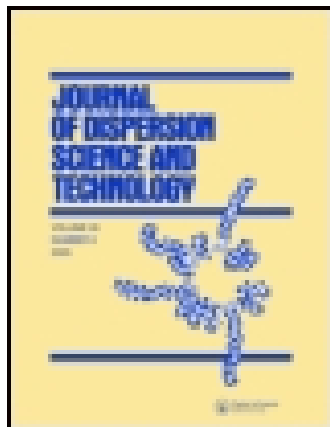


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SURFACTANT-OIL-WATER SYSTEMS NEAR THE AFFINITY INVERSION PART I: RELATIONSHIP BETWEEN EQUILIBRIUM PHASE BEHAVIOR AND EMULSION TYPE AND STABILITY

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SURFACTANT-OIL-WATER SYSTEMS NEAR THE AFFINITY INVERSION
PART I: RELATIONSHIP BETWEEN EQUILIBRIUM PHASE
BEHAVIOR AND EMULSION TYPE AND STABILITY

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ABSTRACT

A systematic relationship was found between the equilibrium phase behavior of a surfactant-alcohol-oil-water system and the type and stability of the corresponding emulsion.

Formulations are scanned through the three phase transition by changing (one at the time) brine salinity, oil EACN, surfactant nature and alcohol concentration. Whatever the scanning variable, it is found that the electrical conductivity exhibits a large change near the optimum formulation, indicating the inversion of the continuous phase of the dispersed system.

On the other hand, the emulsion stability is found to undergo a deep minimum for formulations corresponding to the three phase behavior at equilibrium.

The large but relatively smooth variation of the conductivity gives some hints on the possible continuity structure of the MOW triphasic emulsions.

INTRODUCTION

Surfactant-oil-water systems have been studied recently in relation to their enhanced oil recovery potential (1). It has been shown that under certain circumstances the interfacial tension

could be decreased down to ultra-low values in the 10^{-4} dyne/cm range. In such cases, quasi-miscibility is obtained, and the capillary forces which trap oil in porous media are no longer a match for the viscous drainage forces (2-3).

Owing to the complexity of such systems, most physicochemical studies were carried out with modeled oil and brine phases; the involved variables were recently classified (4) in three groups: a) the formulation variables dealing with the nature or type of substances, i.e. oil, brine, surfactant and alcohol; b) the position variables (on a diagram), which describe the fractional composition of the system; and c) the external variables such as temperature and pressure.

When a surfactant-oil-brine pseudo-ternary approach is considered for the sake of simplicity, it is convenient to neglect the alcohol volume, and to transfer the influence of the nature and concentration of alcohol into a single external variable, the "f(A)" alcohol functional that gathers both effects (4-5).

PHASE BEHAVIOR

Most physico-chemical studies use the unidimensional formulation scan, i.e. the continuous change of a single formulation or external variable, at all others held constant, including composition. For such a scanning technique it is found that, for a so-called optimum formulation, the interfacial tension undergoes a deep minimum; in the presence of a suitable alcohol, most optimal systems exhibit a triphasic behavior, with a middle-phase microemulsion in equilibrium with excess brine and oil phases (4-16).

Optimum formulations are also associated with other characteristic phenomena such as a maximum solubilization of oil and water by the surfactant (6), surfactant balanced affinity for the aqueous and oleic phases (4,7,13,17), and several others described in the recent literature (13,18-22).

Thanks to the introduction of several parameters able to describe quantitatively the characteristics of the system components and other relevant variables such as the alcohol effect, recent

publications have shown that the conditions for obtaining an optimum formulation, and thus a surfactant affinity balance, may be written as:

$$\sum_i c_i X_i = 0 \quad \{1\}$$

where the c_i are coefficients, and the X_i the formulation and external variables such as: brine salinity or its logarithm, oil equivalent carbon number - EACN, a measurement of oil lipophilicity (23) - type and concentration of alcohol or alcohol functional (4), a surfactant characteristic parameter (HLB or related), and temperature. Such correlations were reported for anionics (5), nonionics (9,12), and mixtures (24) of surfactants.

