

## The fundamental basis for the action of a chemical dehydrant. Influence of the physical and chemical formulation on the stability of an emulsion

*Processes of dehydration which are used to break up emulsions of crude oil and water, such as those that occur in the secondary recovery of petroleum by the injection of water or brine, were studied. The stability of representative systems comprised of hydrocarbons, brine and surfactants (both anionic and nonionic), and sometimes cosurfactants (alcohols) was determined experimentally. The behavior of such emulsions is represented on a graph, with the surfactant affinity-difference (SAD) as the ordinate and the water-oil ratio (WOR) as the abscissa.*

The stability of an emulsion of petroleum and water results principally from the presence of natural surfactants adsorbed at the interface. Dehydrating agents interact with natural surfactants to produce extremely unstable emulsions. The influence of the physical and chemical formulation on the conditions of stability and instability of an emulsion were determined for representative conditions. The reasons for this instability are discussed, and the process of dehydration is interpreted graphically in terms of the ratio of water to crude oil.

### Introduction

Sooner or later, a petroleum well begins to produce a greater percentage of water than is acceptable. Removal of this water by dehydration or desalination [1-3] is then necessary.

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A portion of the water, called free water, is easily separated from the crude by the action of gravity as long as the velocity of the fluid is sufficiently low. The remaining produced water is intimately combined with the crude in the form of an emulsion, i.e., a stable dispersion of fine droplets of one of the fluids in the other [4-5]. The more common dispersions of water in oil are known as W/O (water-in-oil) emulsions. Emulsions of O/W type are occasionally formed. These are called "inverse" in the petroleum industry.

Just as with mayonnaise (an O/W emulsion), petroleum emulsions are produced when a mixture of oil and water undergoes agitation, the fluid-mechanical effect of which is a shear near the interface between the fluids. This shear results in an interfacial instability due to mechanisms which have been discussed elsewhere [6]. In conventional primary production of oil and also in the secondary production by water flooding, the fluids arrive at the bottom of the well in the form of two-phase flow. Thus, the emulsion must result from agitation of the mixture of water and crude in the production equipment: pumps, restrictions, expansion valves, etc.

This clearly suggests how to avoid the production of an emulsion. However, this is not often possible because of technical and economic considerations. Furthermore, stimulation by acidification and enhanced recovery methods, such as thermal or chemical, can themselves produce emulsions [7-8].

A petroleum production engineer must thus be resigned to living with emulsions and learning how to break them up.

### Phenomena involved in the breakup of an emulsion

The breakup of an emulsion is a multistage process which may occur due to inhibition or enhancement of one of the phenomena which command stability. By simplifying the analysis of Jeffreys and Davies [9], it may be said that the principal stages are:

(1) Macroscopic agglomeration of droplets of the dispersed phase until the formation of a floc (typical distance = 0.5 - 1 micron). At the end of this stage, the droplets are flattened and are separated by a film.

(2) Drainage of this film until it thins out to the order of 0.1 micron or less.

(3) Rupture of the film and coalescence of the droplets with the appropriate geometric rearrangement.

The third stage involves capillary forces of considerable magnitude, and can be considered to be instantaneous with respect to the first two. The first stage corresponds essentially to gravitational sedimentation and is governed phenomenologically by the analog of the laws of Stokes or Hadamard [10] for a single droplet. The rate of agglomeration increases with the buoyant force, i.e., with the density difference, with the size of the droplet, and the gravitational force, and inversely with the viscosity of the external phase.

Processes of dehydration are designed to increase the rate of this first stage; they all involve physical changes such as heating, which reduces the viscosity of the external phase and, to a lesser extent, increases the density difference between the fluids. Another physical effect is the introduction of a large amount of the internal phase, as in desalination, e.g., to reduce the average distance traveled by each droplet before it contacts another one. Forces other than natural gravity can also be used to increase the probability or the velocity of contact and/or the size of the droplets: artificial gravity by centrifugation [11], capillary forces in precipitation filters [12], or electrostatic forces in Cottrell type separators [13].

The mechanisms of the first stage obey these well-known laws of physics and, hence, are not considered in the present article.

The second stage — drainage of the thin film involves two simultaneous phenomena. On the one hand, approach of the two interfaces and, on the other hand, motion of the fluid contained in the film in a direction parallel to the interfaces.

In both cases, interfacial phenomena related to the presence of adsorbed surfactants are involved.

Surfactants are substances whose molecules have a polar part with affinity to water and a nonpolar part with affinity to oil. These substances cannot satisfy this double affinity, except when they are located at the boundary between the water phase and the oil phase, with the polar part immersed in water and the nonpolar part in oil. Surfactants are generally adsorbed at the interface, which results in a decrease in the free energy of the system [14, 15]. Such substances occur naturally in the majority of crudes, e. g. naphthenic acids, resins, asphaltenes, etc. [16-18].

Being adsorbed at the interface, these surfactants can naturally retard considerably the culmination of the second stage [19-22]. Figure 1 indicates schematically the four retarding effects that the presence of an adsorbed surfactant can produce on the drainage of a film and the agglomeration of droplets of water (in a W/O emulsion).

