

Emulsion Instability in the Three-Phase Behavior Region of Surfactant-Alcohol-Oil-Brine Systems

RAQUEL E. ANTON AND JEAN-LOUIS SALAGER

Lab. FIRP, School of Chemical Engineering, Universidad de Los Andes, Mérida, Venezuela

Received May 10, 1985; accepted July 17, 1985

The stability of the emulsion is estimated from a dual criterion, i.e., from both oil and water phases settling. The two criteria overlap and swap their respective meaning (coalescence vs clearing) in the three-phase zone. Three-phase emulsion breaking is interpreted with the help of a simple model. The removal of one of the phases prior to emulsification produces an emulsion as unstable as the triphasic ones. The middle phase appears to behave as a trap which hinders the surfactant from stabilizing a macroemulsion.

© 1986 Academic Press, Inc.

INTRODUCTION

In the past decade concentrated research effort has been applied to surfactant-oil-water systems in relation to their potential for enhanced oil recovery. It is now recognized that the required ultralow interfacial tension can be attained when a microemulsion, the so-called surfactant phase or middle phase, is in equilibrium with both excess oil and water phases.

These systems were labeled by Winsor (1) as type III or 3, and from the thermodynamic point of view they are obtained whenever the affinity of the surfactant toward the aqueous phase exactly balances its affinity toward the oleic phase (2, 3). Such a case may be reached with a proper combination of the physicochemical variables, i.e., surfactant HLB, oil type, brine salinity, alcohol content, as well as temperature, and is referred to as an optimum formulation. Correlations for the attainment of such optimum formulations have been found empirically (4, 5), and were recently interpreted from thermodynamic arguments (3,6).

Most physicochemical studies make use of the method of the unidimensional scan, i.e., the continuous change of a single formulation variable, while all others are held constant.

Whenever the affinity of the surfactant toward the water (respectively oil) phase predominates, a $\underline{2}$ (respectively $\bar{2}$) biphasic behavior is observed. In this mnemotechnic symbolism, the position of the bar indicates the surfactant-rich phase.

The phase behavior transition $\underline{2} \rightarrow 3 \rightarrow \bar{2}$ or vice versa, is a general phenomenon which may be obtained by scanning any formulation variable.

Since such surfactant-oil-water systems may emulsify in porous media, several studies have dealt with macroemulsion properties (7-12). In a recent series (13-16) it was shown that, whatever the scanning variable, the optimum formulation is associated with the emulsion inversion, and with a minimum in both viscosity and stability. This coincidence is very important in surfactant flooding since it is the key feature to ensure displacement (17, 18). However, the instability of macroemulsions at optimum formulation may have many other applications such as emulsion breaking.

The connection between a nonequilibrium process such as emulsion instability and the phase behavior at equilibrium is rather unexpected (13). The aim of this paper is to bring some light on this puzzling coincidence.

EXPERIMENTAL PROCEDURES

The surfactants were used as received. Witco TRS 10-80 is a petroleum sulfonate with EMW of 425. MAKON X are polyethoxylated nonyl phenols manufactured by Stepan Chemicals, where X stands for the average number of ethylene oxide groups per molecule. The oil phase is a kerosene cut with equivalent alkane carbon number (EACN) of about 11. Sodium dodecyl sulfate (SDS) and all other chemicals are pure grade or analytical reagents.

In the reported data, salinity is expressed in %wt NaCl in the brine, while surfactant %wt and alcohol %volume are with respect to the whole system. The water/oil ratio (WOR) stands for the volume ratio between brine and kerosene.

The surfactant-oil-brine systems are prepared in 50-ml batches and left to equilibrate at constant temperature in graduated tubes for at least 2 days. The phase behavior is determined by visual inspection.

The optimum formulation is attained by scanning an appropriate formulation variable, which is the salinity with anionics; with nonionics it is the ethylene oxide number (EON) calculated according to a linear mixing rule on a molar basis.

