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SHORT COMMUNICATION

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Physicochemical parameters influencing the emulsion drop size

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Abstract The stirring-mixing energy is the most obvious factor in the drop size reduction process, but it is not necessarily the most important one. Both the physicochemical formulation and the composition variables are shown to play a determinant role, at constant stirring condition.

The generalized formulation versus water/oil ratio diagram allows to map emulsion properties such as emulsion type, stability and viscosity. It is used to discuss the combined effect of the formulation and composition upon the emulsion drop size, through their influences on the interfacial tension, and the emulsion viscosity and stability.

Key words Emulsion – drop size – bimodal – distribution

Introduction

The emulsion type and other properties have been shown to depend upon the physicochemical formulation, i.e., surfactant type, oil nature, brine electrolyte content, temperature etc, as well as the composition variables, i.e., the water/oil ratio and the surfactant concentration, and mechanical mixing conditions (1–2).

When the effects of all formulation variables are gathered in the so-called generalized formulation, the phenomenology can be represented on a formulation-water/oil ratio map that has been used by us and other research groups (3–8). Figure 1 illustrates the main features of such a map. The shaded zone corresponds to the three-phase behavior at or near optimum formulation. The formulation variable scale is such that the hydrophilicity increases from top to bottom. Above (respectively below) the three-phase behavior region, a Winsor II or $\overline{2}$ (respectively Winsor I or $\underline{2}$) phase behavior occurs (9–10). The symbols indicate a two-phase behavior in which the surfactant rich phase is the upper phase, i.e. the oil phase ($\overline{2}$) or the lower phase, i.e., the water phase ($\underline{2}$), depending upon the top or bottom position of the mnemotechnical bar.

As far as the emulsion type is concerned, the measurement of the electrolytic conductivity allows to determine the high (O/W) and low (W/O) conductivity emulsions, and to draw the inversion line (bold line in Fig. 1) as the boundary between the associated regions.

As shown in Fig. 1, the map can be divided into three vertical regions, labeled A, B and C, with the + or − superscript, depending on the position with respect to the optimum formulation (3).

In the central region (A), the emulsion type is associated with the phase behavior, while the extreme (B) and (C) regions exhibit an emulsion type in which the external phase is the one in higher proportion. Typically the A region extension ranges from 25 to 75% water or oil.

Emulsions produced by stirring equilibrated systems whose formulation-composition is located in the A^+ (and B^+) regions, as well as A^- (and C^-) regions have been called normal emulsions. They are stable, whenever their formulation is not too close from optimum formulation.

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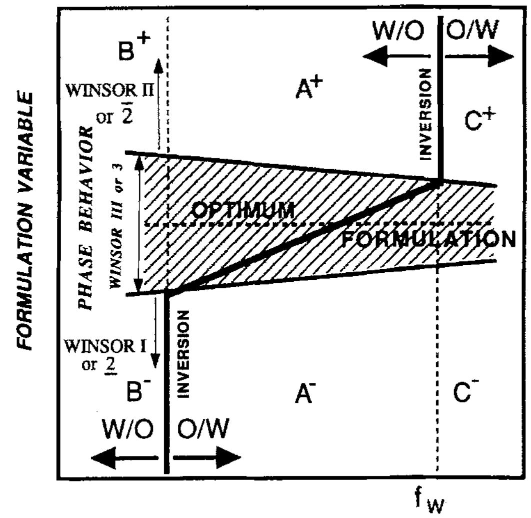


Fig. 1 Formulation-water fraction bidimensional map, showing the phase behavior at equilibrium, and the emulsion inversion line

On the contrary the C^+ and B^- so-called abnormal emulsions, are often multiple emulsions with a rather low stability (3–4).

In any case, a change of formulation along a vertical line results in a minimum in both the interfacial tension and the emulsion stability at the optimum formulation (11–14), which is essentially located in the middle of the three-phase behavior region. The stability minimum at optimum formulation has been attributed either to the percolation through liquid crystals located across the thin film, or to the trapping of all the surfactant in the microemulsion (15–16). It is important to note this duality to understand the following discussion. In effect, as optimum formulation is approached (either from above or from below) both the tension and the emulsion stability decrease. As far as the emulsion drop size is concerned, the two resulting effects are opposite, since a decrease in tension tends to enhance the efficiency of the stirring-mixing process and thus tends to produce smaller droplets, while a decrease in emulsion stability tends to favor the coalescence, and thus results in larger drops.

Other studies have shown that the emulsion viscosity undergoes through a minimum when the three-phase region is crossed (17–18). On the other hand, the emulsion viscosity is found to increase in the A^- (respectively the A^+) region when the internal phase ratio increases, i.e., when the A^-/B^- (respectively A^+/C^+) inversion line is approached. The change in viscosity can be several orders of magnitude; as a consequence it can alter the mixing-stirring process to such a point that a new mechanism of emulsification, referred to as high internal phase ratio (HIPR) has been proposed in these cases (18).