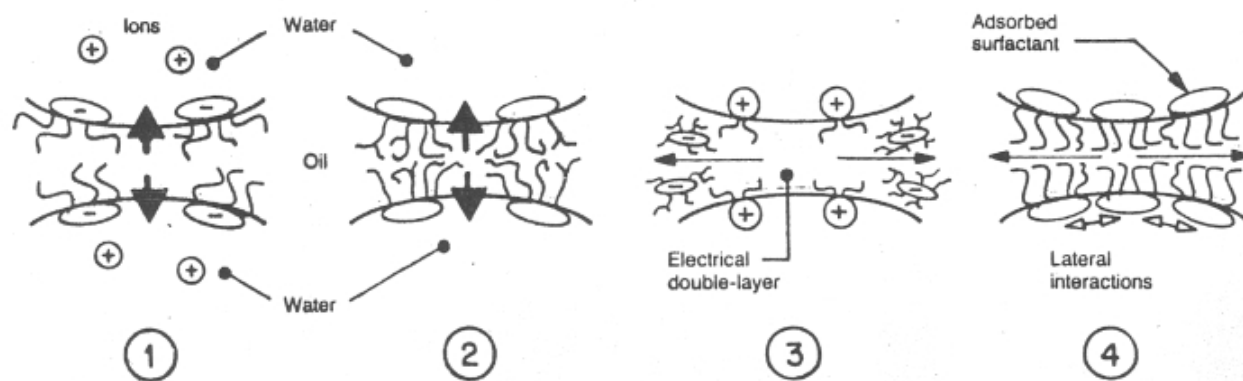
In case (1), an anionic surfactant, e. g., a carboxylate, is adsorbed at the interface, and its cations are in a double layer in the interior of the droplets. As charged interfaces approach one another, an electrostatic repulsion is produced between the droplets.

Case (2) illustrates the steric repulsion produced by interactions between lipophilic groups of the surfactant molecules. With surfactant molecules of the asphaltene type, the side chains can considerably intrude into the oil phase, and steric repulsion can maintain the interfaces at a distance sufficient to inhibit coalescence.

Dissociation of the natural surfactant into an adsorbed ion (here cation) and a liposoluble anion in the electrical double layer on the oil side is considered in case (3). As the film between droplets drains, a drag occurs on the ions of the double layer, producing a charge delocalization, and resulting in the electrokinetic effect known as "streaming potential". The electrical field which is created tends to return the ions to their initial position, i. e., a force opposing drainage of the film is produced.

Case (4) illustrates the formation of a rigid film resulting from lateral interactions between adsorbed molecules of the surfactant and from the immobilization of the oil layer which solvates the lipophilic tails.

This produces a considerable increase in the interfacial viscosity and in the apparent viscosity of the oil in the film between the droplets. Both of these effects oppose drainage.



**Fig. 1.** Sketch of the four effects which retard film drainage resulting from the presence of a surfactant adsorbed at the interface. (1) Electrostatic repulsion; (2) Steric repulsion; (3) Electroviscous effect; (4) Increase of the interfacial viscosity.

### Action of a "chemical" dehydrant

In almost all field installations, a small amount of a solution of synthetic surfactants, called a "chemical" dehydrant, is added to the fluids which are produced. This addition is performed as soon as possible after the oil gets out of the ground, and can even be done "down-hole" [23] in order to guarantee adequate mixing such that the surfactants migrate to the interfaces of the emulsion before arriving at the separation equipment [1,2].

The many conjectures regarding the physico-chemical mechanism for the action of dehydrating agents have not been very successful; in general, they do not explain the extreme specificity of a type of dehydrant on a particular system of crude and brine. The only valid generalizations concerning effective dehydrating agents are that they possess a high molecular weight (comparable to that of natural surfactants), and, when used as emulsifying agents, they tend to establish an emulsion opposite in type to that which is stabilized by natural surfactants [1-5]. This explains why literally thousands of products have been patented and commercialized for such purposes, since the pioneering work of William Barnikel and his Tret-O-Lite Company. Today, the selection of a dehydrating agent is still made from bottle tests, i.e., by trial and error.

This situation is probably due, in part, to the confidentiality maintained by the firms which manufacture such products, but also, until recently, due to a lack of understanding of the relationship between the composition of a surfactant-water-oil mixture and the resulting interfacial properties, even for pure ternary systems, much less for systems which involve

crudes and natural surfactants. Since a surfactant can be effective at a concentration of the order of 1 ppm, thousands of substances in a crude can be responsible for interfacial effects, and their explanation from one aspect of the phenomena is useless.

Systems whose composition is perfectly defined and controllable must be used to analyze and comprehend the effects involved in the stabilization or destabilization of an emulsion. This article analyzes the phenomenology encountered in such systems.

### Materials and procedures

For the reasons mentioned above, idealized systems were employed, which nonetheless are realistic within the framework of those encountered in the field. The surfactants were of the commercial type with a wide distribution of molecular weight—both anionic (alkylaryl sulfonates, alkyl sulfates, petroleum sulfonates) and nonionic (nonylphenol polyethoxylates). An alcohol was often added as a cosurfactant to eliminate the eventual formation of gel mesophases, which can solubilize the surfactants and complicate observation of the behavior.

The aqueous phase was a sodium chloride brine of variable salinity. Hydrocarbons, ranging from analytically pure substances to refinery cuts such as kerosene, gas oil, paraffins, and lubricating oils, were used as the oil phase.

Except as noted, surfactant-water-oil samples (50-100 ml) were prepared and allowed to equilibrate at a constant temperature for at least 24 hrs prior to their emulsification. The purpose was to assure that the phases which comprised the emulsion were in physicochemical equilibrium, thus avoiding mass

transfer between the phases during the process of rupture, which would complicate the interpretation of the results. This pre-equilibrium situation corresponds reasonably to what occurs in the oil reservoir.