The equilibrated systems are stirred with a turbine blender and the emulsion properties, i.e., electrolytical conductivity and stability, are measured according to the procedure reported in previous papers (9, 13). Since the aqueous phase contains an electrolyte, the value of the conductivity readily indicates the type of emulsion, i.e., O/W or W/O. The different ways to measure the emulsion stability are discussed in the next section.

In some experiments a part or the whole of a phase is removed from the equilibrated system by pumping it out with a syringe. It is actually impossible to withdraw the whole middle phase by this method; instead, the system is equilibrated in a long burette, and while 80% of the oil phase is pumped with a syringe, 80% of the aqueous phase is

removed from below. The withdrawn phases are contacted again without being contaminated by traces of the middle phase.

EMULSION STABILITY

By simple observation of the evolution of the aspect of an emulsion left at rest in a test tube, it is easy to state whether it is stable or not. However, the quantification of the concept of stability, which is required to carry out comparison is not an easy task (11, 12).

Not considering the case of multiple emulsions, any two-phase system becomes, upon stirring, either a O/W or W/O emulsion. When the emulsion is left to settle, several complex processes take place (19-21).

After some time the partially broken emulsified system exhibits in most cases three zones. A central opaque zone and two clear zones above and below it. The central zone corresponds to a compacted emulsion, so-called cream, while the others are the coalesced internal phase and the cleared external phase.

The volume of these last two phases was monitored versus time, resulting in sigmoid variations (13). The time at which the coalesced or cleared volume reached 60% of its final value is taken as a criterion of stability. In a previous paper (13) it was shown that the results are very insensitive to the selected percentage.

Figure 1 indicates the variation of the emulsion stability versus formulation for both criteria. Since the emulsion inverts inside the three-phase region, a different meaning applies to each curve depending upon the type of emulsion. For the circle dots data, which refers to the water phase, the left side (W/O) corresponds to a coalesced internal phase, whereas the right side (O/W) indicates a cleared external phase. The opposite applies to the oil phase. While there is evidence in this case that the coalesced phase criterion exhibits higher values on both sides, the main feature is that both data point to the same information, i.e., emulsions formulated in the

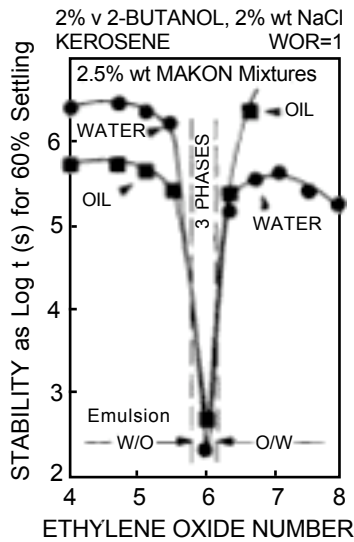


FIG. 1. Stability of macroemulsion through an EON scan as the time for 60% of either coalescence or clearing of oil or water phase.

three-phase region are several orders of magnitude less stable than their off-optimum counterparts.

Furthermore, these results show that the stability maxima on both sides of optimum formulation are not always located at the boundaries of the three-phase zone, as claimed recently (8, 22). As a matter of fact this was expected from Griffin's original method to estimate the HLB of a surfactant (23, 24).

When the three-phase region is wide enough, as in Fig. 2, the two curves may be observed to cross at or near optimum formulation. This representation gives more information than the truncated curves (11), since it indicates the continuity of the phenomenology through the three-phase region. This evidence tends to corroborate a recent model (25) which represents this "transitional" inversion through the three-phase region as the consequence of a continuous shift in phase composition, rather than a sudden change of the interface curvature.

If only an overall visual observation is used to determine the stability of the system, then a weak maximum of stability is found in the

center of the three-phase zone at the cross of the two curves as noted earlier (8).

INTERPRETATION

The observation of the three-phase emulsion breaking shows, after a few moments, that both oil and water separated bulk phases increase their volume with time by a coalescence process which takes place at the interface with a central zone, which consists of the middle phase containing rising oil and falling water droplets. It is observed that when an oil drop reaches the limit between the middle phase and the separated oil, it coalesces instantly; the same applies to the water drops at the water-middle phase limit.

