Review on the Surfactant Characteristic Parameter used in EOR, Crude Dehydration and Other Formulation Applications

A simple physicochemical concept useful in practice but complex in real cases

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with the help of Raquel E. Antón, Ana M. Forgirini, Johnny Bullón, Ronald Marquez and José G. Alvarado
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Abstract
The surfactant characteristic parameter (SCP) is numerically related to its amphiphilic interactions with oil and water phases. Basic ideas have resulted in the energy balance concept so-called the hydrophilic-lipophilic deviation from optimum formulation (HLD linear equation) which integrates the effects of 6 variables: surfactant and co-surfactant, oil phase nature, brine salinity, temperature, and pressure. The HLD is very important because it allows to model and predict the phase behavior, interfacial tension, micro-emulsion solubilization, as well as emulsion and foam properties. However, this expression is too simple to be applied for real cases involving surfactant mixtures; it should therefore be better modeled.

Keywords: Surfactant Characteristic Parameter, physicochemical formulation, HLD, microemulsion, surfactants

1. Introduction
Surfactants are amphiphilic molecules going to surfaces and interfaces to produce specific effects. Typical interfaces are the limits between two immiscible phases, e.g. two fluids like water/air, and water/oil or solid/liquid. Surfactants tend to crucially determine the properties on the equilibrated systems (surface and interfacial tension, adsorption, association, bulk solution solubilization, and phase behavior) as well as those of multiphasic dispersions (e.g. emulsions, foams, suspensions), which vary both with the selected surfactant(s), and with the nature of the other ingredients.

The surfactant is generally described according to its chemical formula, e.g. type and typical characteristics of hydrophilic and lipophilic group(s), ionic or nonionic head, linear or branched structure, single or multiple head(s) and tail(s), pure species or mixtures for which some average tail and average head group may be estimated some way. However the formula is not a definite characteristic concerning the effects because different formula surfactants could produce similar effects and result in similar properties; on the other hand surfactants with a very small difference (like a single methyl group added somewhere in the molecule), could behave very differently.

Surfactants are used in hundred of products in the classical domestic and industrial applications, e.g. detergent and cleaning, personal care products, pharmaceutical and cosmetic vehicles, foods and beverages, paints, corrosion inhibition, waste water treatment, paper making, ore separation and concentration, lubrication, petroleum recovery and treatments, etc.
However, the surfactant classification according to the application is not necessarily useful because the association between surfactant(s) and other ingredients used in complex systems is far from unique, and, it can sometimes be somewhat contradictory. For instance the same surfactant can stabilize an emulsion or break it, depending on the aqueous and oil phases used and on the temperature and the way it is handled. The classification according to its behavior in water (i.e. soluble or insoluble, ionic or nonionic) is somewhat useful but it is often too simple and in general insufficient in critical cases. A practical classification must thus be related to some determinant behavior, or some attained characteristic property of interest, in water solution or in multi-phase system, such as those containing oil and water, or solid and water.

It is worthwhile mentioning that in the petroleum-petro-chemical industry the efficient use of surfactants in complex oil-water systems implies a highly precise formulation and a much more accurate surfactant characterization than in most other domestic and industrial applications. The corresponding knowledge and know-how has been developed since 1974 to solve enhanced oil recovery formulation issues and other exploration-production-refining problems, e.g. formation damage remediation, crude oil dehydration at well or for hydrocarbon cut desalting in petroleum refinery. The present review updates the quantification of the surfactant characterization proposed 20 years ago.

2. The principle of characterization of surfactant-oil-water systems

The first and simplest way to characterize a surfactant from the physicochemical point of view, was first considered to be independent of the nature of other ingredients, but according to its general behavior as far as a property of interest was concerned.

The principal phenomena are:
- The phase behavior with one solvent fluid, i.e. completely or partially soluble, in particular the concept of cloud point for nonionic surfactants that indicates the importance of temperature in polyethoxylated surfactant case.
- The surfactant molecules association in a solvent fluid, e.g. the formation of micelles or other aggregates in water or in oil.
- The association structure of surfactants with two immiscible fluids, e.g. oil and water, as in micro-emulsions, liquid crystals, vesicles, liposomes, etc...

Particularly important properties in petroleum applications are:
- The phase behavior with several phases, i.e. 1, 2 or 3, in a surfactant-oil-water (SOW) ternary, or in a quaternary system when adding a second surfactant or a co-surfactant like an alcohol.
- The surface or interfacial tension at fluid/fluid limits (e.g. air/water, oil/water) that varies with the content as well as with the nature of the ingredients.
- The adsorption at interface and its consequences as far as the tension and wettability are concerned.
- The interfacial effects concerning dispersions with a high surface area, as in emulsions, foams, and suspensions.

The fact is that these physicochemical properties that depend on the surfactant also depend on the other ingredients (water, oil, and other solvents nature) and conditions (temperature, pressure). What is more, a good characterization could imply to handle not only a single surfactant molecule specification but, in practical situations, many other issues as well. This is because, in general, the surfactant is not a single substance but a mixture of two or more different commercial types so as to gather advantageous properties, and also because, for economic reasons, each commercial surfactant is already a mixture of similar species.

The other ingredients, in particular in a petroleum application, involve the use of several variables to describe their composition, such as the water (from an aqueous solution of sodium chloride to different salts composition in reservoir brine or in waste water or blood) and the oil phase (from pure n-alkane to edible triglyceride oils or complex crude oils), as well as alcohols co-surfactants or substances influenced by pH in particular applications. In all these cases the temperature exerts an influence on many different phenomena, and in petroleum well and refining units the pressure is also critical for the 2 or 3 liquid phase behavior or the occurrence of gas or solid.
Some applications only require an approximate characterization and thus a simple way to handle the formulation is enough in practice, as it happened at first with pioneering proposals such as Bancroft's rule (1915)\(^3\), Langmuir wedge theory (1917)\(^4\), and Griffins' hydrophilic-lipophilic balance (HLB in 1949)\(^5,6\). Then, as the surfactant systems used were getting more sophisticated, a more complete approach was proposed. It took into account all the formulation variables, but was still as a qualitative description such as Winsor's R ratio (1954)\(^7,8\), and its extension as Beerbower's cohesive energy ratio (CER in 1969)\(^9\), as well as the geometrical approach of Israelachvili's critical packing parameter (CPP in 1976)\(^10-12\). Shinoda's phase inversion temperature (PIT in 1964)\(^13-16\) was proposed to describe a temperature characteristic value limited to polyethoxylated nonionic surfactants, but quite accurate and also depending on the system oil phase or aqueous salinity.

It was finally during the first years of research in enhanced oil recovery with surfactants that a systematic one-dimensional formulation scan with anionic surfactant was used according to Winsor's principle\(^17\), with a proposed basis on chemical potential equations\(^18\). A study on bi- and multidimensional scans produced a numerical expression of a physico-chemical correlation for the attainment of three-phase behavior and minimum tension\(^19\) for ionic and nonionic surfactants\(^20,21\). The generality of the correlation for the occurrence of an optimum formulation and related phenomena was expressed as the surfactant affinity difference (SAD in 1983)\(^22-24\) and its dimensionless equivalent hydrophilic-lipophilic deviation (HLD in 2000)\(^25\).

The state of the art at this time can be found in a general book on interfacial phenomena\(^26\), four books specifically dealing with microemulsion\(^27-30\) and some articles\(^31-38\).

It is worth noting that many related fundamental studies on phase behavior and interfacial tension have been carried out on systems containing pure surfactants of the polyethoxylated nonionic type with the temperature as the formulation variable. These were conducted by Kahlweit and Strey in Germany, Shinoda and Kunieda in Japan, and Langevin and Aubry in France. Theoretical and advanced results can be found in journals like Langmuir, J. Colloids and Interface Science, J. of Physical Chemistry, Colloids and Surfaces A, J. of Dispersive Science and Technology, Colloid and Polymer Science.

3. One-dimensional formulation scan

The basic technique to study a SOW system, i.e. its phase behavior (and associated interfacial tension), was the one proposed by Winsor after determining the variables likely to produce a change in the interactions between the surfactant molecules adsorbed at interface and the oil and water phases. In the very simple case of pure surfactant, NaCl aqueous solution, and n-alkane oil, these variables were the following: the head and tail nature of the surfactant (i.e. its hydrophilicity and lipophilicity), the salinity (S) of the water phase, and the alkane carbon number (ACN) of the oil, as indicated in Figure 1, as well as the temperature and pressure.

By continuously changing one of these variables in a so-called formulation scan, the ratio of the interactions of the surfactant with oil (Aco) to its interaction with water Acw (i.e. the Winsor's ratio R = Aco/Acw) changes in a monotonous way, eventually from below to above unity or vice-versa.

Consequently, at some point of the scan, the R ratio must be unity. This physicochemical occurrence (R = 1 according to Winsor interaction ratio) was called optimum formulation for the scanned variable value because it also corresponds to the minimum interfacial tension, sometimes ultralow, which is the main goal in enhanced oil recovery purpose. If there is no minimum tension in the performed scan, it means that the range is not the proper one to attain somewhere an optimum formulation, i.e. a balanced interaction of the surfactant for oil and water for the given fixed conditions.

In such a case the surfactant has to be changed for a more hydrophilic or more lipophilic one or alternatively some other conditions should be changed to attain R = 1 somewhere in the scanned variable range.

Figure 2 indicates the variation of the interfacial tension and of the phase behavior along a formulation scan (here the changing variable is the aqueous phase salinity) which exhibits an optimum salinity (indicated as S*).
It is seen that close to the optimum formulation a three-phase behavior takes place with a middle-phase micro-emulsion in equilibrium with excess water and excess oil phase. These excess phases contain a very small concentration of surfactant, typically at or lower than its critical micelle concentration, as seen essentially to be zero in the ternary triangle in the center of the Winsor III diagram.

All the surfactant is in the micro-emulsion in a complex bi-continuous structure containing both oil and water. This has been extensively studied in review books. In the three-phase system there are two interfaces in a test tube, thus two interfacial tensions, so-called $\gamma_{mo}$ and $\gamma_{mw}$. At optimum formulation (which happens at the crossing of these two tension curves), the third interfacial tension between excess oil and excess water $\gamma_{ow}$ is at its minimum, slightly higher than the crossing value between $\gamma_{mo}$ and $\gamma_{mw}$. More detailed information may be found elsewhere. In practice, the range with three-phase behavior is relatively narrow; it is actually narrower when the minimum tension is lower, at the usual surfactant concentration for EOR, i.e. around 0.5 wt% and eventually below.

