

## **SURFACTANT-OIL-WATER SYSTEMS NEAR THE AFFINITY INVERSION PART III: THE TWO KINDS OF EMULSION INVERSION**

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### **ABSTRACT**

The inversion locus is represented on a generalized mixed bidimensional scan (formulation-WOR), where the formulation variable may be the salinity, oil ACN, alcohol type or concentration, surfactant parameter such as EON, or temperature.

At near unity water/oil ratio the inversion locus (Phase Inversion Formulation: PIF) approximately matches the optimum formulation for minimum tension and phase behavior. In this region the inversion depends essentially upon physico-chemical factors. At extreme water/oil ratios, the inversion locus depends essentially upon the volumetric proportion of the phases, i.e., a physical factor.

A general classification of emulsion type is proposed according to the optimum formulation and phase inversion lines.

The alterations of the inversion locus with surfactant type, oil viscosity and conditions of emulsification, are discussed.

### **INTRODUCTION**

In previous papers [1-3], it was shown that there is a relationship between the phase behavior at equilibrium and the emulsion properties of surfactant-oil-water systems. The reported results were limited to near unity water/oil ratio and low viscosity oil phase. Within such limits, the phase behavior at equilibrium determine the type of emulsion, whatever the formulation variable used to scan through the three-phase transition zone.

The inversion takes place in the three-phase region in a microemulsion-oil-water (MOW) emulsified system.

On the other hand, it is well known that the increase in internal phase ratio may also produce the inversion; most of the reported results refer to the case of an emulsion to which internal phase is added (continuously or by increments) under constant stirring. This procedure increases the internal phase volume fraction " $f_i$ ", until the emulsion inverts, typically at  $f_i = 0.7-0.8$ .

When emulsification takes place with preequilibrated surfactant-oil-water systems, the obtained emulsion also depends upon the WOR, for a given mixing scheme. The inversion limit for this second case is fixed, but not necessarily equal to the one obtained from continuous addition experiments, in which an hysteresis phenomenon may occur, especially with viscous liquids and rigid surfactant films [4].

## CHEMICALS

Sodium dodecyl sulfate (SDS) was MERCK™ pure grade reagent; STEPAN™ Petrostep MMW, a 50% active petroleum sulfonate with EMW 435, was used as received from the manufacturer.

MAKON™ X nonionic surfactants are STEPAN™ ethoxylated nonyl phenols, where X stands for the average number of ethylene oxide; ethylene oxide number scans were obtained by mixing MAKON 4, 6, and 8 in different amounts according to a linear scaling rule on a molar basis [5-7].

Alcohols and sodium chloride were analytical reagents; oil phases of different types and viscosities were made out of one or several of the following hydrocarbons: pure grade alkanes, commercial kerosene, and an aromatic lube oil base (viscosity 4100 cP at 25 °C)

## EXPERIMENTAL

The general experimental procedure to preequilibrate and emulsify the surfactant-oil-water systems has been reported in previous papers [1-3].

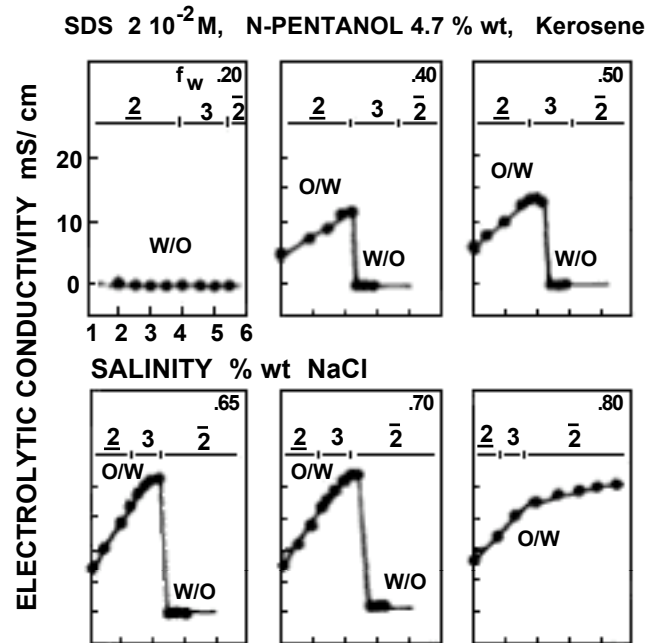
The electrolytic conductivity is measured under gentle stirring with a platinized platinum cell, and a TACUSSEL™ CD 78 digital conductimeter. Since the aqueous phase contains a certain concentration of sodium chloride (1 wt% or more), the inversion is easily monitored by a change of two or more orders of magnitude in conductivity (mS/cm for O/W, and  $\mu$ S/cm for W/O).