Experimental procedures

Sodium dodecyl sulfate (SDS) is a reagent grade product manufactured by Merk. The ethoxylated nonyl phenol with an average of 13 ethylene oxide group per molecule was supplied by Gaf Chemical (Antarox trade name). N-pentanol (4.8 vol %) was added to the SDS system in order to reduce the surfactant hydrophilicity. Oil phases are either an hydrocarbon distillation cut of low viscosity (3 cP) or a heavy crude oil (> 10000 cP at 25°C) from the Hamaca oil field in eastern Venezuela.

The anionic system formulation is changed by scanning the aqueous phase salinity (NaCl) while the temperature is used for the nonionic system.

The emulsions are prepared from pre equilibrated systems according to a standard procedure, with a Ultraturrax T4558 turbine blender; light cut emulsions are stirred at 3000 rpm for 15 seconds at 25° C, while the heavy crude emulsions are stirred at 8000 rpm for 45 seconds at the selected temperature.

The drop size distribution is measured on O/W emulsions diluted to a 1/1000 oil/water proportion with a 0.5% sodium pyrosphosphate solution, with a Malvern Mastersizer laser diffraction apparatus. The reported drop average diameter is the so-called D(V,0.5) average, i.e., the diameter below which half of the volume distribution occurs.

Formulation scan

Figure 2 shows the variation of the droplet average diameter along a salinity scan for an anionic surfactant system. Since these systems contain 80% water, only O/W emulsions are produced in the whole scan (3), as indicated by the arrow position in the inserted formulation-WOR diagram. When salinity increases from below optimum formulation, the drop diameter first decreases (point 1 to point 2), then it increases; it passes through a minimum (point 2) which is located at a formulation near the three-phase zone. The presence of this minimum may be explained by the previously mentioned opposite effects. As optimum formulation is approached (point 1 to point 2), the first dominant effect is a very strong decrease in interfacial tension, which results in smaller droplets. When the formulation gets closer and closer to optimum, then the emulsion becomes very unstable, and the dominant effect turns out to unbalance the break up/coalescence equilibrium the other way, with a resulting increase in drop diameter.

The drop size increases considerably in the three-phase zone (up to point 3). The decrease from point 3 to point 4 is due to the fact that abnormal emulsions located in the

C^+ zone are unstable, but not so unstable than the emulsion located at optimum formulation (15–16).

Figure 3 shows another physico-chemical formulation scan with hydrophilicity still increasing from top to bottom; however, this time the change is produced by the variation of temperature in a nonionic system. In effect, an increase in temperature is known to drive the dehydration of the polyethylene oxide chain, thus resulting in a less hydrophilic surfactant. The O/W emulsion contains a high internal phase ratio (70 vol. % oil), and its inversion takes place near the optimum formulation for minimum interfacial tension, which is here an optimum temperature. As before, the drop diameter first decreases (point 1 to point 2), then it increases as optimum formulation is approached (point 2 to point 3). The expected physical effect of the temperature, i.e., a decrease in viscosity, is hidden by the formulation effect, i.e., the decrease of hydrophilicity of the nonionic surfactant as the temperature increases.

It is not known why the drop average diameter exhibit a light increase from 50 to 60° C. It is only known for sure that below 50° C, the heavy crude oil is extremely difficult to emulsify and the collected experimental data is not very reliable.

The conclusion from Figs. 2 and 3, is that in both cases the minimum drop size is found at some distance from optimum formulation.

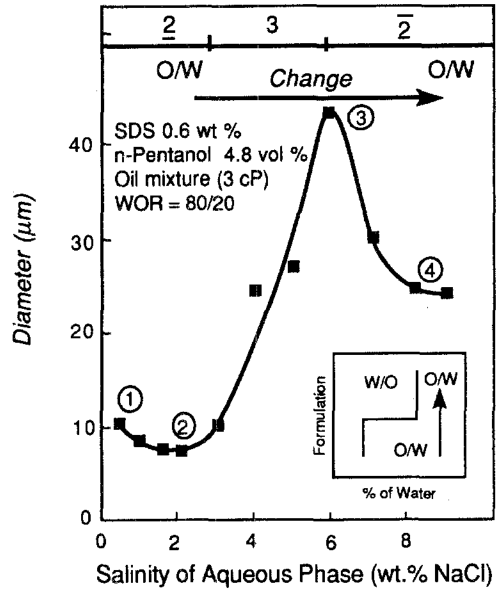
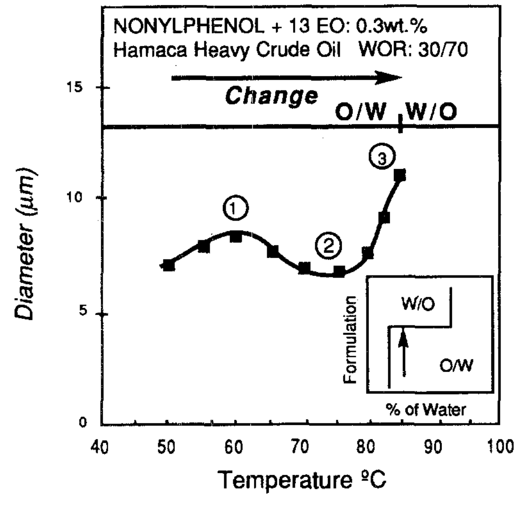