On the WI diagram (here at lower salinity) R < 1, i.e. the surfactant has more interactions with the water phase in which it forms a (gray) micro-emulsion water phase in equilibrium with excess oil, whereas in the other two-phase diagram WII (here at higher salinity), R > 1 and the surfactant is in a (gray) oil micro-emulsion in equilibrium with an excess water.

The phase behavior change produced by an increase in brine salinity is usually shown as the diagram transition WI > WIII > WII indicates. The actual phase behavior at the square point in the multiple phase system is noted in the diagram WI-WIII-WII. Above the micro-emulsion point in the WIII diagram, the behavior is monophasic and it is often indicated a WIV.

The formulation variation through an optimum value has been found to be a very special event in which many different phenomena are taking place. This is exhibited in Figure 3 where the scanned variable is indicated as V* at optimum, with the horizontal arrows showing the direction of increasing change for salinity, surfactant tail length, surfactant head hydrophilicity (e.g. ethylene oxide number for polyethoxylated nonionic), temperature for both ionic and polyethoxylated nonionic, and pressure.

Fig. 2: Interfacial tension and phase behavior along in a formulation (salinity S) scan.
It can be seen that, aside the minimum tension previously mentioned as the way to determine the optimum formulation $V^*$ at the center of the three-phase behavior (WIII) zone in Figure 3.1, the solubilization (as the amount of excess phase incorporated in the swollen micelles or bicontinuous structure) passes through a maximum in figure 3.2 and the partition coefficient is close to unity (for ionic surfactants) in Figure 3.3.

It has been shown experimentally\textsuperscript{17} and explained by means of a micro-emulsion theoretical model\textsuperscript{41} that the tension varies inversely to the square of the solubilization parameter. In other words, the optimum formulation to attain a low tension in a scan is also the optimum to solubilize more oil and water into a single phase for a given amount of surfactant. A performance index PERFIND, taken as $-\log_{10} \gamma_{\text{min}}$ where $\gamma_{\text{min}}$ is the minimum tension in a scan, has been recently introduced and precisely related to the different variables for a very simple system\textsuperscript{36,37,42}.

An emulsion made by stirring an equilibrated SOW system also exhibits particular characteristics at optimum formulation\textsuperscript{43-45}. It inverts, as indicated by a large change in conductivity in Figure 3.4, where it passes from O/W to W/O as the phase behavior changes from WI to WII. Its stability passes through a deep minimum in Figure 3.5, i.e. the emulsion becomes very unstable, probably because the surfactant has a lower chemical potential in a micro-emulsion middle phase than at the oil-water interface where it could generate stabilization mechanisms. Consequently, it may be said that the surfactant is trapped in the micro-emulsion and that the oil/water mixture dispersed by the stirring would coalesce instantly as in absence of surfactant. This specific emulsion strong instability at optimum formulation has recently been found to match and thus to be due to a very low interfacial rheology elastic modulus\textsuperscript{46-48}.

Figure 3.6 also shows that the emulsion viscosity is particularly low, probably because the low tension favors the elongation of the drops when the emulsion is submitted to a shear. More detailed information about these many specific properties at the optimum formulation of a scan may be found in details elsewhere\textsuperscript{1}.

![Diagram](https://via.placeholder.com/150)

**Fig. 3**: Different occurrences taking place at the optimum value ($V^*$) of a single variable scan, whatever the formulation variable $V$.

### 4. Surfactant Characteristic Parameter (SCP) and its applications

Before going to more generality about the number of formulation variables, it is worth remarking that attaining an optimum formulation by continuously changing a single variable is an extremely useful method in different petroleum exploration-production-refining applications. When a petroleum reservoir is selected the water salinity is equivalent to some NaCl brine, the oil nature is practically described by some equivalent alkane (EACN), and the temperature is fixed. Consequently, the variable selected to be scanned and to attain an optimum formulation is principally the surfactant characteristic parameter, the so-called SCP in what follows\textsuperscript{49,50}.

It is known that SCP increases with the tail length\textsuperscript{35,36,51} and that it decreases when the head group is more hydrophilic for instance when passing from alkyl carboxylate to alkyl sulfate, or when increasing the number of ethylene oxide groups for ethoxylated nonionics, with no change in the rest of the molecule.
Consequently a scan of the SCP variable carried out by changing the surfactant is a way to pass through an optimum formulation, either with a proper surfactant or with an adequate mixture of two (or more) of them in order to accurately attain the required SCP value, as was proposed in the late 1970’s\textsuperscript{52}. This is summed up at the end of this review.

In enhanced oil recovery an optimum formulation would result in a minimum interfacial tension in a single variable scan, which, if low enough (< 0.001 mN/m), could be a partial solution to start moving the crude oil trapped in the porous medium.

The fact that the emulsion is very unstable at this optimum formulation means that any emulsified system produced by the displacement, is likely to coalesce thus avoiding the formation of viscous emulsions with very small droplets. On top of it, the low viscosity of the emulsion at optimum formulation is an additional reason for an easy displacement of the crude oil.

In the well perforation a drilling fluid is used to cool and lubricate. It thus contains oil and water as an emulsion, generally with solid particles such as clays and high-density solids. The drilling fluid tends to form a filter cake at the perforated wall and to penetrate into the porous medium. Both effects tend to be detrimental when the petroleum production is started because they limit the flow. Such a formation damage may be eliminated before starting production by dissolving the drilling fluid in a single phase and pumping it back. This can be done by forming a micro-emulsion single phase down hole so that what is formed by mixing the injected fluid with the plugging emulsion-dispersion correspond to the WIV part in a SOW ternary diagram.

Since Winsor WIII diagram is the one with the higher solubilization in the formulation scan, it is again the system corresponding to optimum formulation that will produce the more efficient solubilization of the plugging drilling fluid\textsuperscript{53,54}. It is of course not that simple since the injected fluid often requires acids in its water phase to dissolve solids and solvent to destroy any gel, but the main goal is to attain an optimum formulation with a high performance index.

After a few years or even a few months only of starting producing from a reservoir well, water is mobilized and dragged with the oil. Since the lift from down hole by pumping through tubing results in some shear and some stirring, a water-in-oil emulsion is produced from the well and it is often very stable because of the presence of asphaltenes, naphthenic acids, or resins. Because these chemicals act as lipophilic amphiphiles, the corresponding phase behavior of the emulsified system at the wellhead is WII. The dehydration process mainly consists in altering the formulation, displacing it to the WIII phase behavior case at which the emulsion is extremely unstable and thus breaks quickly. In practice a surfactant solution containing a so-called demulsifier hydrophilic surfactant is injected, so that the mixture of the natural surfactants and the demulsifier exactly attains the optimum formulation in the SCP scale.

In a petroleum refinery, some cuts have to be treated to remove salt either as solid crystals or in remaining brine droplets. To do so, some water is generally added and a W/O emulsion is made so that salts quickly transfer to the water drops. The emulsion must be quickly broken in a process that is similar to crude oil dehydration. Again, an appropriate demulsifier is added to attain the optimum formulation where the emulsion stability becomes extremely low, and the water separation is fast in a process called desalting.

5. Multidimensional scans and optimum formulation relationships

Figure 2 shows that the increase in some formulation variable produces a transition opposite to the transition generated by the increase of other variables, i.e. they are likely to compensate if they are both increased. For instance an increase in salinity produces a WI > WIII > WII transition, while an increase in ACN produces the opposite WII > WIII > WI.

Figure 4 displays the two-dimensional S-ACN space in which both formulation variables can be changed. For the sake of simplicity, numerical values are indicated in abscissa for ACN and in ordinate for lnS. The lnS is used instead of S because it is well known that in chemical potential estimations the concentration effect is always through its logarithm because of the usual general expression:

\[
\mu \sim \mu^* + RT \ln C \tag{1}
\]
Two scans are going to be carried out for a system containing a given alkylbenzene sulfonate and a fixed 3 vol% 2-butanol content at a fixed temperature$^{20}$. Two variables are to be changed, i.e. the aqueous phase salinity as the sodium chloride concentration and the ACN of the n-alkane oil. Using a hexane oil phase a first salinity scan is carried out along a vertical line at ACN = 6 and a transition WI > WIII > WII takes place with an optimum salinity $S_6^* = 0.85$ wt% for the minimum tension of the center or the three-phase behavior zone. Then the oil phase is changed to decane without changing the surfactant, alcohol and temperature, and a second salinity scan is carried out. It was found that the optimum formulation is displaced to $S_{10}^* = 1.6$ wt% NaCl. If a third scan is realized with hexadecane, the optimum salinity is found to be at 4.0 wt% NaCl. Figure 4 shows that the points indicating the optimum formulation are located along a straight line whose equation is

\[ \ln S = 0.16 \text{ ACN} + \text{Constant} \]  

(2)

where Constant is depending on values of other variables.

Using another alkylbenzene sulfonate, another temperature, and another alcohol content, the same relationship is found with a different value of the Constant. For this kind of surfactant, a linear relationship thus exists between the variable salinity (expressed as $\ln S$) and the oil ACN, which is independent of the other variables. It is found that the coefficient can change with the type of surfactant head. It is 0.16 for alkyl benzene sulfonates, 0.10 for alkyl carboxylate or sulfate, 0.17 for alkyl ammonium, and 0.19 for trimethyl alkylammonium$^{31}$.

In other words a general differential relation of equivalence between two formulation variables (salinity and ACN) double change may be written generally as:

\[ \text{dln} S = k \text{ dACN} \]  

(3)

Another two-dimensional study was carried by changing $\ln S$ and temperature and the result is another differential equation

\[ \text{dln} S = -a_T \text{ dT} \]  

(4)

where the coefficient $a_T$ is around 0.01 for all anionic surfactants.