## FORMULATION SCANS AT DIFFERENT WOR VALUES

Inversion may be due to a change in the physico-chemical conditions of the system, or to an increase of the internal phase volume fraction ( $f_i$ ) beyond a certain value. The literature does not clearly mention whether and how these two phenomena are linked, but in a study on the relationship between the PIT and WOR [8].

In order to study an eventual relation between them, both phenomena are gathered in a "mixed" bidimensional scan; first, several series of formulation scans at different WOR are carried out as described in Part I paper [2]; Fig. 1 indicates the conductivity variation versus salinity for different values of the water volumetric fraction. On each graph the phase behavior ( $\underline{2}$ ,  $3$ ,  $\bar{2}$ ) is noted versus salinity.

- Between 35% and 65% water, the conductivity exhibits a rapid change inside the three phase region, in accordance to the previous results [1-2]. However, it is worth noting that the exact position of the inversion point changes from the lower boundary of the three-phase region for  $f_w = 0.40$ , to the upper boundary for  $f_w = 0.65$ ; it may be seen that at  $f_w = 0.70$ , the inversion occurs even slightly outside the three-phase region. Because of this displacement of the inversion point, it is seen that the MOW three-phase emulsion may exhibit a conductivity similar to O/W or W/O emulsions, depending of the case.
- Below 30% and above 70% water, there is no rapid change in conductivity when the salinity passes through the optimum formulation for three-phase behavior. In the conditions of emulsification, the external phase is the one with higher volume fraction. However, it is worth noting that at  $f_w = 0.80$ , the conductivity variation exhibits a change of trend, right at the boundary of the three-phase region. It may be

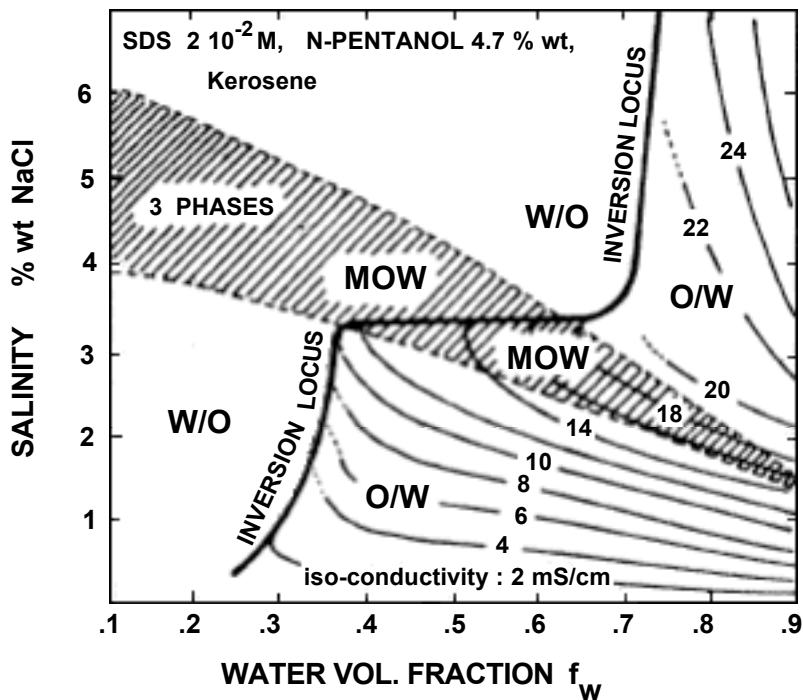


**Fig. 1.** Variation of the electrolytic conductivity of the emulsified system vs. salinity - Influence of the water volume fraction  $f_w$