The three-phase emulsion breaking may be analyzed according to the following simple model. First it is assumed that the emulsification process produces a dispersion of both oil and water droplets, in either the microemulsion or the alternate phase. The relative size of these droplets would depend on the corresponding interfacial tensions. The

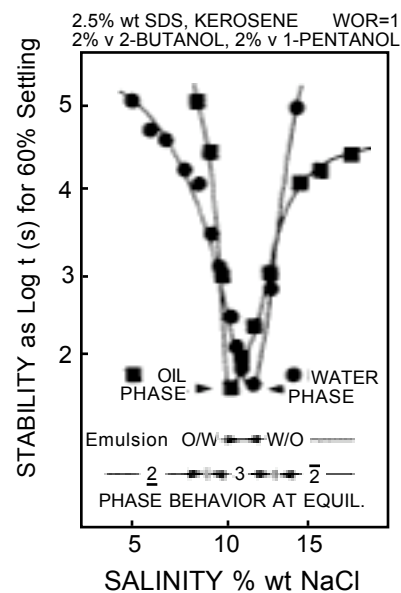


FIG. 2. Stability of macroemulsion through a salinity scan for both used criteria.

three-phase dispersion exhibits a continuous variation of the conductivity (13) through the three phases; this is compatible with a model involving a microemulsion external phase, the composition of which changes continuously from aqueous to oleic. As a matter of fact multicontinuity may be also conjectured (13).

Because of the lower tension between the middle phase and both excess phases, relative to the tension between these excess phases themselves (26), and because of its character as an external and thus continuous phase, the middle phase gathers quickly in the center of the system, which may be observed experimentally.

Since oil and water droplets coalesce instantly on contact with their separated bulk phase, the settling time corresponds mainly to the sedimentation time, specifically the time required to cross the middle-phase layer. For both species of droplet this time depends chiefly upon the droplet size and the density difference according to Stokes's law.

Figure 3 is a composite plot of the properties needed for this discussion, through a salinity scan. The variation of the interfacial tensions is well known (26). The shaded area in the test tubes represents the microemulsion, which is the middle phase in three-phase systems. The change of density of the microemulsion has been found to be practically linear in the three-phase region (27). The density difference between the microemulsion middle phase and the excess phases depends considerably on the exact location (B-D) of the formulation inside the three-phase range. For the sake of simplicity, the middle-phase microemulsion, and the excess oil and water phases will be referred to as M, O, and W respectively.

First consider case B, located inside of the three-phase region in between the center and the $2-3$ boundary. In this system, M contains more water than oil; as a consequence the difference of density between M and W is lower than between M and O.

Moreover, the tension between M and W is

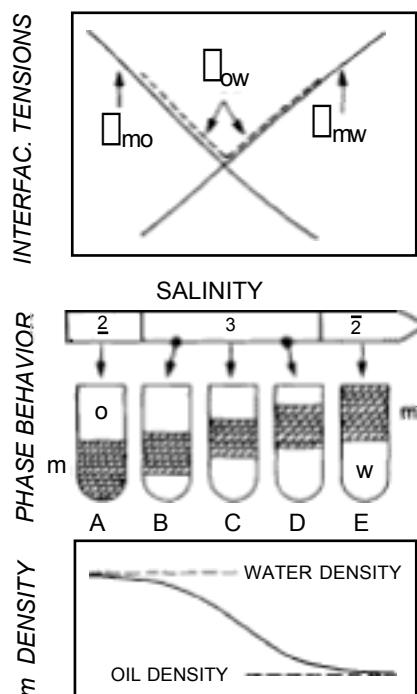


FIG. 3. Typical variation of interfacial tensions, phase behavior, and microemulsion density for a formulation scan through the three-phase region.

lower than the tension between M and O; consequently the water drops are likely to be smaller than the oil drops.

In case B, W drops are smaller and present a lesser density difference with M than O drops. Both trends produce a slower sedimentation rate of W drops through the M layer, i.e., the settling of the W phase would be slower than the one of the O phase, which is exactly what Fig. 2 shows.

The opposite occurs for a formulation located at case D, near the $3-2$ boundary.