Fig. 4: Bidimensional (water salinity and oil ACN) formulation scan$^{19}$. The same kind of relationship was found for all pairs of variables$^{20,35}$. Generally it may be written as:

\[ \text{d}X_i = k_{ij} \text{ d}X_j \]  

(5)
where i and j indicate the two variables and the k’s are constant coefficients for a given surfactant type. As discussed later, instead of a unit constant before \( dX_i \) and a \( k_{ij} \) constant before \( dX_j \), the equation can be written in a more general way for any \( ij \) pair with two coefficients, i.e. with one coefficient characteristic of each variable.

\[
  k_i \, dX_i + k_j \, dX_j = 0 \tag{6}
\]

This kind of expression has been said to represent the equivalence of chemical potential differential dual changes\(^{55}\) to keep the Winsor R constant. By the way, by passing from an optimum formulation to another optimum formulation, the \( R = 1 \) equation stays valid along a straight line in the two variables space.

Another way to express the Winsor relation is to write it not as \( R = \frac{A_{co}}{A_{cw}} \) ratio but as a difference \( D = A_{co} - A_{cw} \) which is a deviation from \( A_{co} - A_{cw} = 0 \) that occurs at the optimum formulation.

The equilibrium of the surfactant interactions in the oil and water phases in equilibrium with the intermediate bi-continuous micro-emulsion may be written as follows

\[
\mu_w = \mu_o \tag{7a}
\]

with \( \mu_w = \mu_w^* + RT \ln C_w a_w \) \tag{7b} \]

and \( \mu_o = \mu_o^* + RT \ln C_o a_o \) \tag{7c} \]

The star indicates a standard reference, the \( C \) the surfactant concentration, and the “a” its activity coefficient. For a three-phase system at optimum formulation the \( C \) are very small (close to the CMC); the activity coefficients are thus close to unity for a normal surfactant like a typical ionic one used in EOR\(^{24,55,56}\). As found in the literature, the partitioning coefficient is found to be unity\(^{19,57-61}\) for such surfactants and thus the standard chemical potentials are equal

\[
\mu_w^* = \mu_o^* \tag{8}
\]

It means that the affinities of the surfactant (affinity is the negative standard chemical potential) for water and oil excess phases are equal. Taking the affinity as the molecular interactions \( A_{cw} \) and \( A_{co} \), the surfactant affinity difference (SAD) may be written as\(^{19,20}\)

\[
  SAD = \mu_w^* - \mu_o^* = A_{cw} - A_{co} \tag{9}
\]

When \( SAD < 0 \) (respectively \( SAD > 0 \)), a Winsor WI (respectively WII) phase behavior is produced, and the optimum WIII case happens at \( SAD = 0 \).

**Fig. 5:** Variations of the chemical potential of the surfactant in oil and water phases along a formulation scan passing through an optimum system.
As can be seen in Figure 5 (left), an increase in salinity results in an increase in $\mu^*_w$ that produces the transition $W_I > W_{II} > W_{III}$ since $\mu^*_o$ does not change because the salinity does not alter the oil phase. Figure 5 (right) shows that an increase in oil ACN from case (1) to case (2) produces an increase in $\mu^*_o$, but that both $\mu^*_o$ values stay constant as $S$ changes in the scan.

Figure 5 (right) shows that an increase in oil ACN from ACN$_1$ in case (a) to ACN$_2$ in case (b) produces a displacement of the standard chemical potential in oil from $\mu^*_o$ thus resulting in a change of optimum salinity $S^*$ from $S_1$ to $S_2$ as experimentally attained according to equation (3) which may be written for $a$ as

$$d\mu^*_o = (\partial \mu^*_o / \partial ACN) dACN$$  
(10)

$$d\mu^*_w = (\partial \mu^*_w / \partial \ln S) d\ln S$$  
(11)

by substitution in equation (3)

$$(\partial \mu^*_o / \partial ACN) = K (\partial \mu^*_w / \partial \ln S)$$  
(12)

This expression does not depend on the value of $S$ or ACN or any other fixed variable, and it refers to a change in water and a change in oil that are, of course, independent. These partial derivatives must thus be constant, as experimentally shown in the initial work in the late 1970’s$^{20,21}$.

To make things even clearer, a simple mathematical expression should be remembered here. Assume that the difference $A_{Co-Cw}$ (or its affinity equivalent difference $\mu^*_o-\mu^*_w$) is written as a function $F$ of only two formulation variables “$X$” and “$Y$”, e.g. $\ln S$ and ACN. The Taylor polynomial expansion of the function $F(X,Y)$ around a reference point $(X=0, Y=0)$ may be written as

$$F(X,Y) = F(0,0) + \frac{\partial F}{\partial X}(0,0) X + \frac{\partial F}{\partial Y}(0,0) Y + \frac{1}{2} \left[ \frac{\partial^2 F}{\partial X^2}(0,0) X^2 + 2 \frac{\partial^2 F}{\partial X \partial Y}(0,0) XY + \frac{\partial^2 F}{\partial Y^2}(0,0) Y^2 \right] + \text{etc}… \quad (13)$$

It is clear from this equation that if the first derivatives are constant, the second derivatives and the higher ones are zero; the appropriate expansion defining the optimum formulation line is thus a linear equation as shown in (6)

$$F(X,Y) - F(0,0) = k_x X + k_y Y$$  
(14)

By carrying the same argument for all other pairs of variables the overall reference chemical potential change in oil and water is as follows for all the variables altering the oil or water phases, where the $K_i$ are constants.

$$dF(X,Y) = d\mu^*_o - d\mu^*_w = \sum (\partial \mu^*/\partial X_i) dX_i = \sum K_i dX_i$$  
(15)

By integrating this differential equation the following expression for optimum formulation is attained

$$SAD = \mu^*_o - \mu^*_w = 0 = \sum K_i X_i + CST$$  
(16)

where CST is the integration constant.

A one-dimensional similar equation is written as $SAD/RT = HLD$, where the HLD is the Hydrophilic-Lipophilic Deviation from optimum formulation$^{25}$. HLD contains the surfactant characteristic parameter SCP.
(as the HLB was supposed to do) but it also contains the influence of water salinity and oil nature, as well as alcohol nature and concentration effects, temperature and pressure. It also contains an integration constant according to the relation (16).

This equation is formally similar to the optimum formulation empirical equation found in 1979 and improved later with the CST corresponding to a value that makes HLD = 0 when the actual experimental values of all the Xi producing a WIII are introduced, i.e. the S, ACN, surfactant parameter, alcohol effect, temperature and pressure.

For anionic surfactants the correlation with an arbitrarily zero constant was written as

$$\text{LnS} - K\text{ACN} - k\alpha C_A - a_T (T-T_{\text{ref}}) + b_p (P-P_{\text{ref}}) + \sigma = 0 \quad (17)$$

in which $S$ is the salinity (wt% NaCl), ACN the alkane carbon number, $C_A$ the alcohol concentration, $T$ the temperature, $P$ the pressure, and $\sigma$ the surfactant characteristic parameter including the constant too. The added pressure effect comes from recent publications and is useful for what happens in a reservoir, not for atmospheric conditions in the laboratory. The $K$ coefficient depends on the nature of the surfactant head group. This equation was found to be valid for cationic surfactants systems, which are however not used in enhanced oil recovery.

For polyethoxylated nonionic surfactants a similar relationship was found, this time with a very small effect of salinity expressed by a simple linear effect $b\text{S}$, where $b$ is 0.13 if $S$ is expressed in wt% NaCl. The pressure effect was added too, as for the ionic case.

$$b\text{S} - K\text{ACN} - k\alpha C_A + c_T (T-T_{\text{ref}}) + b_p (P-P_{\text{ref}}) + \beta = 0 \quad (18)$$

where $\beta$ is the surfactant characteristic parameter, first introduced as ($\beta = \alpha - \text{EON}$), $\alpha$ the contribution of the tail, and EON the average number of ethylene oxide groups. In this case it is a that includes the integration constant.

It is worth noting that since the (17-18) summations are zero, they can be multiplied by any coefficient and still be equal to zero. In general, the coefficient in front of the scanned variable is arbitrarily taken as unity, i.e. the equation is divided by this coefficient with no change in its meaning. For anionic surfactants, the scanned variable is generally the salinity, thus the coefficient in front of $\text{LnS}$ is unity as in previous equation (17). For nonionic surfactants, the usual scan is the surfactant hydrophilicity, as its ethoxylation number EON, and thus the coefficient in front of EON (or in front of $\beta$) is taken as unity.

Studies carried out with ethoxylated nonionics by Shinoda and Kunieda used the temperature as the scanned variable and the corresponding equations on the PIT (phase inversion temperature) which are identical to HLD = 0, used a unit coefficient in front of the temperature.

The very early scans were using the n-alkane length as the scanning variables; thus, the ACN would have been the one with a unit coefficient in a multidimensional relation. It is worth noting that there is another reason to take the unit coefficient in front of the ACN variable; it happens to be the variable that has exactly the same meaning in the two correlations (17 and 18) for ionic and nonionic surfactants systems. It thus can allow to handle some combination of the two equations when ionic and nonionic surfactants are mixed. On top of it, in referenced systems (T-T_{ref}) and (P-P_{ref}) are taken to be equal to zero, as well as the effects of salinity (LnS or $S=0$) and alcohol (in absence of it $C_A=0$), then

$$\frac{\alpha}{K} = \text{PACN} \text{ or } \frac{\beta}{K} = \text{PACN} \quad (19)$$

The surfactant characteristic parameter is then called the Preferred Alkane Carbon Number (PACN) in a real or extrapolated ACN scan. This optimum ACN or $n_{\text{min}}$ has been called the EPACNUS (as Extrapolated PACN at Unit Salinity and no alcohol for anionic surfactants) which is a precise, but somewhat anachronistic definition which is not used in the literature.
Then, in the $\text{HLD} = 0 = \sum K_i X_i + \text{CST}$ equation of the optimum formulation one of the $K_i$ is taken to be equal to unity; in general, it is the one corresponding to the scanned variable (lnS for ionics, EON for nonionics, and sometimes ACN because it has the same expression scale for both kinds of surfactants).

The remaining issue is the integration constant variable CST. In the original empirical equations (17) and (18), the CST is actually introduced in the only parameter which was not known with an actual value, i.e. the surfactant characteristic parameter $\sigma$ or $\beta$.