said that at 5 wt% NaCl, the obtained O/W emulsion differs in structure from the one obtained at 1 wt% NaCl. In effect, if they were similar, the conductivity of the emulsion would continue to increase with the same trend, with increasing salinity of the external phase. As a matter of fact a multiple emulsion may occur at 5% NaCl.

## MIXED BIDIMENSIONAL SCAN

In order to obtain the variation of conductivity versus both variables (salinity and internal phase fraction), various series of  $f_w$  scans are carried out at different salinities, in the regions where the previous salinity scans did not give a precise information, i. e., around 30% and 75% water.

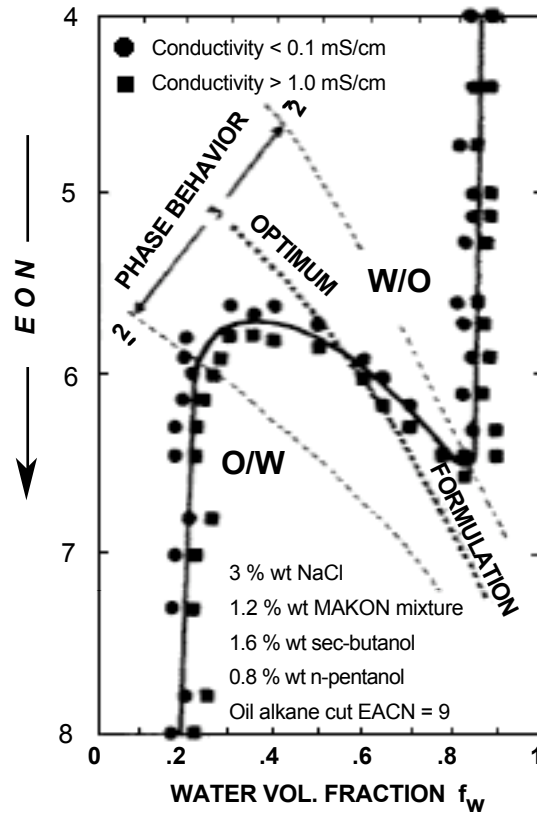


**Fig. 2.** Mixed bidimensional scan showing the phase behavior at equilibrium and the emulsion properties (anionic surfactant)

With the two kinds of scan, a mixed bidimensional plot of conductivity versus both salinity and water volume fraction  $f_w$  is constructed. Fig. 2 shows the three-phase region (shaded), and the contours of iso-conductivity on such a plot. It is noted that the iso-conductivity lines all tend to gather into an asymptote, which is indicated as a heavy line.

On the right and lower part, the conductivity of the emulsion is of the same order of magnitude as the conductivity of the corresponding aqueous phase; the slight slope of the iso-conductivity curves is due to the increasing proportion of external phase from left to right.

On the other side of the asymptote (left and upper part of the graph), the conductivity of the emulsion is of the same order of magnitude as the conductivity of the oil phase.



**Fig. 3.** Mixed bidimensional scan (nonionic surfactant)

Actually the heavy line indicates the geometrical locus of the points where the conductivity drops two or three orders of magnitude, i.e., the emulsion inversion locus on a mixed bidimensional scan, which may be called the phase inversion formulation (PIF) [2], in the same way as Shinoda's phase inversion temperature PIT [9-10].