By changing any of the X_i , the left side of equation {1} can be made smaller, equal or greater than zero, leading to a surfactant affinity leaning towards the aqueous, the middle or the oleic phase (17). These different cases correspond respectively to the three observed phase behavior types I, III and II according to Winsor (25), or $\underline{2}$, 3 and $\bar{2}$ as mentioned in other papers (26).

EMULSION TYPE

The transition through an optimum formulation is a general phenomenon, and the associated effects on phase behavior, interfacial tension, and surfactant partitioning are also quite general, and comparable from case to case on a qualitative basis. One may wonder whether such generality applies to the emulsified systems.

For several unidimensional scans, the studied systems which contain in most cases sodium dodecyl sulfate/sodium chloride brine/kerosen/n-pentanol with a water-oil ratio near unity, are equilibrated at constant temperature and the phase behavior is noted; then the preequilibrated systems are emulsified with a turbine blender according to a consistent procedure.

The electrical conductivity of the emulsion is immediately measured, under gentle magnetic stirring, with a platinized Pt cell. Under these conditions the obtained value remains constant for a long time, and is found to be relatively steady ($\pm 5\%$).

Because of the salinity of the aqueous phase (1 to 5% wt. NaCl) the electrical conductivity of the oil-in-water emulsions is of the 10 mS/cm order of magnitude, whilst it is one hundred to one thousand times lower for water-in-oil emulsions. Thus the conductivity measurement yields a quick determination of the emulsion external phase; these results are corroborated by microscopic observations.

Figure 1 shows the conductivity variation versus the salinity of the aqueous phase, all other parameters being held constant. The $\underline{2}$, 3 and $\bar{2}$ symbols (26) indicate the phase behavior at equilibrium and the surfactant affinity (towards aqueous, middle and oleic phase respectively), while O/W and W/O refer to the diphasic types of emulsion. In the three phase region, the emulsion is labeled MOW for microemulsion-oil-water (27); however no dash is included since the external phase is not readily determined, as discussed later on.

In the $\underline{2}$ region the conductivity increases steadily with salinity, as may be expected with a continuous aqueous phase; on the other side in the $\bar{2}$ region, the conductivity is lower than 10 μ S/cm, and thus essentially zero on the illustrated scale.

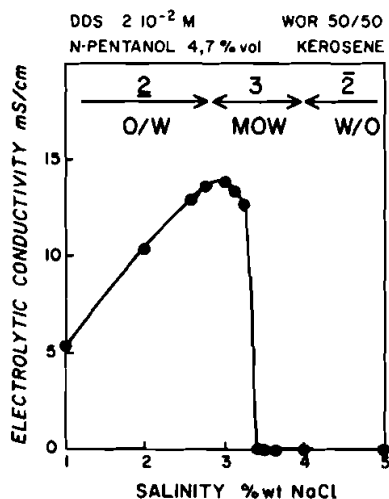


FIG. 1. Variation of the electrolytic conductivity of the emulsified system for a salinity scan.

As far as the 3 region is concerned the conductivity exhibits a sharp fall in the mid-range; however the tendency to decrease is apparent already at the $\underline{2}$ -3 boundary. Such smoothing effect, although non visible on the figure because of the scale, also happens near the $3-\overline{2}$ limit; in some cases an intermediate value of the conductivity (equivalent to, say 5 mS/cm on the graph) is observed in the center of the three phase region. This "non-catastrophic" drop tends to indicate that the transition from complete water-external to complete oil-external emulsion occurs over a narrow but finite range of formulation. It is worthwhile recalling here that from left to right in the 3 region, the middle phase composition varies from, say, 90% to 10% brine, with an associated drastic change in its own conductivity (8,28,29).

There is not enough evidence to decide about the structure of the triphasic emulsion MOW on the sole basis of conductivity; it may be bicontinuous (water|middle phase, or middle phase|oil) on the left and right part of the 3 region, and for the sake of a smooth transition, middle phase continuous or even tricontinuous in the center. The whole picture is further complicated by the attractive possibility of multicontinuity for the middle phase itself (30,31).

However, the conductivity drop does not always happen in the center of the 3 region as in figure 1; we have found systems in which the change occurs at the $\underline{2}$ -3 or $3-\overline{2}$ boundaries, and even slightly outside the three phase region depending of the water-oil ratio; these observations will be reported in a forthcoming paper.