For a very complete study with super pure alcohol ethoxylates, and pure n-alkane, in absence of salt and alcohol, temperature scans yield the following HLD equation $^{21,67}$.

$$\text{HLD} = 2.00 + 0.34 \text{SAT} - \text{EON} - 0.15 \text{ACN} + 0.005 (T-25) = 0 \quad (20)$$

where the variable with a unit coefficient is taken as the EON and where the SAT is the surfactant n-alkyl tail length, i.e. the number of carbons in the surfactant straight tail. According to the previous equation the surfactant characteristic parameter could be taken as

$$\beta = 2.00 + 0.34 \text{SAT} - \text{EON} \quad (21)$$

In this case, and if $\beta$ only contains the values dealing with the surfactant molecule, i.e. SAT and EON, then the CST = 2.00. However, if the reference temperature is not 25 °C but 0 °C, then the CST has to be 1.875. If the reference were containing some salt or some alcohol, then the CST would be different. This means that if the constant is introduced in the surfactant characteristic parameter, the meaning of this parameter is not dependent on the surfactant only but also on the references for the formulation variables.

It is thus wrong to say that the surfactant parameter has to do with the curvature, as found in its naming as $C_c$ (characteristic curvature) in some articles $^{68-73}$. Such an anachronism was detected in a review book $^{74}$ which used the $C_c$ abbreviation but changed its meaning as surfactant CharacteristiC.

It is recommended to include the constant in the surfactant characteristic parameter as in equation (21) because this parameter does not include the head (EON) and tail (SAT) only, but also the branching in the tail(s), and the presence of double bounds, cycles and other characteristics, such as multiple heads, which are not easy to handle in particular complex cases as, for example, when the asphaltenes are considered as lipophilic surfactants in the dehydration process $^{21,35,75}$.

In a recent article $^{42}$, Figure 4 equivalence with three independent variables exhibits a plane for the equation (20). Adding the well known salinity (S) effect on the ethoxylated non-ionics the equation (20) becomes

$$\text{HLD} = \beta + 0.13 S - 0.15 \text{ACN} + 0.005 (T-25) = 0 \quad (22a)$$

An equivalence to the previous equation is to take an unit coefficient in front of ACN by dividing it by K (0.15 for nonionics), so that an HLDN normalized according to ACN is:

$$\text{HLDN} = 6.67 \beta + 0.87 S - \text{ACN} + 0.033 (T-25) = 0 \quad (22b)$$

In such a case, illustrated in Figure 6, the three parameters plane (V1 = ACN, V2 = S and V3 = T-25) intercepts the ACN axis, i.e. at $S = 0$ and $T-25 = 0$, at a $V_1^* = \beta/K$ value which is the surfactant preferred CAN PACN, EPACN if it is extrapolated out of the liquid n-alkane range.
In the original studies on the numerical correlation for optimum formulation \((20,21)\) the integration constant was thus taken to be zero, which is basically the same as saying that the integration constant was incorporated in the surfactant characteristic parameter \(EPACNUS\) value. The logic when the two kinds of surfactants are used is to have the same scale for the HLD of both kinds of equations, which means that there should be an unit coefficient in front of the only variable which is exactly the same in both cases, i.e. the oil \(ACN\) (or \(EACN\)).

For ionic surfactants the correlation with zero constant and unit coefficient in front of \(ACN\) may be written as follows by dividing equations \((17-18)\) by \(K\).

\[
\frac{1}{K} \ln S - k_A/K C_A - a_T/K (T-T_{ref}) + b_P/K (P-P_{ref}) + \sigma/K = ACN \quad (23a)
\]

In this ionic surfactant case, the surfactant is an electrolyte; the standard salinity is thus taken as unity so that \(\ln S = 0\). The characteristic parameter is then deduced from a reference in which there is no alcohol and at 1 % NaCl salinity.

A similar relationship was found for polyethoxylated non-ionic surfactants \((21)\). There is a very small effect of salinity expressed by a simple linear effect \(b_S\), where \(b\) is a 0.13 coefficient if \(S\) is expressed in wt% NaCl. The pressure effect was added as for ionic case.

\[
b/K S - k_A/K C_A + c_T/K C_A (T-T_{ref}) + b_P/K C_A (P-P_{ref}) + \beta/K = ACN \quad (23b)
\]

In this case the standard reference was taken at zero salinity, no alcohol, ambient temperature and atmospheric pressure. As for the characteristic parameter for an ionic surfactant, the integration constant is taken as zero, or, to be more precise, it is incorporated in the surfactant characteristic parameter \(\beta\). It is worth noting that the salinity reference is not exactly the same for ionic (\(S = 1\) wt%) and nonionic surfactants (\(S = 0\)). This is due to the fact that the logical reference with non-ions is no salt since it eliminates a variable, as it is the case in many studies \((67)\). The problem is that for ionic surfactants \(S = 0\) cannot be used as a reference, firstly because of the logarithmical scale, and secondly, because \(S = 0\) cannot exist because the surfactant is a salt, thus contributing to salinity. Even if the equation for ionic surfactant could be valid at low salinity, i.e. below 0.5 wt% down to 0.2 wt%, if the equivalent salinity (in Na\(^+\)) produced by the surfactant is introduced as an extra NaCl equivalent amount, the accuracy is not appropriate for a reference.

A same reference of \(S = 1\) wt% NaCl for the nonionic surfactants is thus recommended. Compared with the usual \(S = 0\) reference, this result in producing an error of 0.13 on the \(\beta\) value or 0.87 on SCP (\(\beta/K\)), which may be estimated as a small inaccuracy.
Studies with different kinds of surfactants have shown the effect of the surfactant tail length, with essentially n-alkyl tails, without strong branching. The surfactant characteristic parameter SCP (\(\sigma/K\) or \(\beta/K\)) indicated in Figure 7, for pure and commercial products, have been found to vary exactly the same way with the surfactant tail size\(^51\).

For the reasons mentioned above, the surfactant characteristic parameter SCP will be numerically taken as \(\sigma/K\) or \(\beta/K\) in HLD equations (23) so that a unit coefficient is selected in front of the ACN variable. It should be remembered that a very general relationship between the surfactant characteristic parameter and the length of its linear alkyl tail was found to be as follows for all the surfactants\(^{19,25,51}\)

\[
SCP = SCP_0 + 2.25 \text{ SAT} \tag{24}
\]

where SAT is the surfactant alkyl tail carbon number (i.e. the number of carbon atoms in the tail). K is the coefficient of ACN in the original correlations (17-18) which was found to be 0.16 for alkylbenzene sulfonates, 0.15 for polyethoxylated alkylphenols or n-alcohols, 0.10 for alkyl carboxylates and sulfates, 0.17 for alkyl ammonium and 0.19 for alkyl trimethyl ammonium and alkyl piridinium.

This means that for an alkylbenzene sulfonate or an alcohol/alkylphenol-ethoxylate (for which K \sim 0.15-0.16), 0.444 additional carbon atoms (equal to 6.2 molecular weight increase) in the tail increases SCP (\(\sigma/K\) or \(\beta/K\)) by one unit as noted in equation (24) and confirmed by the examples on Figure 7.

Figure 7 shows the pure products series, i.e. the linear alkyl-benzene sulfonates (LABS), the alkyl orthoxylen sulfonates (AOXS) and the nonionic surfactants (CiEj), which are all perfectly following equation (24), as indicated by a straight line.

For both ionic and nonionic surfactants, the SCP<sub>0</sub> – i.e., the value corresponding to the head group (i.e. when the SAT is extrapolated to 0) – was found to depend on the head group. Some values are found in the following list\(^51\) mostly for relatively pure surfactants. These values are only approximations for commercial products, the interfacial SCP<sub>0</sub> of which also depends on the partitioning of the different species and is altered by the surfactant concentration and the water-to-oil ratio in the system\(^{52,76}\).

<table>
<thead>
<tr>
<th>Surfactant Type</th>
<th>(\sigma_0/K)</th>
<th>(\beta_0/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na n-alkyl carboxylate</td>
<td>-50</td>
<td></td>
</tr>
<tr>
<td>Na n-alkyl sulfate</td>
<td>-57</td>
<td></td>
</tr>
<tr>
<td>Na iso-alkyl benzene sulfonate</td>
<td>-30</td>
<td></td>
</tr>
<tr>
<td>Cl n-alkyl trimethyl ammonium</td>
<td>-50</td>
<td></td>
</tr>
<tr>
<td>Cl n-alkyl pyridinium</td>
<td>-51</td>
<td></td>
</tr>
<tr>
<td>iso-alkyl phenol ethoxylate</td>
<td>+23</td>
<td>+13</td>
</tr>
<tr>
<td>n-alcohol ethoxylate</td>
<td>+13</td>
<td>-1.5</td>
</tr>
</tbody>
</table>

When the products are quite pure, a fair coincidence is found even if they are made by different companies as for instance a PACN value of -2.5 for a sodium linear dodecyl benzene sulfonate with 99% purity, comparing well with the Figure 7 LABS data which is of -3.0.

So it may be said that the general tendencies are significant, but are not absolutely precise because the actual data depends on small structure details such as the isomerism or the branching of the tail, or of the exact content of similar substances in commercial mixtures.
For instance a substantial difference is found between two carefully prepared commercial C14-17 LAS Na products with a PACN value of + 0.30 for the first one (#1) and − 0.45 for the other one (#2) at 28°C and 0.2 wt% concentration.

If the temperature is shifted to 60 °C the variation of these products is from PACN = + 0.53 to - 0.30, which is consistent with more branching in the tail of the #2. It is thus seen in Figure 7 that for anionic products where the basic difference is in the tail structure, the shift could be 2-3 units, as well as a similar variation with the surfactant concentration, as seen for instance for TRS-10-80 in Figure 7 as well as in Figure 8.

More variations are likely to happen when the head group is not well defined as in ethoxylated nonionic products, which are more sensitive to the effects of temperature and to concentration, with a possible variation of 4-5 units between the PACNs of products supposed to be the same chemicals.

Since the required accuracy for application like EOR and dehydration is less than a PACN unit, it is obvious that an experimental measurement of the used product SCP at the proper concentration has to be carried out to get the right data.