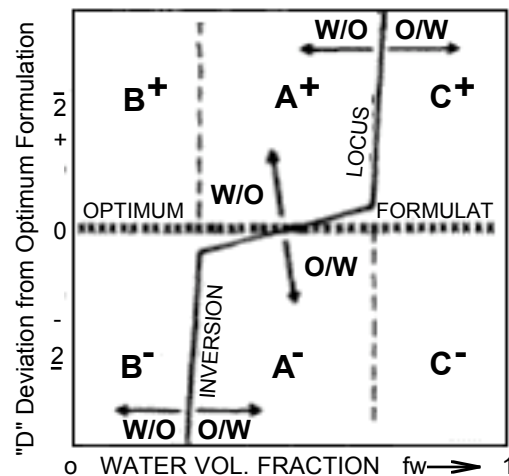
Fig. 3 shows a mixed bidimensional scan with nonionic surfactants; this time the formulation variable is the average ethylene oxide number (EON) of the ethoxylated nonyl phenol mixture. Since lipophilicity increases when EON decreases, the ordinate scale reads from top to bottom, in order to keep the same orientation as Fig. 2 data.

This figure was obtained from EON scan inside the region  $0.10 < f_w < 0.90$ , and from  $f_w$  scans near the 0.20 and 0.80 boundaries. Only two experimental points are shown for each scan, i.e., the last with low conductivity and the first with high conductivity. The inversion locus is thus squeezed in between these points.

In a study with nonionic surfactants where the temperature plays the role of the formulation variable, Shinoda and Arai [8] reported that the inversion locus, i.e., their PIT [9-10], exhibits for several oil phases, the same variation as mentioned here.

## REMARK ON THE VARIATION OF OPTIMUM FORMULATION WITH WOR

It is worth noting here that the three-phase region center line in Fig. 2 and 3 presents a slope, i.e., the optimum salinity decreases as  $f_w$  increases. This phenomenon seems to be typical of surfactant/oil/water systems containing an hydrophobic alcohol such as n-pentanol. In effect, as  $f_w$  is changed, the total amount of alcohol in the system is maintained constant. Assuming a constant partition coefficient of the alcohol between phases, this means that as  $f_w$  increases, the actual concentration of alcohol in the aqueous phase increases. It was shown recently [11] that such an increase in pentanol concentration produces a shift of optimum salinity towards lesser values. The magnitude of the change was related to an alcohol function  $f(A)$ , which depends on the type of alcohol and on its concentration; the stronger the lipophilicity of the alcohol, the stronger the shift effect for a given concentration. This concept applies similarly for the EON shift for nonionic surfactants [6].



**Fig. 4.** Scheme of a mixed bidimensional scan with inversion locus and different regions.

## ANALYSIS OF A MIXED BIDIMENSIONAL SCAN

In spite of the shift in the position of the different branches of the inversion locus, Fig. 2 and 3 are very similar. To analyse the information content of a mixed bidimensional scan, a typical schematics of it is represented in Fig. 4. In order to eliminate the shift of optimum formulation with WOR, the ordinate scale is taken as the deviation "D" from the optimum value of the scanning variable at the same WOR. That is

In Fig. 2 case  $D = S - S^*$

In Fig. 3 case  $D = EON^* - EON$

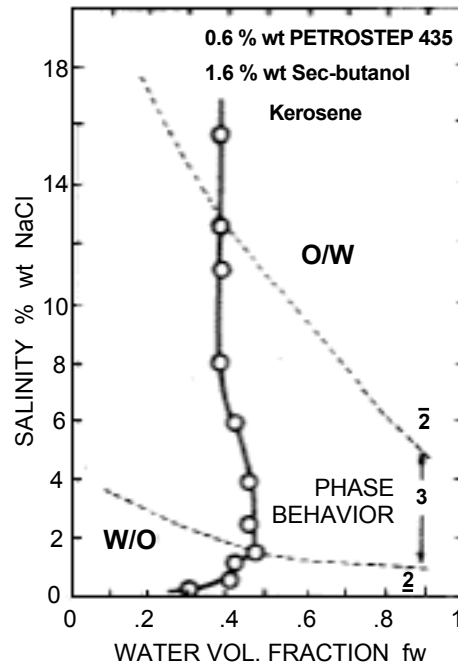
A positive value of "D" indicates a  $\bar{2}$  system, while a negative value corresponds to a  $\underline{2}$  system. This representation is linked with the difference in affinity of the surfactant for the oil phase and the aqueous phase, and is quite general, since "D" may represent salinity, oil EACN, alcohol type and concentration, surfactant type or temperature [11].