### Formulation of a surfactant/oil and water (SOW)

Formulation of a SOW mixture embraces two types of variables. First are the composition variables, which define the fractions or percentages (mass, molar, or volumetric) of each one of the components. Second are the formulation variables, which correspond to the physicochemical nature of each one of the components and to the effects of external variables such as temperature and pressure.

Numerous studies related to the SOW mixtures used in the enhanced oil recovery by micellar drainage have led to the definition of the following formulation variables, each one of which characterizes a component or an effect [24-29]:

- Salinity of the aqueous phase (S, in % NaCl with respect to water). With anionic surfactants, the natural logarithm of the salinity (ln S) is generally used as the variable.
- ACN (alkane carbon number), or the number of carbon atoms in a molecule of n-alkane. If the oil is not an n-alkane, then its EACN is defined as the carbon number for a molecule of the equivalent n-alkane, i. e., one which has the same affinity for the surfactant as the oil [30]. For complex oils, including crudes, linear mixing rules based upon mole fractions are employed [31].
- A parameter characterizing the surfactant which defines the balance of the affinities for water and for the oil. The HLB of the surfactant [32, 33] supplies an estimate for this property; today, more precise parameters such as the EPACNUS (extrapolated preferred EACN) are being used [34].
- A function which accounts for the effect of the alcohol, and which depends upon both the type of alcohol and its concentration. Both effects are combined into a single function, and thus treated as an additional component or additive [34, 35].
- The temperature [35].

Each one of these variables of formulation contributes to the affinity balance of the surfactant for the aqueous and oil phases.

Figure 2 illustrates the different interactions possible between surfactant molecules adsorbed at the interface and molecules of water and oil.

The letter C represents the interfacial zone where the surfactant is adsorbed. The subscripts indicate the nature of the interactions: O for oil, W for water, L for the lipophilic part of the surfactant, and H

for its hydrophilic part.

The different interactions are classified into those which favor the presence of the surfactant at the interface, such as  $A_{LCO}$  for the lipophilic side and  $A_{HCW}$  for the hydrophilic side, and those which tend to inhibit it, correspondingly, the interactions which occur in the absence of a surfactant at the interface, such as  $A_{OO}$ ,  $A_{LL}$ ,  $A_{WW}$ , and  $A_{HH}$ . The ratio between the interactions on one side and the other of an interface, denoted as R, indicates the affinity balance

$$R = \frac{A_{CO}}{A_{CW}} = \frac{A_{LCO} - A_{OO} - A_H}{A_{HCW} - A_{WW} - A_{HH}}$$

This concept, proposed by Winsor 30 years ago [36], is extremely useful for the qualitative understanding of what is happening at an interface. When for instance, the interactions of the surfactant with the oil phase are greater than those with the aqueous phase, the "lipophilic tail" side of the surfactant will be more solvated by the oil molecules than the "hydrophilic head" side by the water molecules. This produces a swelling which results in concavity of the interface toward the aqueous phase (see Figure 3).

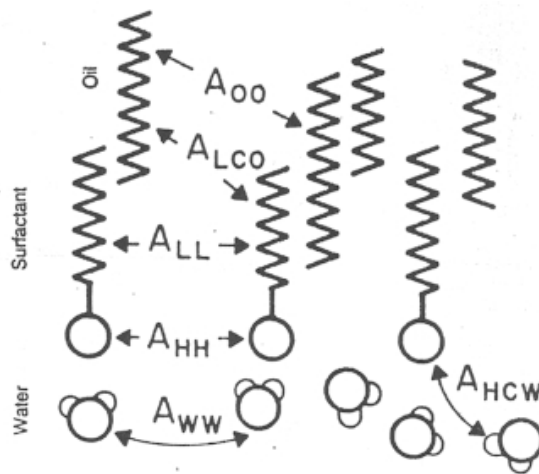


Fig.2. Sketch of the interactions between a surfactant adsorbed at the interface and water and oil molecules, following the Winsor's terminology.

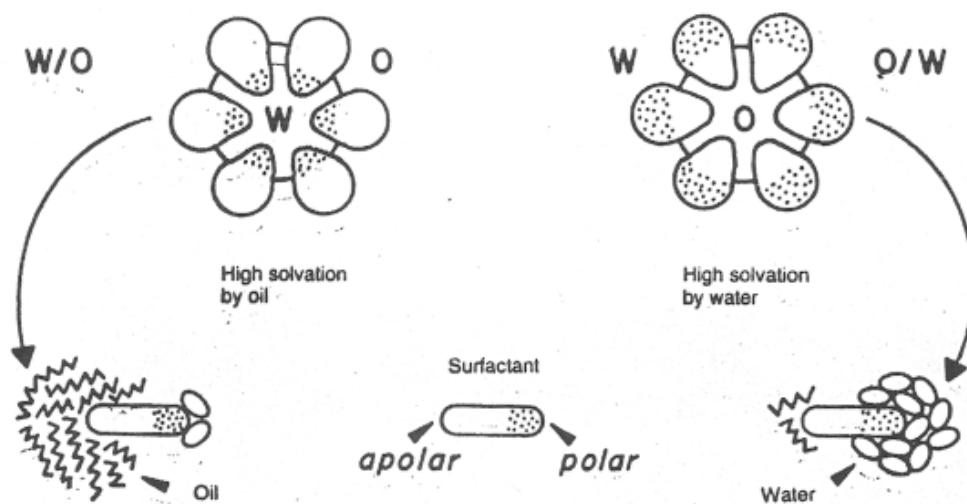


Fig. 3. Influence of the balance of interactions on solvation of a surfactant molecule at the interface, on the curvature, and on the type of resulting emulsion.