Exactly at optimum formulation (case C, the tensions are equal and the microemulsion contains the same amount of oil and water. Both factors would lead to an equal settling rate, which is what happens at the crossing of the two stability curves. The slight overall maximum at this point is due to the fact that neither the tensions nor the density difference exhibit their more favorable values.

REMOVAL OF ONE OF THE 3 PHASES

Figure 4 is a blow-up of Fig. 2 in the three-phase region. The previous data on settling of O and W phases in MOW emulsions are indicated by lines without experimental data. The circle and square dots refer to the settling of W and O in biphasic WM and OM emulsions, obtained by removing one of the excess phases. The consistency of the data with the three-phase case tends to indicate the validity of the model. It is worth noting that biphasic emulsions tend to settle a little bit more slowly than their three-phase counterparts; this may be attributed to the fact that all drops are formed in contact with M and thus at a lower average tension; this would produce a smaller average size and then a slower sedimentation rate.

It was recently reported (26) that the interfacial tension between excess O and W follows the higher of the tensions M-O and M-W (see Fig. 3 above). This tends to indicate that the actual volume and even the presence of a sizeable volume of middle phase has no influence on the phenomenon.

It is found that if the middle phase is completely removed from the system, an

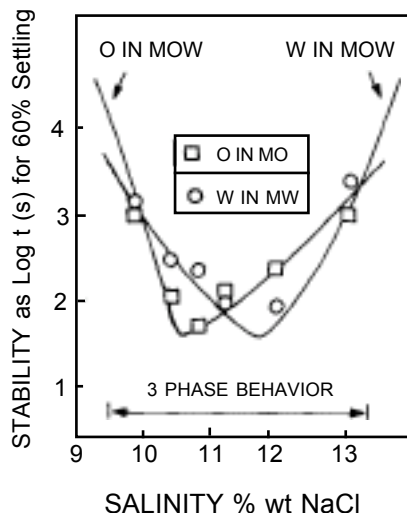


FIG. 4. Stability of three-phase emulsion (lines) and two-phase emulsions (circles and squares) obtained by removing one of the excess phases, for both criteria used.

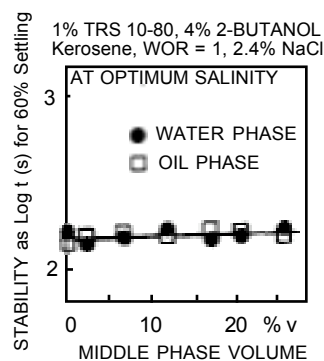


FIG. 5. Stability of three-phase emulsion at optimum formulation versus middle-phase content.

unstable biphasic dispersion is obtained. If its stability is measured according to both previous criteria, the result is essentially the same as that obtained at the minima of stability of MOW emulsions.

Figure 5 indicates the stability according to both W and O settling for a formulation exactly located at optimum, versus the middle phase relative volume. It is clear from this data that the presence of a certain amount of middle phase has no effect on the stability of the dispersed system other than a short lag time for the droplets to cross it.

CONCLUSIONS

In the three-phase region, surfactant-oil-water emulsified systems exhibit a marked minimum in stability.

Regardless of the selection of the coalescence or clearing of W or O excess phases as a criterion of stability, the result is essentially the same. However the exact location of the minimum depends on the criterion used. A simple model based on physical properties allows the interpretation of this difference.

Exactly at optimum formulation, both criteria lead to the same instability, independently of the amount of middle phase in the system.

The presented data give evidence that at optimum formulation, the surfactant "prefers" the complex zero-curvature structure of the

microemulsion middle phase (28), to the highly curved interface of the fine droplets in a macroemulsion.

The middle phase behaves as a reservoir in which the surfactant is trapped, and is thus unavailable to stabilize the macroemulsion.

ACKNOWLEDGMENT

The authors thank the Research Council of Universidad de Los Andes for supporting this project under Grant CDCHT-I-186.

