potentials are indicated with an asterisk, while the concentration references bear the subscript ref. If the partition coefficient is defined as $K = C_w / C_o$, then:

$$\begin{aligned}RT \ln K + \text{constant} &= \mu_o^* - \mu_w^* = \Delta G_{(w \rightarrow o)} \\ &= -\text{SAD}.\end{aligned}\quad (11)$$

The constant is the partition coefficient between the two reference states. As a matter of fact, the value of this constant does not matter, since it does not change with the formulation variables that influence the μ^* s. By measuring the partition coefficient with different systems exhibiting a variety of oils, surfactant characteristics, alcohol content, brine salinity, and temperature, Marquez was able to correlate the term $RT \ln K$ with the formulation variable in a linear relationship very similar to SAD expression by the correlations, according to a splitting-

contribution technique suggested by Cratin [16]. For instance, these studies allow the experimental determination of the molar free energy of transfer $\Delta\mu^*(w \rightarrow o)$ of a ethylene oxide group or to a methylene group by showing that:

$$\begin{aligned}RT \ln K(\text{EON, SACN}) &= \text{EON} \times \Delta\mu^*(\text{EO group}) \\ &+ \text{SACN} \times \Delta\mu^*(\text{CH}_2 \text{ group}) + \Delta\mu^*(\text{remaining}),\end{aligned}\quad (12)$$

where EON is the number of ethylene oxide groups in the oligomer molecule and SACN is the number of methylene groups in the surfactant hydrophobe. Marquez et al. [15, 17] were also able to determine the contribution of temperature, water salinity and alcohol content. The determination of these physico-chemical parameters is fairly straightforward if the formulator is able to reach an optimum formulation with the desired system, and provided that he may use one of the modern analytical technique to measure the concentration of the different surfactant species in the excess phases.

Conclusion

Winsor's R concept has now quantifiable equivalents, and the formulator should invest some time in knowing these new approaches that give more reliable results than the early yardsticks such as the HLB number.

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