A W/O type of emulsion is then obtained. An O/W type of emulsion is obtained in the opposite case. In the intermediate case of equality of the affinities, neither type of emulsion would be expected to be applicable. This discussion demonstrates the principles of Winsor's model, and the use of the ratio of the interactions,  $R = A_{CO}/A_{CW}$ . Unfortunately, with the present state of knowledge of the thermodynamics of the liquid state, the magnitude of these interactions cannot be accurately estimated, and other models must be considered [6].

Beginning with studies especially related to the conditions required for a three-phase system [37,38], a thermodynamic model based upon chemical potentials has gradually been developed [6,39,40]. Recently, this balance was quantified by the following expression for the SAD (surfactant affinity-difference) [41]:

$$\begin{aligned} \text{SAD} &= \text{affinity for oil} - \text{affinity for water} \\ &= \mu^*_{\text{w}} - \mu^*_{\text{o}} \end{aligned}$$

Here,  $\mu^*$  represent the standard chemical potentials for the surfactant in the phase indicated by the subscript. The affinities are the negatives of these potentials. For anionic surfactants,

$$\begin{aligned} \text{SAD}/RT &= \\ \ln S - k \text{ EACN} - f(A) + \sigma - a_T(T - 25) \end{aligned}$$

and for nonionic surfactants of the polyethoxylated alcohol or phenol type,

$$\begin{aligned} \text{SAD}/RT &= \\ \alpha - \text{EON} - k \text{ EACN} - \phi(A_1) + bS + c_T(T - 28) \end{aligned}$$

Here,  $\sigma$  is the parameter characteristic for all anionic surfactants, while  $\alpha$  is a parameter characteristic of the apolar part of a nonionic surfactant, and EON is the average number of ethylene oxide groups per molecule. Also,  $f(A)$  and  $\phi(A)$  take into consideration the alcohol effect, and  $K$ ,  $k$ ,  $a_T$ ,  $c_T$ , and  $b$  are positive coefficients in the relative weighting of the effects of the different variables [37,38].

This expression for SAD combines the effects of all of the formulation variables into a single one and, therefore, considerably reduces the problem of formulation. This expression also indicates that a change in one variable can be compensated for by a change in another one.

When the SAD varies from negative to positive, which could be realized for instance by increasing the salinity, the molecular weight of the apolar part of the surfactant (increase of  $\sigma$ ), or the temperature (nonionic surfactants), or by reducing the latter (anionic surfactants), the so-called formulation scan is obtained, and the SOW system exhibits a series of properties, as illustrated in Figure 4, whichever variable is used to modify the SAD.

The phase behavior and a test-tube view of the system are also shown in Figure 4, together with the variations in the interfacial tension and the solubilization parameters (volume of water or of oil solubilized per unit mass of surfactant).

For  $\text{SAD} = 0$ , the affinity of the surfactant for the aqueous phase exactly equilibrates its affinity for the oil phase.

## Type and stability of an emulsion versus SAD

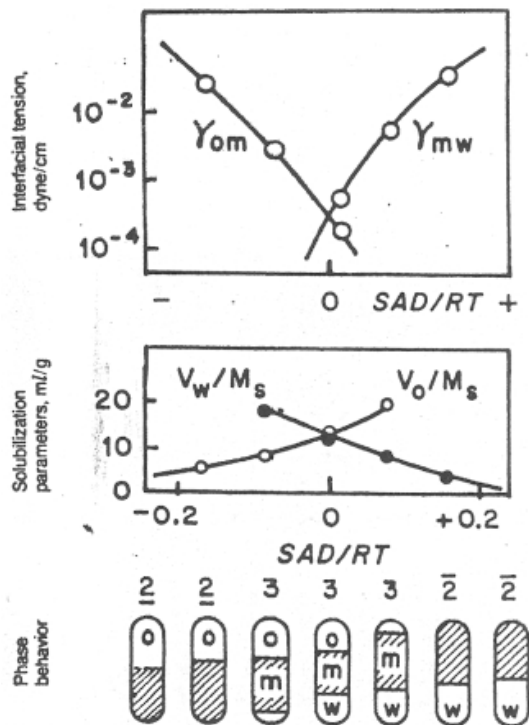


Fig. 4. Phase behavior, interfacial tension and solubilization parameters during a formulation scan. Optimal system: TRS 10-80, 3% sec-butanol, 2% ter-pentanol, 1.0 wt% NaCl, octane. Salinity scan [36].

The solubilization of water and of oil per unit mass of surfactant passes through a maximum, and a third phase, called an intermediate microemulsion, can be formed, producing type 3 phase behavior. When  $SAD = 0$ , the interfacial tension passes through a well-defined minimum, which can reach very low values ( $10^{-3}$  dyne/cm) required for enhanced recovery. This occurrence has been called "**optimal formulation.**"

For negative values of SAD, the affinity of the surfactant in the aqueous phase exceeds its affinity in the oil phase. The surfactant is preferentially distributed in the aqueous phase, and the two-phase system obtained is symbolized by  $\underline{2}$  to indicate that the surfactant is in the lower phase (aqueous) in the test tube. The opposite applies for positive SAD.