Equation (24) is quite exact for linear alkyl chains with the head located at the end of the alkyl group. Nevertheless, it was found that if the tail is not an n-alkyl structure, slight differences in structures can influence the SCP. This is the case with branched or multiple tails, and with the introduction of a central intermediate (as for extended surfactants with a propylene oxide part in the tail) or even with simple changes as recently shown for the addition of a single methyl group close to the head.

Moreover, it is worth noting that using S = 1 wt% NaCl reference for nonionics (instead of S = 0) would introduce a difference of 0.13 in β (or 0.87 β /K), which is relatively small in front of the constant value (2.0) found with the ethoxylated n-alcohol. It is important to mention that such a difference is equivalent to an error of 0.15 on EON, of 0.5 carbon number in the tail (i.e. on SAT) of 1 carbon atom in the alkane scale (ACN) and of 3 °C in the temperature.

This discrepancy is actually small compared to the effect of the surfactant tail structure, in particular its branching which very early research showed that exerts a strong influence. For instance a difference in n_{min} (ACN) of about 10 units was found when passing from the 2φC16 benzene sulfonate to the 8φC16 isomer. This displacement of the benzene attachment point from the end to the center of the C16 linear alkyl tail is equivalent to an increase of 1.5 units in β (or 15 units in SCP₀), which is the same as 4.5 more carbons atoms in the non-branched tail. Additionally, this salinity reference discrepancy is also small for a commercial surfactant, the SCP of which is quite sensitive to its concentration in the system, as discussed further on.

Because of all these effects that are not taken into account in the HLD equation, it may be said that the characterization of the surfactants with one (σ or β) or two (α – EON in equation 24) or even three (2.00 +
0.34 SACN – EON for n-alcohol ethoxylates) parameters is, in actual practice, not sufficient. This kind of insufficiency is also probably due to an error in the characterization of a real oil phase like a vegetable product or a crude oil in which some polar ingredients are likely to be segregated at interface\textsuperscript{94-98} or for actual aqueous phases containing many anions and cations for which only some initial equivalence has been proposed\textsuperscript{99,100}.

The previously reported situation emphasizes two important aspects. Firstly, there is no doubt that the numerical correlations as equations (23) are generally very useful to make predictions in formulations dealing with EOR, dehydration and other applications requiring a much better tool than the simplistic HLB parameter. Secondly, it also indicates that the HLD formulas with only 5-6 basic variables could be somehow quite approximate in practice for real systems.

In the following part of this review, the different reasons of the aforesaid are summarized so that the users of the HLD formulation concepts can determine whether more variables and more complex expressions than equations (23) are worth being dealt with in their application case, particularly as they are related with the surfactant characteristics.

First of all, it should be stressed that there are different methods to detect an optimum formulation. The experimental data are thus not exactly equivalent, in particular for characterizing the contribution of surfactant species.

The point is that real systems are intricate, in particular because they contain several surfactants, and complex studies have shown that the mixtures used in commercial products are not necessarily simple and that their formulation cannot be predicted by a simple linear relation because of a different partitioning of the incorporated species. However, a high level of formulation understanding of the inconveniences, also makes it possible to use several skillful tricks by selecting proper mixtures of 2 or 3 surfactants to reduce the difficulties in actual systems.

Besides these uncertainties dealing with the surfactant components, oil species segregation close to interface is also occurring, thus affecting the accuracy of the EACN concept. This obviously represents a further inconvenience, but the present review does not deal with this aspect because it is dedicated to surfactants species only.

6. Different methods to find the optimum even with extremely pure surfactants

The original method to detect the optimum formulation consists in measuring the interfacial tension along a single variable scan (typically ACN and lnS for ionic surfactants in petroleum applications, and EON and temperature for ethoxylated nonionics in cosmetics or food systems). When the expected tension is low, as in the case of EOR, a spinning drop interfacial tensiometer must be used, and the time necessary to reach a good measurement is at least between 1 and 2 hours for pre-equilibrated systems. Non pre-equilibrated systems could require much more time and could present the difficulty of a water/oil ratio very different from unity. In such cases the small drop could disappear during the measurement, or could at least produce a shift in optimum formulation because of excessive partitioning of some species.

This method is appropriate at low surfactant concentration with a (very) narrow range of WIII phase behavior so that the two tension lines crossing could be easily found extrapolating the trends from the two phases system (WI and WII) ranges. Measuring the tension in the WIII zone would require an accurate measurement of the density of the middle phase micro-emulsion, which is not easy with petroleum oil. Nevertheless, at low surfactant concentration (and narrow WIII range), in actual practice the positioning of the minimum tension in the scan is quite accurate.

However, the low surfactant mixture concentration is a situation in which there is often a strong partitioning that makes the interfacial formulation very sensitive to the surfactant concentration as is discussed here below. Figure 7 shows that, for a petroleum sulfonate surfactant TRS 10-80, the minimum tension at the center of the WIII zone (left plot) or at the unit partition coefficient (center plot) in a formulation scan passing through optimum, changes considerably with the surfactant concentration.
This effect was mentioned as a practical inconvenience in early EOR studies\textsuperscript{19,55}. The same trend was found for commercial nonionic surfactants, particularly the ethoxylated ones in which there is in general a very wide distribution of EON in commercial products that results in an even worse effect\textsuperscript{21,64,94,101,102}.

However, similar experiments carried out with very pure anionic or nonionic surfactants clearly indicate a strong insensitivity to the surfactant concentration\textsuperscript{39,55,103}, which indicates that this phenomenon is due to the mixture as will be corroborated later.

Figure 8 right plot indicates that the deviation from horizontal trend is only slight for a binary mixture of two pure and relatively similar anionic surfactants, thus confirming the trend. Consequently, it can be said that the data obtained for SCP (SPC\textsubscript{3} and SACN) for commercial surfactants – which are often a (wide) mixture – is sometimes inaccurate. Incidentally, this is why the data reported previously from experimental studies can exhibit discrepancies with commercial surfactants.

The other frequent method is the three-phase behavior visual observation of the WIII system detected in a test tube, in general an elongated one. The surfactant concentration should be enough to see a certain volume of the middle phase, i.e. at least more than 0.1%, typically 0.5% wt, so that the partitioning might be less of a worry. Moreover, in phase behavior studies the water/oil ratio is taken as relatively close to unity, i.e. from 0.3 to 3, without any significant effect on the result.

However, if the concentration is greater, the WIII zone could be relatively large. Then, the determination of the optimum formulation just in the middle of a WIII wide zone is not necessarily accurate to coincide with the minimum tension or maximum solubilization. This is the case when a partitioning could result in a non-linear rule between two HLD variables as seen in the extreme case of figure 9 where it is clear that the deviation from T-EON linearity increases when T and EON increase because of a strong dehydration of the ethylene oxide groups\textsuperscript{104}. It is obvious that in this specific case the c\textsubscript{T} coefficient in the HLD equation cannot be considered as a constant; it should therefore be taken as the best approximation in the range used.

The coefficient c\textsubscript{T} is generally assumed to be about 0.05 ± 0.01 with EON ~ 6 for commercial alkylphenols and alcohol ethoxylates producing WIII at ambient or slightly warm temperature\textsuperscript{21}. This value was confirmed for pure products\textsuperscript{68}. However, these data are only valid when the EON belongs to the 5-7 interval; it can change considerably from half to the double (at lower or higher EON) as can be seen on Figure 9. More accuracy can be found by looking at the PIT data published by Shinoda and Kunieda, Kahlweit and Strey and others\textsuperscript{13,14,27,105-110}.

On the contrary, the usual value of a\textsubscript{T} for anionic\textsuperscript{19} and cationic surfactants is about - 0.01 to - 0.02, with no strong variation reported over the 20-60 °C range\textsuperscript{111}.

The partitioning effect also produces a strong variation of the optimum formulation which is easily observed in the fish diagram, i.e. a formulation vs. surfactant concentration plot\textsuperscript{112-114} particularly with a sensitive scan variable as temperature in nonionic systems\textsuperscript{109,110,113,115-119}.
Figure 9: Bidimensional (temperature–EON) formulation scans showing variable WIII zone size and nonlinearity over a large range.

Figure 10 shows that for very pure surfactant (left), the optimum temperature is almost constant (horizontal black line), while it is considerably deviated for a typical ethoxylated commercial mixture when the concentration is changed.

The best way to avoid this deviation is thus to take a highly pure surfactant, but this is not a solution in practice because of the considerable cost increase. Another way to avoid this deviation with surfactant concentration is to detect the optimum formulation at the tail end, i.e. to take the point X at which a phase behavior transition from $3\phi$ to $1\phi$ (single phase micro-emulsion) is observed. In such a case, there is no inconvenience to determine the center of the WIII zone, since it is just a point.

However, in most cases, the tail is at a concentration that is much higher than the one used in practice. Nevertheless, this method is used to make an exact comparison among surfactants and between oil EACN values.

Fig. 10: Fish diagram for very pure surfactants (left) and commercial mixtures (right).

In the WIII zone the maximum solubilization at equal amount of oil and water in the micro-emulsion middle phase also indicates the optimum formulation. This coincidence first reported by Exxon people was demonstrated by using a simple micro-emulsion model and confirmed by many research articles. The equivalence appears in the performance index (PERFIND) used to compare the formulation containing up to three surfactant that results in the lowest tension for EOR as well as the formation of a single phase micro-emulsion for well cleaning, foods, medical creams and cosmetics, vegetable oil fuel, etc.
Other methods were used to determine the optimum formulation in one- and multi-dimensional scans. They resulted from the fact that other properties are associated with optimum formulation. The first connected phenomenon to be noticed was the emulsion inversion, the emulsion type being O/W at HLD < 0 and W/O at HLD > 0 according to the very old Bancroft’s rule\(^3\).

Many studies on the phase inversion temperature PIT were performed later by Shinoda and coworkers\(^{13,106}\), not surely mentioning if they were reporting a phase behavior change or an emulsion type change, until they started to use the HLB-temperature term\(^6\) to refer to the phase behavior. Moreover, the emulsion inversion temperature (EIT)\(^{127}\) in a formulation-WOR plot was shown to exhibit the zone where there is a coincidence (not too far away from WOR = 1) between the emulsion inversion and the WII zone\(^{128}\).