Fig. 2 Variation of the emulsion drop average diameter as the formulation is changed. Case of a transition C^-/C^+ with a change in salinity for an anionic system

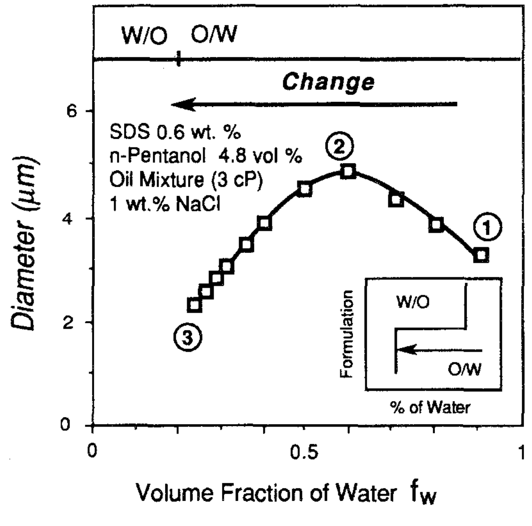
Fig. 3 Variation of the emulsion drop average diameter as the formulation is changed. Case of a transition A^-/A^+ with a change in temperature for a nonionic system



Composition scan

Figure 4 shows the variation of the O/W emulsion drop diameter as the water-to-oil ratio (WOR) is changed. From left to right the internal phase ratio increases and the drop diameter first increases and then decreases. The increase in drop diameter from point 1 to point 2, is attributed to a decrease in stirring efficiency as the number of drops increases, whereas the stirring stays constant. It is worth noting that in this intermediate region, the emulsion viscosity is quite low, i.e., a few centipoises, because it contains less than 50% of dispersed phase.

Fig. 4 Variation of the emulsion drop average diameter as the water/oil is changed. Case approaching transition A^-/B^- with a change in oil internal phase



On the contrary the emulsion viscosity increases very rapidly with the internal phase content, when the inversion is approached. When the O/W emulsion contains less than 30% water, the viscosity increases beyond 1000 cP and the stirring situation changes to the so-called high internal phase ratio emulsification, which has been found to be very effective in reducing the drop size (18). Figure 4 shows that the drop size goes down to 2 μm, a very good stirring performance for such a high internal phase ratio (oil/water ratio 80/20). The drop size reduction is thus attributed to the increase in emulsion viscosity that probably improves the transfer of stirring energy from the impeller to the droplets to be broken.

Conclusions

When identical stirring conditions are applied to equilibrated surfactant-oil-water systems, the emulsion drop size depends upon both the formulation and the water/oil ratio.

Small diameter emulsions are found at some distance from optimum formulation, where the tension is low enough for the droplets to break up easily, whereas the stability is still high enough for the drops not to coalesce instantly.

As far as the effect of the water/oil ratio is concerned, the small diameter emulsions are found in the high internal phase ratio region, located near the catastrophic inversion, where the emulsion viscosity is quite high.

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References

1. Becher P (1977) Emulsions: Theory and Practice, Reprint 2nd Ed, R Krieger, New York
2. Becher P, ed (1983–88) Encyclopedia of Emulsion Technology, 3 volumes, M Dekker
3. Salager JL, Miñana-Pérez M, Pérez-Sanchez M, Ramirez-Gouveia M, Rojas C (1983) J Dispersion Sci Technology 4:313
4. Jarry P, Miñana-Pérez M, Salager JL (1987) In "Surfactants in Solution", K Mittal, P Bothorel, eds, Plenum Press 6:1689
5. Antón RE, Castillo P, Salager JL (1986) J Dispersion Sci Technology 7:319
6. Miñana-Pérez M, Jarry P, Pérez-Sánchez M, Ramirez-Gouveia M, Salager JL (1986) J Dispersion Sci Technology 7:331
7. Dickinson E (1986) Emulsions' Annual Reports C, The Royal Soc of Chemistry 31
8. Brooks B, Richmond H (1991) Colloids and Surfaces 58:131
9. Winsor P (1954) Solvent Properties of Amphiphilic Compounds, Butterworth London
10. Bourrel M, Schechter RS (1988) Microemulsions and Related Systems, M Dekker New York
11. Shah DO, ed (1981) Surface Phenomena in Enhanced Oil Recovery, Plenum Press New York
12. Salager JL, Quintero L, Ramos E, Andérez J (1980) J Colloid Interface Sci 77:288
13. Viniatieri JE (1980) Soc Petrol Eng J 20:402
14. Wasan DT, Milos FS, Di Nardo P (1982) AIChE Symposium Series 78 (vol 212):105
15. Hazlett R, Schechter RS (1988) Colloids & Surfaces 29:53
16. Antón RE, Salager JL (1986) J Colloid Interface Sci 111:54
17. Salager JL, Miñana-Pérez M, Andérez J, Grosso J, Rojas C, Layrisse I (1983) J Dispersion Sci Technology 4:161
18. Briceño M.I, Chirinos ML, Layrisse I, Martinez G, Nuñez G, Padrón A, Quintero L, Rivas H (1990) Revista Técnica INTEVEP 10:5