The SAD concept thus corresponds to a generalized variable of formulation whose reference is at optimal formulation ( $SAD = 0$ ) and whose value defines the deviation from an optimal formulation, based upon the above expressions.

The type of emulsion (O/W or W/O) is easily determined by measuring the electrical conductivity, which is approximately proportional to the conductivity of the continuous or external phase and the volume percent of the said phase in the emulsion. Since the aqueous phase is brine, the conductivity of O/W emulsions is several orders of magnitude greater than that of W/O emulsions. A change from O/W to W/O, termed an inversion of the emulsion, is thus detectable without difficulty.

The stability is an easily estimated property in those extreme cases wherein the emulsion completely coalesces in a few minutes or, on the contrary, remains apparently unchanged with no visible separation for several months. In intermediate cases, however, quantification of the stability for purposes of comparison of emulsions often encounters serious difficulties in experimentation or interpretation [42, 43]. A single absolute measure of the stability would be the variation as a function of time of the number of droplets present in a given sample of the emulsion. The number of droplets in an emulsion can be deduced from a particle-size distribution, but such a measurement perturbs or destroys the integrity of the sample, and thus cannot be implemented on the same sample at different times. Comparative studies in the vicinity of  $SAD = 0$  have shown that a good criterion of stability results from taking the time required for a certain fraction (1/3 or 2/3) of the first phase to separate (coalesce or clarify) [44]. An equivalent criterion, although less selective, is the volumetric fraction not separated from the internal phase (i. e., not coalesced) after a fixed time.

Figure 5 shows the stability variation which results from both criteria over the same formulation sweep.

The symbols  $\underline{2}$ , 3, and  $\bar{2}$  refer to the phase behavior, and the symbols O/W, MOW, and W/O to the emulsion type. MOW indicates a three-phase microemulsion-water-oil dispersion whose conductivity could be of the O/W, W/O, or intermediate type.

The data indicate that around  $SAD = 0$  the emulsion is inverted and the emulsion stability passes through a minimum, irrespective of the criterion. A comparison of these two stability criteria indicates that the time required for separation of 20% of the phase which clarifies first permits a quantitative comparison over the entire sweep, and suggests that the stability can vary by four orders of magnitude in the vicinity of the optimal formulation.

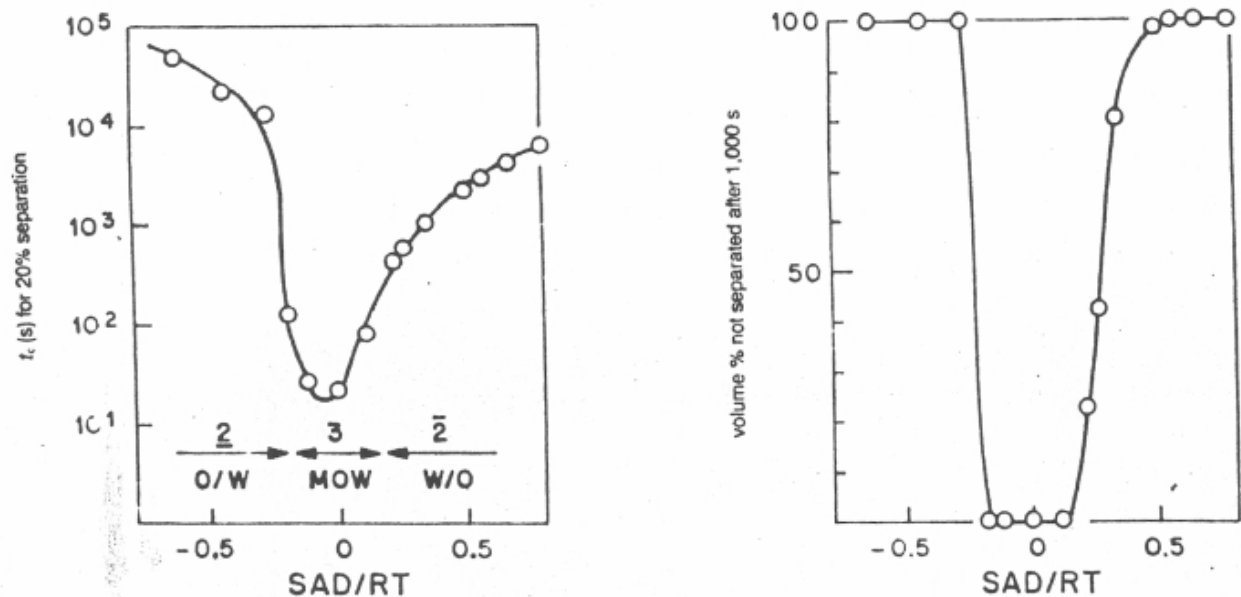


Fig 5 Variation of the stability of an emulsion according to two common criteria during formulation scans. Optimal system: 0.5 % dodecyl sodium sulfate, 6 % n-pentanol, 3.5 % NaCl, kerosene, WOR = 1. Salinity scan.

Such a pattern in the stability variation has been observed in numerous systems containing different types of surfactants, oils with viscosity ranging from 1 to 1,000 cP, and WOR near unity, regardless of the variable used experimentally to change SAD [42-62]. The stability values and the symmetric or asymmetric aspects of its variation with SAD depend upon each particular case, but the general phenomenology is the same; as the optimal formulation is approached, the stability of an emulsion is reduced considerably. Such a reduction in the stability is much greater than that which would result from modification of the physical parameters (viscosity of the external phase, size of droplets, density difference) involved in the first stage of emulsion rupture.