Emulsion inversion is usually detected by a strong change in electrical conductivity, a method that generally requires at least a small salinity in the aqueous phase. Such measurements are very easy to perform and could be detected during a continuous changing of the formulation variable, in particular the temperature, which can be increased or decreased. This is thus a very rapid way to find the optimum formulation since the temperature can be changed very quickly. However, if the temperature is too rapidly changed, the dynamic variation of conductivity could be delayed in time and thus in formulation\(^{129}\) and some minimum pseudo-equilibration time should be respected.

Incidentally, the measured interfacial tension can only be a dynamic value if the equilibration is not attained, with an unreliable result as far as the optimum formulation detection is concerned. This is not discussed in this review, but it is recommended to make sure that equilibrium is reached by having the SOW system prepared and left to equilibrate at least one day before the emulsification is carried out and the conductivity is measured.

The emulsion minimum stability occurrence was systematically studied in many reports describing the involved phenomena\(^{130-132}\). However, it was only in the late 1980’s, that the generalized HLD = 0 was shown to be the most determinant formulation expression to find an emulsion minimum stability\(^{133-135}\). Much later, some fundamental approaches have been proposed to explain this coincidence\(^ {36,47}\).

It is worth noting that this specific property association at HLD = 0 is very important in practice, in particular because it is used to dehydrate crude oil and, in general, to break an emulsion when it is not desired in many other applications. Figure 11 indicates the variation of the stability of many different emulsion cases \textit{versus} the generalized formulation HLD (with different scans). Even if the low stability zone (in the scan) can be in a narrow or wide range, it is always very low. In other words, it means that in a series of emulsion test tubes in a formulation scan, the one to separate first corresponds to the optimum formulation. This is an astonishing coincidence as far as a very short experimental time is concerned. This was first clearly noticed in the late 1970’s\(^ {33,134}\) then afterward applied as the basic trick to crude oil dehydration\(^ {138}\).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11.png}
\caption{Variation of the emulsion stability close to optimum formulation (HLD = 0) from many systems presented in various references\(^ {33,134-137}\).}
\end{figure}
Fig. 12: Variation of emulsion stability close to optimum formulation (in an EON scan) for different surfactant concentrations.

However, even if the detection is very quick and very accurate (as confirmed in figure 12 data), it is also extremely sensitive to the surfactant concentration, as can also be seen in figure 12 for a commercial nonylphenol ethoxylate products having an extremely wide range of EON from 0 to 12, and thus a considerable partitioning, and a strong interfacial formulation change with the surfactant concentration.

A very recent discovery of the occurrence of an extremely low interfacial elasticity modulus measured with an oscillating spinning drop interfacial rheometer, could offer a new way to locate the optimum formulation\textsuperscript{16-48}. This will actually confirm the early micro-emulsion birefringence change found to happen close to optimum\textsuperscript{140}, as well as the minimum emulsion viscosity also reported close to optimum probably because of the easy extension of the drop in low tension systems\textsuperscript{141}.

7. Mixing surfactants is very interesting, easy to use but complex to handle

It is seen that, in practice, many of the variables in HLD have a value that is linked with the applications, for instance the oil EACN, the brine salinity, and the temperature in a petroleum reservoir. For other applications like foods, cosmetics or paints, the restriction might be lighter as temperature and pressure are concerned, and in many cases the surfactant selection and the required properties are likely to be the most important choice.

The SCP value required to be at HLD = 0 or at another value to provide the appropriate property, is not generally found exactly with a given surfactant. The easiest way to adjust the adequate SCP value is thus to mix two similar surfactants with characteristics slightly different from the required one. In practice the mixture is composed of surfactants with SCPs slightly lower and slightly higher than the required one, e.g. the optimum (SCP*). In such conditions a simple binary mixture will provide a solution according to a linear mixture technique\textsuperscript{20} in which

\[
SCP_{\text{mix}} = X_1 \, SCP_1 + X_2 \, SCP_2 = SCP^* \tag{25}
\]

where the Xs are the proportions of the two basic components of the surfactant mixture, i.e. \(X_2 = 1 - X_1\), where the X are in weight, volume or mole fractions, with the last one as the most logical when the molecules are well identified.

This equation makes it possible to perform a study according to the effect of a single variable, which is the composition of the surfactant binary mixture, e.g. \(X_1\), the proportion of surfactant 1. This is the case of figure 13 in which a minimum interfacial tension, i.e. an optimum formulation and thus a SCP*, is found with a proper binary mixture between a Guerbet extended surfactant mixed with two other surfactants.
Fig. 13: Interfacial tension in a formulation scan produced by a mixture of two surfactants, the first one being an extended surfactant with a fraction indicated in the abscissa and the second one being a linear dodecylbenzenesulfonate LAS anionic (upper abscissa scale) or a nonionic dodecyl alcohol ethoxylate (EON=8) (lower abscissa scale).

Figure 14 indicates a similar binary surfactant mixture effect with the optimum determined by the emulsion minimum stability attained by mixing some asphaltenes (a very lipophilic surfactant with a badly known SCP) with a petroleum demulsifier (a very hydrophilic synthetic surfactant) in a system containing diluted crude oil and water.

In this case and according to the usual practice in crude oil emulsion breaking, the total concentration of the surfactant (asphaltene + demulsifier) is not constant, i.e. it is a more complex case in which what is constant is the asphaltene concentration. This is logical since the asphaltene molecular weight is not really known: hence the corresponding X mole fraction cannot be known with any accuracy.

Fig. 14: Stability of water-in-crude oil emulsion versus the added demulsifier concentration.
However, the situation is the same, i.e. there is a mixture, and, as the demulsifier concentration increases at constant asphaltene concentration, the mixture SCP is decreasing after starting with the high value for asphaltenes only. It will then decrease and pass at the lower required SPC* value to attain HLD=0 and the minimum emulsion stability.

Another way to study and properly anticipate the effect of a surfactant mixture vs composition is to plot the experimentally measured SCP versus the binary composition. The usual situations are seen in figure 15 in which the SPC-X relation may be linear (a) or non-linear, with several possible cases: the (b) case in which the non-linearity is almost insignificant, and the other (c-d) cases in which a SCP value out of the SCP1-SCP2 range could be attained. The (d) case shows that there could be a case in which two optimum points are exhibited, which means that there are two mixtures – which may be close together or not – with the same SCP* value.

These complex situations (c-d) in which there is not a monotonous variation between SCP_MIX and the composition of the mixture will thus produce two optimum mixtures, with one of them being better than the other, for some reason. If the two solutions are close enough, this could bring another advantage to the mixture, such as a wider robustness as will be discussed later.

The actual evaluation of the binary mixture can also be studied by measuring the effect of the surfactant mixture composition on a parameter that indicates the optimum formulation.

For that equation HLD=0 (17-18) is written with only one scanned variable (S, ACN, T for instance) and with the X1 composition of the mixture that appears when replacing $\sigma$ or $\beta$ by equation (25), with all the rest constant.

Figure 16 (right plot) shows that for different anionics some slight non-linearity may be found between two quite pure alkylorthoxylene sulfonates. It could be suggested without straightforward explanation that the large variety of species found in the petroleum sulfonates could be thus better lnS* linearity than having two very pure substances only.

This is for instance the well-known case reported in the literature by evaluating the optimum lnS* for a given system containing a binary surfactant mixture which could produce a quite linear relation, or conversely, a highly non linear one, such as in the case of strongly interacting surfactants.

Specific cases of surfactant mixtures and their influence on the physicochemical formulation and trends to optimize more realistic systems are discussed here below.
8. The anionic surfactant mixture case

On figure 16 (left plot) the salinity S is taken as the scanned variable for a mixture of two similar anionic surfactants of the alkylbenzene sulfonate type which are however quite different in hydrophilicity. One has a single C12 tail on the benzene, and the other has a C15 alkyl tail on an orthoxylene ring, i.e. it has 5 more carbon atoms; it is thus more hydrophobic and it exhibits a lower optimum salinity. In this case, it can be seen that there is a very linear mixing rule when the lnS* is used to characterize the optimum formulation so that the linear equation (25) can be deduced from the experimental results

\[ \ln S_{\text{mix}} = X_1 \ln S_1 + X_2 \ln S_2 = \ln S^* \]  

(26)

The same linearity is found in this figure 16 (left plot) when mixing a petroleum sulfonate (TRS-10-80) with a dodecyl benzene sulfonate C12ABS.

![Figure 16: Examples of optimum formulation change with surfactant mixtures.](image)

9. The anionic and nonionic surfactant mixture case

In the case of figure 16 (left and right plots), there are mixtures data with two quite different surfactants as far as the effect of salinity is concerned. The TRS 10-80 is a petroleum sulfonate, i.e. a complex mixture of anionic species which follows very well the HLD = 0 equation with K = 0.16, while the nonionic Igepal species are ethoxylated nonylphenols with different EON\(^{20}\) increasing from 6 to 10.5). For the NPEO6 (EON\(_{\text{average}} = 6\)), it can be seen that the increase in nonionic surfactant in the mixture does not result in any formulation change from 0 to 30%, and that there is a non-linear change after that. It is thus clear that the equations (25) and (26) do not apply for this kind of mixture, and that an experimental measurement is required.

As seen in Figure 16 for a slightly higher ethoxylation (EON\(_{\text{average}} = 7.5\)), the straight line variation now has a slope, i.e. there is a formulation effect (SCP linearly changes with mixture composition) and it is up to 30\% of nonionic.
Finally for a higher ethoxylation as in NPEON7.5, it is a straight line up to 35% nonionic with strong change in lnS*, and an even higher change (more inclined slope) for more ethoxylated nonionic NPEON10.5.

**Fig. 17:** Change in the optimum formulation plane in the 3D space with two independent formulation variables when the mixture of two similar surfactants is carried out.

If the mixture is studied in the three-dimensional space, there are two independent formulation variables and instead of an optimum line in a property-X plot, an optimum plane showing the variation of a property versus X1&X2 is used, with more information as previously seen in a S-ACN-f(A) 3D plot or a S-ACN-T 3D space in figure 6. This is schematically shown in figure 17.

This representation is useful in particular if the two surfactants are similar and thus have a linear mixing rule, but with a different coefficient K in front of ACN in the HLD = 0 equation, for instance in a mixture of sulfate (K = 0.10) with sulfonate (K = 0.16). Figure 17 indicates that the variation of the mixture plane results in a shift parallel to itself if the two Ks are equal or to a crossing plane series if they are different, in a 3D plot in which the 3D selected variables are S, ACN and alcohol contribution f(A) are taken as in the original plot.