Conductivity studies, carried out for different systems and various scanning variables, yield to similar results. Black dots on figures 2 and 3 show the conductivity variation for a EACN scan (obtained by mixing two oils), and a HLB scan (mixture of two surfactants); figure 4 is an alcohol concentration scan according to the concept of alcohol functional as external variable (5), which usefulness was corroborated in a recent study (32).

Since the salinity is constant in these systems, the conductivity of type $\underline{2}$ emulsified system (O/W) does not vary appreciably.

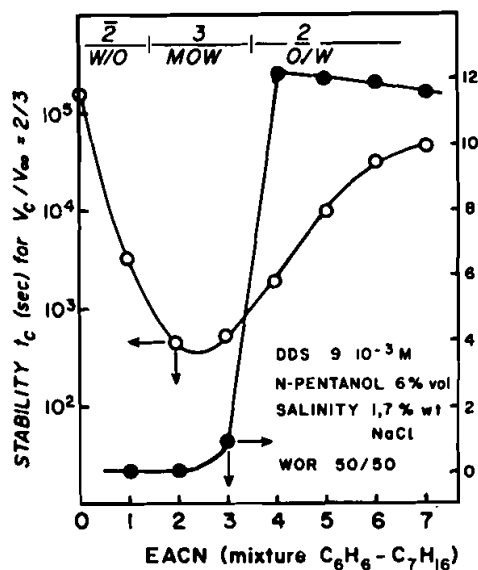


FIG. 2. Variations of the electrolytic conductivity and stability of the emulsified system for an oil EACN (Equivalent Alkane Carbon Number) scan.

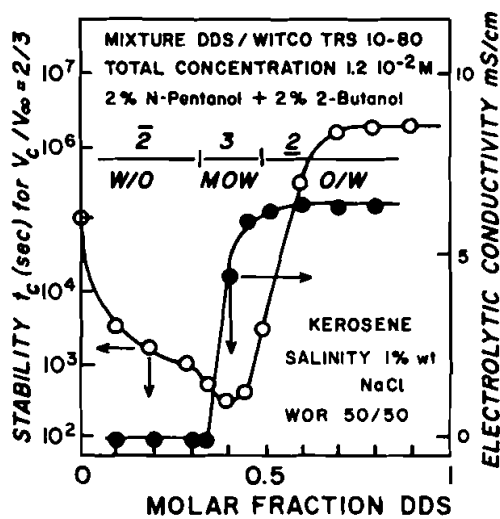


FIG. 3. Variations of the electrolytic conductivity and stability of the emulsified system for a surfactant nature (HLB) scan.

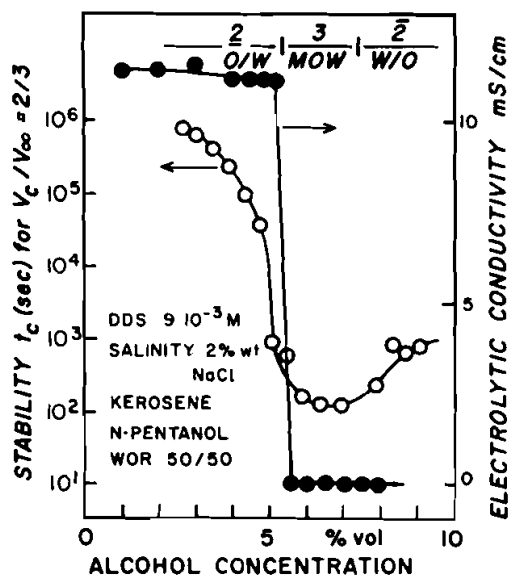


FIG. 4. Variations of the electrolytic conductivity and stability of the emulsified system for an alcohol concentration scan.

However its slight tendency to change in the neighborhood of the 2-3 boundary might indicate an alteration of the charge carrier in the aqueous phase, probably related to the micellar size. Hints for a not-so-sharp change appear in the 3 region as in figure 1 case.

Completing the present results on what may be called a Phase Inversion Formulation (PIF), some authors (20,33,34) have previously reported equivalent effects on phase inversion due to the temperature variation in systems containing nonionic surfactants (PIT).