The characteristics of a formulation at SAD = 0 is thus a key factor in the sense that the effects retarding film drainage in the second stage of emulsion rupture are eliminated.

#### Physicochemical mechanism for destabilization when SAD = 0

In a certain sense, the coincidence of the minimum in the stability of emulsions with the formulation at which the interfacial tension is a minimum, and sometimes extremely low, is paradoxical. For a given degree of agitation, the size of the droplets produced by the process of emulsification depends upon the interfacial tension, such that the lower this tension the smaller are the droplets.

On the other hand, insofar as the droplets are smaller, the time of sedimentation is longer and, consequently, the more stable the emulsion needs to be [4,5].

Experimental evidence has shown that this reasoning does not apply to systems around the optimal formulation, and it thus seems appropriate to determine the reasons.

Beginning with the most obvious factor, although not the most important, the capillary forces are noted to be extremely weak for a very low interfacial tension, and, as a result, the droplets can very easily deform. Visual observation of rupture of an emulsion formulated around SAD = 0 indicates that the droplets are considerably elongated in the direction of the gravitational vector, taking on the shape of a cylinder or a filament. Stokes' law does not apply under such conditions; rather, the lower the tension the greater is the elongation and, consequently, the less the friction and the greater the rate of sedimentation.

Visual observations also indicate that in such systems, coalescence between two droplets occurs instantaneously upon their approach, i. e., the second stage of drainage of the film between droplets is extremely rapid, just as in OW systems which contain no surfactant [63].

As the amount of surfactant is varied in these systems, the stability or, better, the instability, does not depend upon the amount of surfactant [63], which is also contrary to the general tendency [59].

An explanation of this paradox was recently developed [63] by denoting that, at  $SAD = 0$ , SOW systems form a third (microemulsion) phase in equilibrium with the phases of water and oil in excess. The structure of this phase is such that the chemical potential of the surfactant is much less in the microemulsion than in either of the water or oil phase, or at the interface.

Consequently, accumulation of surfactant in this third phase reduces the free energy of the system, which signifies that the process is spontaneous. In the presence of this microemulsion, the molecules of surfactant migrate from the water/oil interface to the microemulsion, leaving the water/oil interface practically without adsorbed surfactant, and, hence, it cannot be stabilized according to the mechanisms of the second stage, as illustrated in Figure 1.

This displacement of equilibrium is equivalent to the rupture of cationic asphaltic emulsions upon contact with a rocky aggregate. The surfactant migrates from the asphalt-water interface to be adsorbed at the rock-water interface, leaving the asphalt-water interface practically without adsorbed cationic surfactant, which is the basis for emulsion stabilization by electrical repulsion.

### Obtaining $SAD = 0$ with surfactant mixtures

A parameter characteristic of the surfactant appears in the definition of  $SAD$ . This parameter can be determined experimentally [64, 65] and related to the structure of the surfactant. For example, for sodium alkyl benzene sulfonates [34],

$$\sigma = -4.80 + 0.35 N_{(CH_2)}$$

where  $N_{(CH_2)}$  is the number of carbon atoms in the alkyl chain of the surfactant.

Upon mixing two surfactants of the same type, e. g., two sulfonates, the characteristic parameter for the mixture is observed to be a linear combination of the characteristic parameters of each of the surfactants [66]. This mixing rule is always linear when the blended surfactants are not substantially different, i. e., essentially when the structural distribution of the mixture is unimodal. Under such conditions, the mixing rule can be used to characterize a surfactant, which means that the value of the characteristic parameter can be found experimentally [64, 65].

If the surfactants are quite different, in particular, if the mixture exhibits a bimodal distribution of structure, then the mixing rule is not linear, and the different species of surfactants, often behave separately and do not form a microemulsion at  $SAD = 0$  [67].

In order to obtain an optimal formulation with a system which already contains a surfactant (e. g., the natural surfactant present in a crude), another surfactant must be added (e. g., a dehydrating agent) in a manner such that the characteristic parameter of the mixture results in  $SAD = 0$ , which then produces an unstable emulsion. In order to apply this rule, the added surfactant must be structurally similar to the initial surfactant; this is corroborated by the knowledge that dehydrating agents are usually polymeric surfactants of high molecular weight, of the ethoxylated resin type, or else block co-polymers of ethylene oxide and propylene oxide. On the other hand, in order to obtain  $SAD = 0$ , a surfactant with an affinity opposite to that of the initial surfactant must be added; the mixture must thus possess a balanced affinity. This also coincides with the observation that dehydrating agents, when used alone, stabilize an O/W emulsion as opposed to breaking it.

Finally, the concentration of the added surfactant must be such that, in combination with the initial surfactant, it produces  $SAD = 0$  exactly. This is in agreement with the observation that dehydration conditions are very specific, and that a small variation in the dehydrant concentration (either below or above the optimum), or in temperature, can produce an unfavorable change in the process.

The parallel between the experiments mentioned above and dehydration assumes implicitly that both the initial surfactant and the added surfactant are present in the system prior to emulsification. Such is the case of injection of a chemical dehydrant down-hole in the well, in which stable emulsions are not produced [23].