In a T- $f_w$  bidimensional mixed scan, "D" would stand for  $T - T^*$ , where  $T^*$  would refer to the optimum temperature for minimum tension or three phase behavior [5-6]. Unfortunately Shinoda and Arai's [8] data do not include the phase behavior.

Fig. 4 exhibits the following main characteristics of mixed bidimensional scans:

- ✓ In the  $f_w$  central region (here  $0.30 < f_w < 0.70$ ), the inversion locus lies in the three phase region, and the inversion is associated with the phase behavior, as reported in detail in a previous paper [2]. This region is labeled "A", with the symbol "A<sup>-</sup>" below the optimum formulation line, and "A<sup>+</sup>" above it. The superscript actually indicates the sign of "D".
- ✓ It is worth noting that the inversion locus crosses obliquely the three phase region, which indicates that the MOW emulsions have a low conductivity (such as W/O) in the upper left, or a high conductivity (such as O/W) in the lower right. In this central "A" region, the position of the inversion point inside the three phase zone depends essentially upon the internal phase ratio.

- ✓ In the left-side region ( $f_w < 0.30$ ), the electrical conductivity of the emulsion indicates an oil external phase, whatever the phase behavior. This region is labeled "B" and divided as previously in "B<sup>-</sup>" and "B<sup>+</sup>" regions, below and above the optimum formulation line. In the "B<sup>+</sup>" region the obtained emulsion is W/O, and the same rule is observed, as in the "A<sup>+</sup>" region for  $D > 0$ . In the "B<sup>-</sup>" region, the phase behavior would favor the occurrence of an O/W emulsion, but there is not enough water ( $f_w < 0.30$ ) to make this the external phase in the conditions of emulsification.
  
- ✓ In the right-side region ( $f_w > 0.70$ ), the electrolytic conductivity of the emulsion indicates a water external phase, whatever the phase behavior. This region is labeled "C", with the notation "C<sup>-</sup>" and "C<sup>+</sup>" as previously defined. In the "C<sup>-</sup>" region, the observed emulsion is O/W, and the rule holds as in region "A<sup>-</sup>" for  $D < 0$ . In the "C<sup>+</sup>" region, the phase behavior would favor a W/O emulsion, but there is not enough oil ( $f_o < 0.30$ ) to make it the external phase in the conditions of emulsification.



**Fig. 5.** Extreme deformation of the inversion locus.

## THE TWO KINDS OF INVERSION

Regions  $A^-$ ,  $A^+$ ,  $B^+$ , and  $C^-$ , are "*normal*" regions in the sense that the emulsion type corresponds to the phase behavior physico-chemical considerations [2], in accordance with the normal curvature requirement of the interface, as predicted by Winsor R [13-14] and cohesive energy models [15-16].

The other regions, " $B^-$ " and " $C^+$ " are "*abnormal*", since the influence of the physico-chemical factors is offset by the volumetric requirement, in the conditions of emulsification.

There are thus two kinds of inversion. The first one corresponds to the transition between regions " $A^-$ " and " $A^+$ ", where the inversion process is controlled by the physico-chemical factors. It was discussed in a previous paper [2] that such an inversion occurs through a sharp but continuous transition.

The other type of inversion is the one occurring at the  $A^+/C^+$  and  $A^-/B^-$  boundaries, which corresponds to a physical effect, i. e., the phase with the higher volumetric proportion becomes the external phase. The position of this inversion is practically independent of the formulation variable, e. g., the lateral branches of the locus are almost vertical.