It is hence rather secure to state, for a water-oil ratio reasonably near unity, i.e. excluding high internal-phase ratio cases, that the optimum formulation transition of the equilibrated system is associated to the inversion of the emulsion, the latter occurring probably through a complex scheme, involving may be liquid crystals (35). The mechanistic difficulty in interpreting emulsion inversion is then partially removed if an acute but continuous emulsion structure transition happens in the three phase region.

In some systems the three phase region is not apparent in a scan; recent studies tend to show that the 3 region range decreases with some formulation parameters, with a barely observable zone for ultra-low tension systems; on the other hand, the surfactant inventory may be so low that it leads to an essentially no-visible middle phase volume, in spite on the evidence of an optimum formulation diagnostic (5,7). In any of these cases it may be conjectured that the transition happens in the same way, but over an extremely reduced and thus non-apparent range of the scanning variable.

STABILITY

Preequilibrated systems pertaining to a formulation scan are emulsified as previously described, and then poured into a graduated test tube. As coalescence proceeds one (or both) of the aqueous and oleic phase tends to clear, and the cleared volume is monitored versus time. When coalescence is completed, the final cleared volume of the observed phase (noted V_{∞}) is taken as a reference, and the relative cleared volume (V_c/V_{∞}) is plotted versus time.

Figure 5 shows such a representation for different systems belonging to a salinity scan. Whilst the logarithmical time scale indicates very large variations, it is worthwhile pointing out the similarity of the experimental curves; after a flocculation process

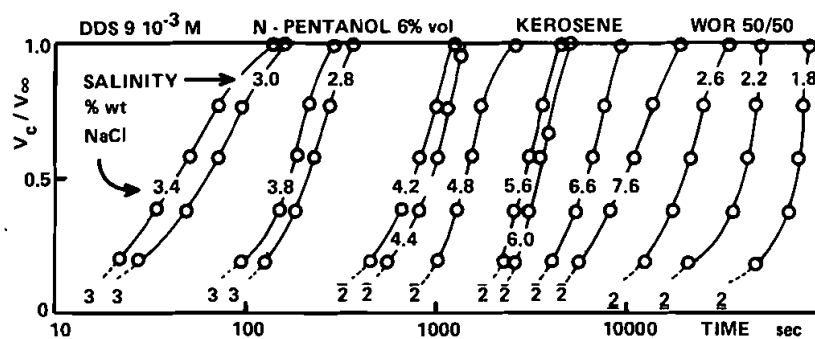


FIG. 5. Relative cleared volume of the aqueous phase (V_c/V_{∞}) versus time for a series of emulsified systems belonging to a salinity scan.

(dashed line) in which the limit of the cleared volume is rather fuzzy, the S-shaped curves exhibit an almost straight line zone.

When salinity increases, the coalescence curve shifts from long times to short ones, then to long times again. The shortest times correspond to the three-phase emulsions, near optimum salinity.

If the stability is measured as the time necessary to clear a certain fraction of the aqueous phase, figure 6 is obtained, with little difference when the given cleared fraction V_c/V_∞ is changed from 1/3 to 2/3.

In accordance to the previously published notes (27,36-38) figure 6 shows how the stability passes through a very deep minimum in the three phase region; this considerable reduction of stability in the neighborhood of the optimum formulation may be used advantageously in the process of transporting a stable emulsion, and breaking it easily afterward, by changing slightly the formulation or temperature.

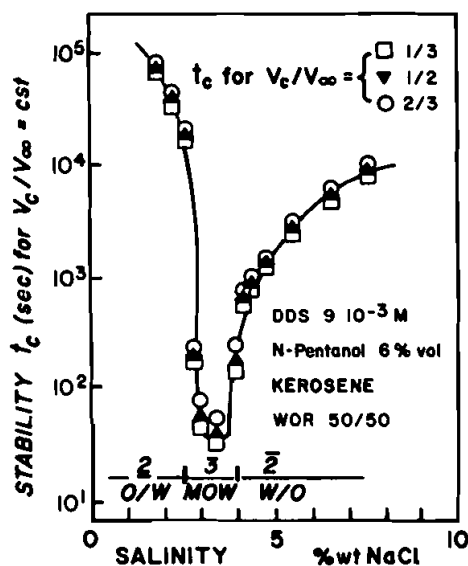


FIG. 6. Stability of the emulsified system, as the time required to clear a given relative volume of aqueous phase, for a salinity scan.