However, in general, the chemical is injected into an already existing emulsion stabilized by natural surfactants. Recent studies [68, 69] have attempted to simulate this realistic situation.

For example, if the original state is not very far from  $SAD = 0$ , the later addition of a "dehydrating" surfactant to the original emulsion produces effects similar to its addition prior to emulsification. Thus, the fundamental basis of the process is conserved, even in the absence of previous physicochemical equilibrium.

## Effect of the water-oil ratio (WOR)

In all of the above, the water-oil ratio (WOR) has been assumed to be close to unity. This assumption merely implies that O/W or W/O emulsions with a large proportion of the internal phase are ruled out. Examination of the influence of the water-oil ratio is therefore appropriate.

In the history of a well, a progressive increase in the percentage of produced water generally takes place; when secondary recovery by water injection is employed, the percentage of water in the production flow can reach a very high value, especially if the selling price of the crude is high. One of the more severe problems associated with an increase in the percentage of water is the rise in the viscosity of W/O emulsions with the content of water. Even with relatively light crudes, the exponential increase of the viscosity with the internal phase content of the emulsion results in pumping problems and in a reduction in production.

In order to find a solution to this problem, it is convenient to study the influence of the composition variables, together with the generalized formulation variable, SAD. For this purpose, let us return to model ternary systems comprised of surfactant, oil, and brine. Such systems have two independent composition variables which are generally expressed as the concentration of surfactant and the water-oil ratio, WOR.

The surfactant concentration has a well-defined general influence [59]. Below a certain "critical" concentration, the amount of surfactant in the system is insufficient to stabilize the emulsion. This concentration probably corresponds to the minimum amount required to cover the interfacial area and to satisfy adsorptive equilibrium. Above this critical concentration the stability of the emulsion tends to increase with the concentration, and then is maintained constant or else decreases. Herein, sufficient surfactant to stabilize an emulsion will be assumed, e.g., between 0.1 and 1%, thus avoiding for now any consideration of the effect of this variable.

On the other hand, the WOR has an effect associated with the formulation which is more difficult to understand. Increasing the water content of a W/O emulsion (formulation  $SAD > 0$ ) is known [4, 5] to end with the inversion into a O/W morphology emulsion when the O phase percentage reaches 70-80%.

In symmetrical fashion, an O/W emulsion (formulation  $SAD < 0$ ) is inverted into W/O when the oil content attains a certain value, which depends notably upon the viscosity of the oil and the fluid-mechanical conditions, and which can be from 40 to 80%.

In order to examine this interaction, a two-dimensional SAD-WOR chart, on which the type of emulsion and its stability are represented [53, 70], is the convenient map. Figure 6 shows such a chart for a typical case. The heavy line indicates a change in the type of emulsion, i.e., the inversion line, while the fine lines denote the iso-stability contours; the numbers correspond to the decimal logarithm of the time (in seconds) for the separation of 2/3 of the phase which separates first. Also presented is the phase behavior of the system before emulsification.

The line  $SAD = 0$  and the inversion lines for the emulsions delineate six zones on this chart. In the central region denoted as A, WOR has a value around unity.

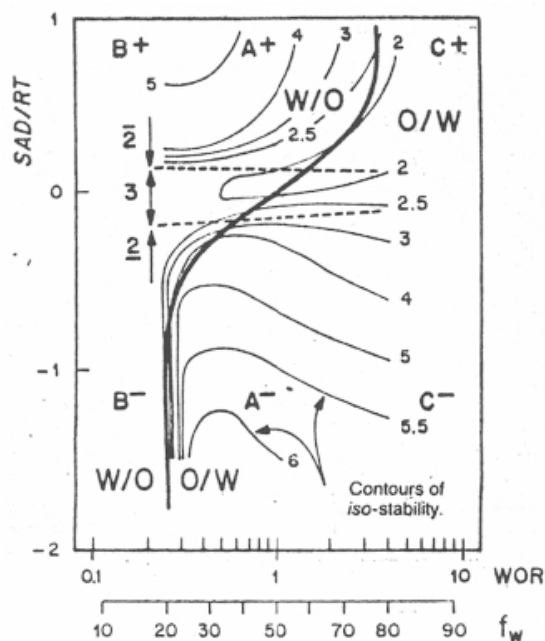


Fig. 6. Two-dimensional formulation-WOR chart, wherein the phase behavior at equilibrium, the inversion curve for the emulsion, and iso-stability contours (the corresponding value is the logarithm of the time in seconds for 2/3 separation) are shown. Optimal system: same as in Figure 5. Salinity scan.

Stable O/W emulsions are observed for  $SAD < 0$ , and stable W/O emulsions for  $SAD > 0$ . The superscript on A indicates the sign of SAD. As  $SAD = 0$  is approached, the stability of the emulsion decreases, both on the  $A^+$  and on the  $A^-$  side. A vertical crossing at  $WOR = 1$  corresponds to the SAD scan seen earlier, with a pronounced minimum in emulsion stability near  $SAD = 0$ . The vertical branches of the inversion line of the emulsion delineate two values of WOR, which correspond to the maximum content of the internal phase for both types of emulsion. In the  $C^+$  region,  $SAD > 0$  and the surfactant is preferentially distributed in the oil, which indicates that a W/O emulsion should be stabilized according to Bancroft's rule. However, not enough oil volume is present in the system (high WOR) to produce such an emulsion, and the external phase is the phase with the greater volumetric percentage — i. e., water. The inverse phenomenon occurs in the  $B^-$  region, wherein a W/O emulsion occurs, even though  $SAD < 0$ .