Because of the above results, in surfactant mixture studies it is very important to understand not only the interfacial effects that are likely to happen between the species, but also how they are likely to alter equation (25).

The first kind of effect is the association of two (or more) surfactants producing some interactions that could result in a new structure at interface, in particular in the cases of ionic/nonionic and anionic/cationic mixtures.

In the previously presented case of anionic/nonionic mixtures it was seen that a small amount of nonionic in the mixture could produce a SCP variation almost linear with the non-ionic fraction, with a more important effect as the ethoxylation grade increases.

This situation is due to the fact that, as seen in figure 18 right pictures, when the nonionic is highly ethoxylated, the nonionic head part is a long enough polyethoxylated chain (EON > 7.5) that acts as a hydrophilic head and also tends to surround the almost spherical anionic head group to partially reduce its interaction with water. This makes the mixed heads slightly less hydrophilic, with a small deviation of the optimum (as lnS*) to a lower value with respect to the linear case.
10. The anionic and cationic surfactant mixture case

When the ethoxylation is quite low (case EON = 5.3), where it is just enough to have solubility in water and when there is a SCP similar to the anionic one, the polyethoxylated head is just sufficient to partially surround all the ionic head and to produce a more lipophilic mixture ($\ln S^* \sim -0.8$) over a very wide range of composition. This width means that the SCP is essentially constant over a large range of mixture (from 40 to 80% of nonionic), thus bringing some robustness to the formulation, an interesting property for some application as discussed elsewhere. For the intermediate case (EON = 6.0 EO) a wide range is also available but this time in another zone (from 0 to 60% of nonionic).
Another well known case is the mixture of anionic and cationic surfactants in which the interactions produce an association with a partial or complete loss of the ionic charge, depending of the mixture composition.

Previous studies have shown that the occurrence of an optimum formulation versus the mixture composition exhibits a typical aspect shown in figure 19. It so happens that in this case a bimolecular component (with a molecule of each species) occurs exactly at the center (in mole %) of the mixture composition. This so-called “catanionic” component is much less soluble in water than its two parts (because the ionic characteristic is lost), and, in many cases it precipitates out of the SOW system: the center zone of the mixture is thus not used, only the lateral sides are.

In figure 19 the optimum formulation (lnS*) for maximum solubilization is shown at different mixture compositions. The data are far from being close to the dashed line indicating a linear variation of lnS* with mixture composition, but it is made instead of two straight lines.

One of these lines starts from the optimum lnS* for the anionic surfactant and goes down to a central point located just in the middle at a very low salinity (indicated with a question mark). The other straight line starts at the optimum lnS* of the cationic surfactant and goes down to the same central point, which corresponds to the real (or more often nonexistent in solution) catanionic bimolecular mixture.

This interesting situation means that the mixing process is still linear as in equation (25), but not between the two basic components. Instead, what happens is a linear mixture between one of the basic components and the catanionic new third component. The actually valid zone for the mixture is limited by the precipitation in the central zone, but it is perfectly valid in most cases when there is more than 80% of one of the basic components.

It is worth noting that, in certain applications, this kind of mixture is often used to lower the optimum salinity of a mixture of very hydrophilic anionic and cationic substances. It is also important to remark that there are two mixtures resulting at an optimum formulation for a given salinity, as indicated by an horizontal line cut at a selected lnS* = 1.6 in figure 19.

The actual position in lnS of the pure basic component and of the catanionic depends on other variables, such as the head and tail of the basic surfactants, the presence of alcohol, and the temperature. Consequently, the precipitation zone may be reduced and even eliminated so that the two optimum compositions may be closely approached or even merged. However, this does not generally improve the solubilization performance, which is often best with only 10 to 20% of one of the basis components, when a liquid crystal zone starts to form.

11. The partitioning phenomena in surfactant mixtures

The second kind of effect which is important with mixtures is that the two or more species are going to interface depending on the situation. This means that their partitioning between the liquid phases and the interface (or between the micro-emulsion middle phase and the excess phases in a WIII system) change with all the variables of the systems as well as with the total surfactant concentration and the WOR.

With a pure ionic surfactant the partitioning coefficient between oil and water excess is very close to unity because of almost equal CMCs in oil and water as seen in figure 20 (left plot). As a consequence the low side of the Winsor’s WIII three-phase behavior triangle is basically horizontal.

This case still applies for a two pure surfactant mixture of very close species, as seen in figure 20 (right plot) with a 50/50 C11-C14 alkylbenzene sulfonates in which the partitioning of both species are the same at the mixture optimum salinity.

This is however an exception and, in general, each species has its own partitioning according to the formulation, specifically for the nonionic ethoxylated surfactants which are very soluble as single molecules in the oil phase, probably without micelles, and with a very low CMC in the water phase. It should be mentioned that for ethoxylated nonionics, the partition coefficient as the surfactant ratio of concentrations is very far from unity at optimum formulation, and to calculate the partition coefficient with a thermodynamic sense, the activity must be used instead of the concentration.
The partitioning of the different surfactant species in a mixture is a complex phenomenon which is not dealt with here in detail. However, this has been extensively studied, and more information is available in the different cases reported in the literature$^{101,154}$. In the present review only the polyethoxylated nonionic case is discussed to show how the interfacial (or middle phase) formulation at optimum can change because of the partitioning variation produced by any of the formulation variables, as well as by the mixture composition (surfactant concentration and water oil ratio)$^{155}$. Figure 21 (left) indicates the distribution of the different oligomers of a commercial ethoxylated nonionic surfactant with an average EON = 5. There are many species with EO ranging from 1 to 12 in a global distribution having a slightly asymmetrical shape with a “tail” on the high EON. The oligomers going to the oil phase are mostly those with short ethoxylation, i.e. EON < 4 and some of the EON = 5-6 species, with none above EON>7.

These oligomers which are lost in the oil phase are not available to participate in the interfacial mixture. Since there is no surfactant species in the excess water because the CMC is very low, it means that the average EON at interface (and in middle phase) is essentially the difference between the global distribution (average EON =5) and the distribution in oil (EON < 4). Consequently, the interface has a higher average (for instance EON$_{average}$ = 6) in figure 21.

Depending on the nature of the other variable (i.e. the salinity, ACN, oil aromaticity, temperature, etc.) the amount of surfactants species lost in the oil can change greatly as indicated in figure 21 (right plot) as the black part of the EON distribution, the remaining white part being what goes to the interface. The surfactant lost is always the low EON part, but it can change greatly, for instance from 25% (in the case of octane-water at 25°C) to 90% (in the case of butylbenzene-brine, 60°C). In this last case only a very small amount of very high EON species will be found to be able to go to interface which has an EON$_{average}$ of around 10 instead of the overall one of 5 in the system.

The distribution available at the interface also depends on the total surfactant concentration and on the water-oil ratio in the system since these two parameters are able to produce changes in the partitioning. Many studies have shown that when the total concentration of a nonionic surfactant is decreased, the interfacial EON tends to increase. Thus, the surfactant influencing the formulation apparently becomes more hydrophilic, i.e. its SCP decreases$^{101}$. The opposite occurs with an ionic surfactant mixture. When its concentration decreases it apparently becomes more lipophilic at interface$^{55}$, and its SCP increases. When the WOR increases, i.e. with more and more water in the system, the surfactant PACN (and its SCP) tends to increase which means that what is going to interface becomes more lipophilic, in all surfactant cases, with a more significant change for very wide mixtures, such as the polyethoxylated nonionics$^{155}$.

![Fig. 20: Left plot: Surfactant concentrations in the different phases and Partition coefficient between oil and water of pure anionic surfactant in a SOW system. Right plot: same case with a mixture of very similar pure surfactants.](image-url)
It is worth remarking that, for any kind of very pure surfactant, i.e. when there is no mixture but a single species (thus no possible different partitioning for the various species), this formulation shift due to concentration does not take place, and there is only a very small effect of the surfactant concentration and WOR\textsuperscript{119}. Of course, this insensitivity is reassuring and straightforward for scientific studies, but it is not a solution in practice because highly pure surfactants are very expensive. There is, however, a trick to obtain some insensitivity with a mixture, which is blending two mixtures with opposite trends, i.e. an ionic mixture with a nonionic one.

![Diagram](image)

**Fig. 21**: Left plot: Ethoxylation distribution in a typical ethoxylated alcohol or alkylphenol. Right plot: Lost lower EON species by solubilization in the oil phase.

Figure 22 indicates the variations of the tension along a salinity scan when the surfactant concentration decreases for an anionic (respectively nonionic) mixture resulting in a decrease (respectively increase) of optimum salinity as indicated by the arrow. When a proper anionic-nonionic mixture is used the two effects are opposite and some insensitivity may be found to exactly compensate the two effects. It happens here with a mixture containing 20% of nonionic and 80% of anionic. Less nonionic is logically required in the compensating mixture, because the variety of the SCP of the components of the ethoxylate mixture (from EON = 0 to EON = 12) is much wider than for the anionic mixture.

The data also show that the optimum formulation for the anionic-nonionic mixture is at a much lower salinity than for the case of the anionic and nonionic mixtures. This is due to the previously explained anionic-nonionic interaction that makes the composite head less hydrophilic, thus with a lower optimum salinity requirement\textsuperscript{156,157}.

It is known that the alkyl polypropoxy polyethoxy sulfates and other so-called extended surfactants\textsuperscript{73,82,83,157,158}, with an ionic head group are actually intramolecular anionic-nonionic mixture molecules with properties similar to extramolecular mixtures.

However, they are known to present much less partitioning in the oil and water phases and are thus more efficient, in particular because the previously noticed loss of the low EO nonionic part does not happen. For this reason such extended surfactant with a proper central alkoxylated part (lipophilic polypropylene oxide plus hydrophilic ethylene oxide) can prevent most of the surfactant concentration effect and exhibit an optimum formulation that is almost insensitive to its concentration\textsuperscript{159}.