REFERENCES

- Winsor, P. A., "Solvent Properties of Amphiphilic Compounds." Butterworths, London, 1954.
- Wade, W. H., Morgan, J. C., Schechter, R. S., Jacobson, K., and Salager, J. L., *Soc. Petrol. Eng. J.* **18**, 242(1978).
- Salager, J. L., *Rev. Inst. Mex. Petróleo* **11**, 59 (1979).
- Salager, J. L., Morgan, J. C., Schechter, R. S., Wade, W. H., and Vasquez, E., *Soc. Petrol. Eng. J.* **19**, 107(1979).
- Bourrel, M., Salager, J. L., Schechter, R. S., and Wade, W. H., *J Colloid Interface Sci.* **75**, 451 (1980).
- Salager, J. L., in "Proceedings, 1st Int. Symp. Enhanced Oil Recovery," INPELUZ, Maracaibo, Venezuela, Feb. 19-22, 1985.
- Vijayan, S., Ramachandran, C., Doshi, H., and Shah, D. O., in "Proceedings, 3rd Int. Conf. Surface Colloid Sci.," Stockholm, Sweden, 1979.
- Bourrel, M., Graciaa, A., Schechter, R. S., and Wade, W. H., *J Colloid Interface Sci.* **72**, 161 (1979).
- Salager, J. L., Quintero, L., Ramos, E., and Andérez, J. M., *J. Colloid Interface Sci.* **77**, 288 (1980).
- Vinatieri, J., *Soc. Petrol. Eng. J.* **20**, 402 (1980).
- Milos, F. S., and Wasan, D. T., *Colloids Surf.* **4**, 91 (1982).
- Baldauf, L. M., Schechter, R. S., Wade, W. H., and Graciaa, A., *J. Colloid Interface Sci.* **85**, 187 (1982).
- Salager, J. L., Loaiza-Maldonado, I., Miñana-Pérez, M., and Silva, F., *J Dispersion Sci. Technol.* **3**, 279(1982).
- Salager, J. L., Miñana-Pérez, M., Andérez, J. M., Grosso, J. L., Rojas, C. I., and Layrisse, I., *J. Dispersion Sci. Technol.* **4**, 161 (1983).
- Salager, J. L., Miñana-Pérez, M., Pérez-Sánchez, M., Ramirez-Gouveia, M., and Rojas, C. I., *J Dispersion Sci. Technol.* **4**, 313 (1983).
- Jarry, P., Miñana-Pérez, M., and Salager, J. L., "5th Int. Symp. Surfactants in Solution." Bordeaux, France, July 1984.
- Wasan, D. T., *et al.*, in "Proceedings, 4th DOE Symp.," Vol. IA, paper B-3. Petroleum Publ. Tulsa, Okla. 1978.
- Salager, J. L., Grosso, J. L., and Eslava, M. A., *Rev. Tecn. INTEVEP* **2**, 149 (1982).
- Becher, P., "Emulsion: Theory and Practice." Krieger, 1977.
- Jeffreys, G. V., and Davies, G. A., in "Recent Advances in Liquid-Liquid Extraction" (C. Hanson, Ed.), p. 495. Pergamon, Elmsford, N. Y., 1971.
- Lissant, K.J., Ed., "Emulsion and Emulsion Technology," Part I. Dekker, New York, 1974.
- Graciaa, A., Barakat, Y., Schechter, R. S., Wade, W. H., and Yiv, S., *J. Colloid Interface Sci.* **89**, 217 (1982).
- Griffin, W. C., *J. Cosmetic Chem.* **1**, 11 (1949).
- Griffin, W. C., *J. Cosmetic Chem.* **5**, 249 (1954).
- Salager, J. L., "5th Int. Symp. Surfactants in Solution." Bordeaux, France, July 1984.
- Pouchelon, A., Meunier, J., Langevin, D., Chatenay, D., and Cazabat, A. M., *Chem. Phys. Lett.* **76**, 277 (1980).
- Thurston, G., Salager, J. L., and Schechter, R. S., *J. Colloid Interface Sci.* **70**, 517 (1979).
- Scriven, L. E., in "Micellization, Solubilization, and Microemulsions" (K. Mittal, Ed.), Vol. **2**, p. 877. Plenum, New York, 1979.