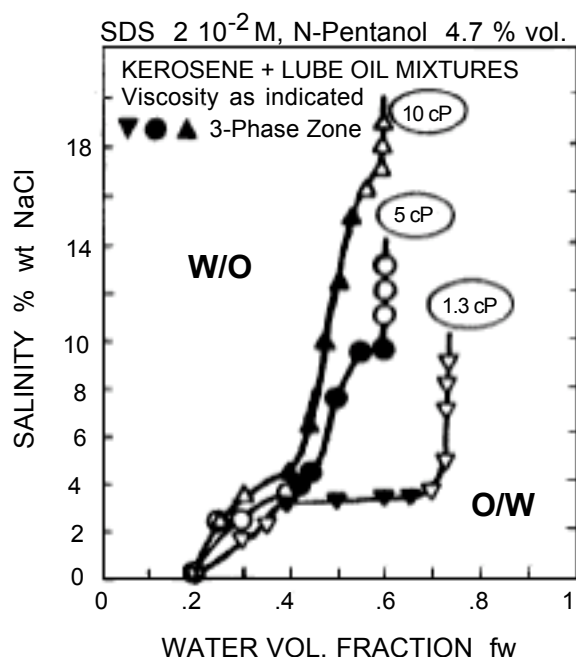
Experimental evidence tends to show that the properties of the emulsion exhibit continuity at the  $A^+/B^+$  and  $A^-/C^-$  limits, while a sharp change in stability is observed at the  $B^-/B^+$  and  $C^-/C^+$  limits. There is some evidence, such as the strong slope of the isoconductivity curves in the " $C^+$ " region of Fig. 2, that the abnormal " $B^-$ " and " $C^+$ " regions may contain unstable multiple emulsions, and that the  $A^+/C^+$  and  $A^-/B^-$  inversion may occur in some "catastrophic" way [17]. These results will be discussed in a forthcoming paper.

## FACTORS INFLUENCING THE INVERSION LOCUS

The central branch of the inversion locus, i. e., the  $A^-/A^+$  inversion, depends essentially on the position of the optimum formulation transition. However, it does not always correspond to an almost straight line crossing obliquely the three phase region. With systems which exhibit a wide three phase regions (vertically) and narrow " $A$ "

region (horizontally), there is no neat plateau, as with the pure systems shown in Figs. 2 and 3. With some systems containing impure commercial anionic surfactants, some large deformations are found as in Fig. 5. The extreme width of the three-phase region and the emulsion behavior tends to indicate that the surfactant different components may fractionate separately, and thus, the collective behavior of the surfactant mixture does not apply in these cases.

The position of the lateral branches of the inversion locus were found to depend upon different factors. Comparison of Fig. 2 with Fig. 3 data, which were obtained in similar emulsification conditions, shows that the width of the "A" region might depend upon surfactant type and alcohol formulation. Ethoxylated nonyl phenols seem to be able to produce emulsions with higher internal phase ratio than sodium dodecyl sulfate.



**Fig. 6.** Influence of oil type and viscosity on the inversion locus (in each case, the black dots indicate three-phase systems)

The type of oil may also alterate and shift the inversion locus. Fig. 6 shows the inversion locus on a bidimensional mixed scan for three systems with different oil viscosities, obtained by mixing kerosene with a viscous lube oil base. As the oil viscosity increases, the  $A^+/C^+$  boundary shifts to lower values of  $f_w$ , while the  $A^-/B^-$  boundary remains unaltered.

Under the same emulsification conditions, it is then more difficult to produce high internal phase ratio W/O emulsions when the oil viscosity increases, while no noticeable change occurs for high internal phase ratio O/W emulsions. This well-known trend is accompanied by a (horizontal) narrowing of the "A" region, and a (vertical) expansion of the three-phase region where the experimental points are figured as black dots.

Since the widening of the three-phase region is linked with an increase of the minimum interfacial tension [18], it is worth noting that the change in aspect of the inversion locus with oil viscosity, may be also due to a change in the interfacial tension.

The influence of the emulsification conditions were not studied exhaustively; however, some experiments, carried out with an adjustable-speed turbine blender, showed that the position of the lateral branches of the inversion locus are shifted by an increase in the mechanical energy input during emulsification, the tendency being to widen the "A" region.