In some cases it is not possible to follow the volume clearing for both aqueous and oleic phases, but only for one of them, or for the corresponding continuous phase. When it is feasible to monitor both phases clearing over almost all the range through an optimum formulation, as in figure 7, it is seen that the coalescence times of both observations yield to the same conclusions; although the coalescence time of the continuous phase is generally shorter (oleic on left side of figure 7, aqueous on right side), the stability undergoes a minimum in the 3 region, where values are essentially identical. This is another hint that MOW emulsions behave quite differently from their diphasic counterparts, independently of the fact that their conductivity is high or low (conductivity change is indicated by an arrow on figure 7).

As for the conductivity studies, different kinds of systems and various types of scan were investigated. Blank dots on figures 2, 3, and 4 indicate the stability versus an oil (EACN), a surfactant type, and an alcohol concentration scan respectively. These figures show that, for any kind of formulation scan, the stability

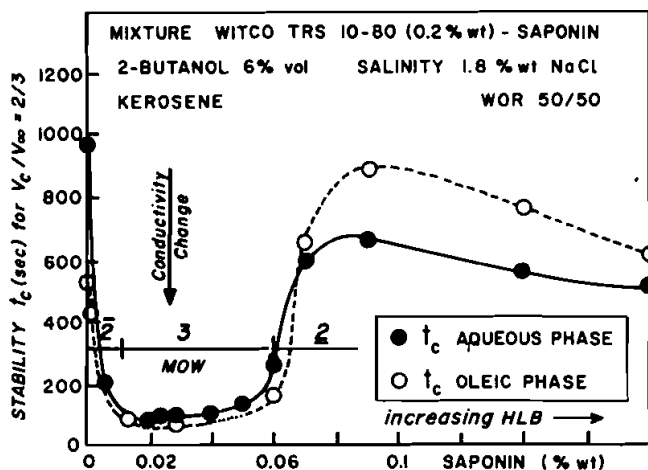


FIG. 7. Stability of the emulsified system, as the time required to clear a 2/3 relative volume of either aqueous (black dots) or oleic (blank dots) phase.

of the emulsion undergoes a minimum in the three phase region. The experimental evidence is not however accurate enough to decide whether this minimum correspond exactly to the optimum formulation (minimum tension) and/or to the conductivity drop. Studies on more stable systems are under way to bring a more precise knowledge on this point.

It is worthwhile noting that a stability minimum is somewhat paradoxical. Indeed, the near optimum systems exhibit a very low tension value, but the size of the produced interfacial area does not seem to increase in the same way as the tension decreases. As a consequence the free energy drop due to the coalescence of the MOW systems, i.e., the product of the tension by the vanished interfacial area, is much smaller than in adjoining W/O and O/W emulsions. Although the thermodynamical gain in coalescence is smaller, the three phase emulsions coalesce much more rapidly. It may be thought that the mechanism is controlled by a kinetic effect, or that the enhanced free energy of the microemulsion shell is insufficient to counteract the enhanced Van der Waals potential (39).

When the coalescence of a two phase emulsion is observed through a microscope, it is possible to follow the drop approaching the bulk phase, the film drainage step, and the final coalescence burst. In accordance with a recent paper (39), we found that with MOW emulsions, the whole picture is quite different. First, the dispersed volumes are far from spherical, exhibiting pear-shaped drops and worm-like behavior; interface contours change constantly and the film drainage lag-time seems non-existent. Finally, the coalescence burst appears to be smoother than in diphasic cases.

CONCLUSIONS

There is a definite relationship between the phase behavior of surfactant-oil-water systems at equilibrium, and the corresponding emulsion properties.

It is found that, at near optimum formulation in the three phase region, the electrical conductivity exhibits a sharp drop

indicating an inversion of the continuous phase, while the stability undergoes a deep minimum, whatever the scanning variable.

Other marked effects on viscosity and related rheological properties were also found, and will be reported in a forthcoming paper.

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