Opposite effects with ionic and nonionic surfactants are also shown in the HLD equation with different signs in front of the temperature coefficients. When the temperature increases, an ionic surfactant becomes more hydrophilic and an ethoxylated nonionic more lipophilic, which is equivalent to an actual change of the SCP with temperature. This means that the comparison of the SCP of two surfactants must be done at the same temperature.

In practice mixing ionic and nonionic surfactant could result in insensitivity to temperature, which makes it possible to eliminate the T variable in HLD.
A similar feature can be attained with an intramolecular mixture in the case of anionic extended surfactants, i.e. as the temperature increases, the dehydration of some polypropylene oxide units close to the interface occurs, which makes the surfactant more hydrophobic. The anionic part of the surfactant with the same increase in temperature makes it more hydrophilic.

**Fig. 22:** The SCP of anionic and nonionic commercial surfactants changes in opposite direction when their concentration is reduced. A proper mixture of the two (80/20 AI/NI) can produce a compensation and thus insensitivity to concentration.

These opposite trends make some extended surfactant with polypropylene oxide central group insensitive to temperature, or at least much less sensitive than the ethoxylated ones. Nevertheless the interesting property of these surfactants is that they become slightly more lipophilic when temperature increases because of the dehydration of the first propylene oxide group which are part of the tail, but also are very close to water and thus hydrated.$^{86,160}$
12. Trends to optimize formulations with surfactant mixtures

Figure 23 (left plot) indicates the variation $\partial \ln S^*/\partial T$ of the optimum salinity versus temperature (at other formulation variables constant) from which the variation of the SCP of the mixture may be estimated with respect to temperature in such anionic-nonionic structures. It can be seen that insensitivity to temperature is found for a certain mixture composition (at the crossing of the horizontal dashed line). It can also be seen that the required nonionic surfactant fraction to result in insensitivity to temperature depends on the ethoxylation (EON), with a trend indicating that more ethoxylation implies a lower SCP at constant temperature, but also a stronger temperature effect\(^{161}\). This is a quite logical result since the increase in temperature dehydrates the ethylene oxide groups and it is thus more significant in formulation if there are more such groups.

When the studies are carried out in a bidimensional plot including temperature and anionic-nonionic mixture composition, interesting results are obtained for practical uses, in particular the possibility of a double insensitivity as can be seen in figure 23 right plot\(^{162}\). This wide WII zone is due to the fact that the temperature effects are exactly opposite in a very wide T range, and that the surfactants are selected to have the same optimum temperature T*.

Insensitivity to a formulation variable means that this variable disappears from the HLD equation, and that the mixture SCP is found from an expression without this variable. However it should be noted that the insensitivity to one variable as far as the HLD=0 equation is concerned, does not mean that the performance, e.g. the minimum tension value or the emulsion minimum stability, is going to be insensitive too.

A recent analysis of the performance\(^{36}\) indicates that the structure of the surfactant is of critical importance. It also indicates that complex mixtures typically containing branched sulfo-nates, extended surfactants with a sulfate head and nonionic ethoxylates result in a considerable performance improvement\(^{37,42}\).

For instance figure 24 indicates that a typical good mixture between 75% of an alkylbenzene sulfonates and 25% of a long propylene oxide extended surfactants can be kept to produce a low minimum tension when the salinity increases in the use of a sophisticated EOR salinity gradient method\(^{163-166}\) simply by adding a proper amount of a simple and cheap nonionic.

It is worth remarking that in this complex case, the tension is even better at very high salinity with a cheaper surfactant mixture containing only a very small amount (~ 10%) of the expensive extended surfactant species\(^{37}\). Since such mixtures contain an anionic-nonionic binary, they can also be relatively insensitive to temperature and surfactant concentration; they can thus be quite appropriate for some applications, such as EOR where the surfactant concentration decreases as the slug move in the reservoir.

The concept of robustness of a formulation was recently studied to describe the insensitivity of a formulation to an external change which is difficult to control in the application\(^{38}\). Such a change can for instance be the variation of a surfactant mixture by the adsorption of some of its species on a solid surface, producing a chromatographic effect in a petroleum reservoir.

Many tendencies and complex tricks and artifacts, particularly those that use amazing surfactant mixture effects, have been proposed to increase the performance and the robustness of a formulation containing mixed surfactants\(^{37,38}\).

However, the precise calculation of the SCP of such mixtures to produce an outstanding behavior is not available yet, although it could be a very good tool to save time and money in many applications with surfactants to attain a particular property associated with the Winsor phase behavior determined by the HLD.

A few published examples have recently related the characteristic parameter of a very pure surfactant to its molecule shape for very clean systems\(^{42,65,167,168}\), but, mixing them to attain synergetic effects is currently too complex to be easily understood and modeled.
Many cases that have been proposed to get a HLD complex variation that would produce the solution of a real problem, but the experiments were often conducted by trial and error without any explanation related to formulation.

Before concluding this review paper, we will present two cases with a combination of a surfactant mixture and a formulation variable effect clearly related to the HLD concept. Changing the surfactant mixture SCP with another formulation variable such as salinity (i.e. with two changes at once), is a very common practice for applications.

The fact that a double control on the salinity and on the nonionic surfactant amount in a ternary mixture can keep the low tension for an EOR application very steady, as previously shown, indicates how to use the HLD to attain what is required to produce a very attractive result.

Another example is for instance that an increase of pH with an oil-water system containing an organic acid (typical case in EOR with some crude oils) will produce a WII > WIII > WI formulation scan that could be interpreted as a variable mixture of two surfactants, i.e. the acid RCOOH species (nonionic lipophilic surfactant) and the salt RCOO- Na+ (anionic surfactant).

Figure 25 (left plot) shows that when the pH is changed (in this case increased from left to right), the acid-salt mixture is changed from a lipophilic mixture with WII phase behavior to a hydrophilic one. Such a change is passing through an optimum SCP* (square point with WIII) at which a low minimum tension occurs, as well as associated phenomena for micro and macroemulsions.
As discussed elsewhere, it can be seen that the optimum formulation occurrence takes place at a very quick variation of pH, in particular because the pH scale is logarithmical.

The pH change is produced in practice by adding some alkaline chemical like caustic soda (NaOH) which also contains Na⁺ ions and thus produces the effect of the salinity formulation variable in HLD. Figure 25 (right graph) shows that, if the pH goes above the value corresponding to the SCP* (x₁a), the mixture SCP stays on the hydrophilic (SCP2) case with a WI phase behavior for some range; it is thus increased because of the salinity increase, and the mixture becomes lipophilic again close to the SCP1 case, after passing a second time through the optimum formulation at x₁b.

This results in two optimum formulations with a low tension at WIII (square dots) and the macroemulsion inversion as well as other effects. Depending on how this is done, i.e. depending on the acid-salt nature and the alkaline used, the two optimum formulations can be far away, close together or almost merging, in which case there is a high robustness of the system properties as discussed elsewhere.

Regarding applications, amazing results can also be attained with an anionic-nonionic mixture whose component SCPs vary with the temperature with opposite effects, in combination with the occurrence of some interaction between them that tends to make the mixture SCP higher, i.e. more lipophilic. Figure 23 showed that an AI-NI mixture containing two surfactants with exactly the same inversion temperatures can result in a very large cross shape WIII zone for the proper application for bitumen EOR.

In the case in which the inversion temperature condition is T* NI > T* AI, there is a central zone between the two inversion temperatures in which both components are hydrophilic surfactants; the phase behavior thus has a WI strip zone, as shown elsewhere.

In some specific cases when the anionic/nonionic interaction is very strong, their mixture with similar amounts can become lipophilic and produce a small WI phase behavior zone, only in the center part of the twisted WIII cross, as can be seen in the upper graph of Figure 26.

The phase behavior effects resulting from such a case makes it possible to produce WI-WIII-WII changes in many different ways, sometimes twice by moving in the same direction. Changing the temperature as in the left lower diagram or changing the anionic/nonionic mixture composition as in the right diagram of Figure 26, results in altering the surfactant mixture characteristic parameter in very different situations, and, in particular in solving formulation issues to produce stable W/O cosmetic emulsions or, on the contrary, to break them as in the dehydration or desalting of crude oils in refinery, as discussed elsewhere.

It is clear that the characteristic parameter SCP value of used surfactants species and its variations in mixtures could result in extremely complex but astonishing effects, which are not very well explained.

Thus, in practice, these effects should be still experimentally tested in proper ways. It is however evident that the formulation experts who, in general, keep the current know-how (and do not divulgate it), are the only ones who could find a solution in a short amount of time and at a lower cost.
13. Conclusions

In a real system formulation problem, not only the typical variables (i.e. S, ACN, SCP, T and possibly P) must be dealt with. Moreover, the fact that there are many candidate surfactants in a SOW system with possible interactions, such as association, segregation, and selective partitioning between phases and adsorption at interface, is extremely significant. What is more, the nature of the oil and of the brine and their often complex composition could be critical and could result in considerable changes in the description parameters for SCP, EACN and S at interface.

Consequently, the HLD = 0 correlation with 4-5 global variables must be completed by some useful information on the mixing rules for surfactants (and co-surfactants), oils and electrolytes. These rules involve a much larger number of variables and cannot be estimated with precision for at least two reasons. Firstly, the preferential properties looked for at interface and secondly, the so-called synergy due to non-linear molecular interactions.

In this kind of multivariable systems, the present review argues that the Surfactant Characteristic Parameter (SCP) can be an important tool to optimize formulations, without affecting the other HLD variables in simple as well as in more complex cases.

There is no doubt that the application performances must be experimentally estimated, but, of course, this has to be done with the sound advise of people with top know-how so as to avoid a disastrous waste of time and money if the effects of 10 to 15 variables have to be tested.

The result of the use of a surfactant binary or ternary mixture, eventually with an additional temperature or pH variation which could produce opposite effects, is often amazing, since it can produce systems with any kind of property, such as low tension, high solubilization, single phase micro-emulsion, stable or unstable macroemulsion of any type, etc.

But of course the actual property depends on the HLD value, and a very good understanding on how to attain the required formulation is necessary. This could be extremely complex in practice, as has been shown by Lab. FIRP research over the past 40 years.

Fig. 26: Cooperative effect of the temperature with a binary surfactant mixture.
14. Referencias


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A review on the surfactant characteristic parameter used in EOR, crude dehydration and other formulation applications

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