## APPLICATIONS

The knowledge and mapping of the inversion locus on a mixed bidimensional scan may have several applications of practical importance.

For low and medium internal phase ratios, it shows that for a system at equilibrium, the type of emulsion depends essentially upon the physico-chemical formulation; thus the adjustment of the formulation variables must be the predominant concern. If an emulsion is to be prepared at little energy expense, the adequate "A" region should be selected inside or near the three phase zone, where the interfacial tension is very low, and from which a fine drop emulsion would result. Shinoda's rule of emulsification [19] near the PIT corresponds to such a technique, since temperature is one of the variables appearing in the correlation, with the consequence that "D" may be expressed as " $T - T^*$ ", which is roughly equivalent to " $T - PIT$ " in the central region (see following remark on PIT).

Since the optimum formulation separates the "normal" and "abnormal" zones in the "B" and "C" regions, a change in formulation may be used advantageously. For example, the introduction of a lipophilic surfactant, the increase in salinity, or the introduction of a lipophilic alcohol, in a stable O/W emulsion laying in the "C" zone, may shift it to the

"C<sup>+</sup>" zone, where stability is much lower. These effects are already well known and applied in emulsion breaking processes.

Since the lateral branches of the inversion locus may be shifted by the surfactant type, the "C<sup>+</sup>" and "B" abnormal regions may be reduced or expanded when needed, to produce or avoid high internal phase ratio emulsions.

Since the lateral branches of the inversion locus may be shifted by a change in emulsification conditions, emulsions laying in the "A" region, but near the A<sup>+</sup>/C<sup>+</sup> and A<sup>-</sup>/B<sup>-</sup> boundaries, are susceptible to invert when submitted to a strong shear field as in centrifugal pumps. The mixed bidimensional scan may allow the definition of "safe" and "dangerous" zones, as far as the emulsion handling is concerned.

Mayonnaise is typically an O/W emulsion in the "A<sup>-</sup>" zone, near the boundary A<sup>-</sup>/B<sup>-</sup>. By switching the emulsification device from spoon to turbine blender, the A<sup>-</sup>/B<sup>-</sup> boundary is moved from right to left, and to obtain a mayonnaise, oil may be added all at once (low  $f_w$ ), instead of drop by drop (high  $f_w$ ). It is worth noting that by adding all the oil at once on vinegar-egg (aqueous phase), and stirring with a spoon, the cook is likely to obtain instead an "abnormal" result, e. g., something like a vinaigrette or Italian dressing (B<sup>-</sup>) rather than a mayonnaise.

### **REMARK on PIT**

The previous discussion on the bidimensional mixed scan shows that the inversion locus crosses the optimum formulation line, only at one point. When the scanning variable is the temperature, the inversion locus is the PIT, which is not strictly equivalent to the optimum temperature for minimum tension or three phase behavior, but only at the crossing value of  $f_w$ .

At water/oil ratio outside the "A" region and for cases where the inversion locus and the optimum formulation lines have quite different slopes, the use of PIT as a measurement of optimum formulation at equilibrium may be grossly in error. In such cases the PIT cannot be used to characterize the surfactant hydrophilic-lipophilic property with the general indirect method discussed elsewhere [20].

## CONCLUSIONS

The mapping of the inversion locus on a mixed bidimensional scan (formulation-WOR) indicates two types of inversions:

- At water/oil ratio near unity, the emulsion type is linked essentially with the phase behavior at equilibrium; the Phase Inversion Formulation (PIF) nearly matches the optimum formulation for minimum tension and three phase behavior.
- At extreme water/oil ratios, the type of emulsion depends essentially upon the volumetric proportions.

The inversion locus divides the formulation-WOR plane in 4 normal and 2 abnormal regions; several changes may occur at the boundaries which limit these regions.

The inversion locus shape may be altered by the surfactant type, the alcohol, the conditions of emulsification and the oil viscosity.

Shinoda's PIT concept is equivalent to the PIF. As a consequence, it does not strictly coincide with the optimum state but for one value of WOR, and may deviate considerably from it in certain cases.

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