Both the  $C^+$  and  $B^-$  regions correspond to "abnormal" emulsions which possess a very low stability; microscopic observations and measurements of conductivity indicate that multiple emulsions of the W/O/W type can be produced in  $C^+$  and O/W/O emulsions in  $B^-$ , that is, drops of the internal phase contain, in turn, included smaller droplets of the external phase [58]. Whereas the external emulsion is then less stable, the inner emulsion may be quite stable.

The  $C^-$  and  $B^+$  zones correspond to emulsions of the same type as in the  $A^-$  and  $A^+$  zones, respectively, but with a low content of the internal phase, which favors phase separation by sedimentation, and, with the chosen criterion, can then result in a lower stability.

The phenomena indicated in the SAD-WOR chart have been encountered for many systems. Similar charts have been obtained by using classical formulation variables for the SAD scan [58, 62, 70-72], in addition to the pH in the presence of acids [73] or the temperature [74], both for anionic and nonionic surfactants. The width of the A zone apparently depends upon the viscosity of the oil [70], the energy of agitation [58], and the interactions of the surfactant with the water and oil [75].

### Application to dehydration

This type of map is extremely useful for explaining the action of a chemical dehydrant which is added to an oil-crude mixture down-hole, i. e., prior to the formation of an emulsion.

In order to treat a system susceptible to produce a stable W/O emulsion located in  $B^+$  or  $A^+$  ( $SAD > 0$ ), as it happens due to the effect of natural surfactants, a hydrophilic surfactant dissolved in an oil phase must be added in such a manner that when combined with the natural surfactants,  $SAD = 0$  or  $SAD$  is slightly negative (Figure 7, case 1). Under such conditions, an unstable W/O emulsion is obtained.

If a hydrophilic surfactant dissolved in a significant amount of water is added to the same system in such a manner that the resulting  $SAD$  is zero at the  $A^+/A^-$  boundary or slightly negative in  $A^-$ , an unstable O/W emulsion is obtained (Figure 7, case 2). This could be a better result than with the preceding treatment if the crude is viscous, since a W/O emulsion can be difficult to pump.

If a hydrophilic surfactant and water in sufficient quantities are added to produce  $SAD < 0$  in the  $A^-$  zone, a stable O/W emulsion can be obtained (Figure 7, case 3), which may be of interest for certain applications such as the transport of heavy crudes [76] or in the production of combustible emulsions.

These arguments are applicable analogously to the injection of a dehydrant down-hole, i. e., before emulsification. However, the problem is generally different, and consists of adding a chemical dehydrant to an emulsion already stabilized by natural surfactants. Some studies have been performed on this topic [77-78].

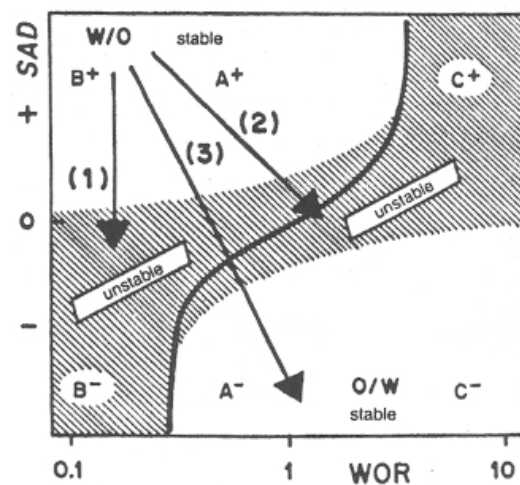


Fig. 7. Use of the formulation-WOR map for treating emulsions of the W/O type: (1) dehydration, (2) desalination, (3) production of stable W/O emulsions.

The inversion line is found to be unchanged for a crossing of the  $A^+/A^-$  limit in any direction, but hysteresis is exhibited for  $A/C^+$  and  $A/B^-$  crossings between normal and abnormal regions. The difference between these two types of inversion, called transitional and catastrophic, has recently been interpreted in a qualitative fashion, with the use of catastrophe theory [79, 80].

With regard to applications of dehydration, a change from  $B^+$  ( $SAD > 0$ ) to the  $B^+/B^-$  limit ( $SAD = 0$ ) or to  $B^-$  ( $SAD < 0$  or near zero), as well as a change from  $B^+$  to  $A^+$  at the  $A^+/A^-$  limit ( $SAD = 0$ ) or to  $A^-$  ( $SAD < 0$ ), produce essentially the same effects as for a preequilibrated system.

If the objective is to apply this analogy to crude/water systems, the appropriate mixing rule between the natural surfactants and the chemical dehydrant must be followed.

It is worth noting too, on the other hand, that the dehydrating agent should migrate rapidly to the interface in order to combine with the natural surfactants. This last requirement implies that the dehydrating agent must be incorporated into the system in a vehicular solvent miscible with the external phase of the emulsion to be broken.

## Conclusions

Experimental evidence on a representative system indicates that the most effective mechanism for destabilization of an O/W or W/O emulsion is the removal of the surfactant from the water-oil interface by trapping it in a microemulsion.

This phenomenon then leads to the optimal formulation of the SOW system, which corresponds to an ultra-low interfacial tension and the formation of a three-phase system.

The physical and chemical phenomena involved in dehydration processes can be interpreted by simulating both the surfactants which occur naturally in the crude and the addition of a chemical dehydrant.

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