

EFFECT OF HYDROPHOBIC CLAY PARTICLES ON THE FORMULATION AND PROPERTIES OF AN EMULSION

EFFET DE PARTICULES D'ARGILE HYDROPHOBÉE SUR LA FORMULATION ET LES PROPRIÉTÉS D'UNE ÉMULSION

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RESUME

On ajoute souvent des particules solides à des systèmes émulsifiés, comme par exemple des aliments, peintures, cosmétiques et autres, et leur effet n'est pas toujours bien interprété, souvent parce que les comparaisons ne sont pas adaptées à la situation.

On sait que les propriétés des émulsions (type, stabilité, viscosité) dépendent de la formulation physico-chimique suivant une phénoménologie générale. Quand on balaye la formulation de façon systématique on passe par une formulation appelée optimale, pour laquelle le système présente un comportement de phase de type Winsor III, et qui coïncide avec un changement de morphologie de l'émulsion ainsi qu'un minimum de stabilité.

Quand on ajoute des particules d'argile hydrophobée on constate que cette phénoménologie est altérée, et que, aussi bien pour des systèmes anioniques que non-ioniques, l'ajout de particules solides se solde par (1) une modification apparente de la formulation, (2) une amélioration de la stabilité des émulsions E/H, du fait de la mouillabilité des particules.

ABSTRACT

Solid particles are frequently added to emulsified systems, as in foodstuff, paints, drilling fluids, cosmetics and others, and their effect is not always well interpreted, most often because the comparison is not carried out the right way. Emulsion properties (type, stability, viscosity) are known to vary with the physico-chemical formulation according to a general pattern.

When a formulation variable is scanned, the value corresponding to Winsor III (three) phase behavior, so-called optimum formulation, coincides with the change in emulsion morphology and a deep minimum in emulsion stability, as well as other characteristics.

It is shown how these properties can be altered when hydrophobated clay particles are added to an emulsion. Experiments on systems containing anionic or nonionic surfactants indicate that the effect of added solid particles is (1) a modification of the apparent formulation, as detected by a shift in optimum formulation with associated properties, (2) an improvement in emulsion stability mostly for W/O type because of the particle wettability.

Mots clés : formulation, émulsion, particule, solide, surfactif
Key words : formulation. emulsion. particle. solid.

1. INTRODUCTION

1.1. Systems stabilized by solid particles

Many complex systems are formulated as both an emulsion and a solid particle suspension. They contain two non-miscible liquids, a surfactant, and a powdered solid which can be either dispersed in one of the liquids or stuck at the liquid-liquid boundary, in which case it plays an interfacial role and is likely to alter the properties of the dispersed system. In some cases a high stability is sought as for instance in paints, drillings muds, or many foodstuffs, whereas in other cases the multiphase dispersion has to be resolved into its separated components, as in many industrial products or waste treatments, particularly in the petroleum and shale oil production.

In these emulsion-suspensions the surfactant could play a role of emulsifier of the liquid-liquid system as well as a dispersing agent of solid particles in one of the liquid. Both cases have been studied and a lot of information is available in the literature on these subjects.

On the other hand the solid particles alone can stabilize the liquid-liquid dispersion as reported by Pickering [1], almost a century ago. The available information on this case is not considerable but several studies, some of them quite old, have linked the results to the wettability of the solid particles [2-4].

The stabilization mechanisms of a liquid-liquid dispersion by a surfactants [5, 6] and solid particles [7-12] are known to be very different. As a consequence, their combination is not obvious and it is important in practice to know how surfactants and fine solid particles can interact.

The present study addresses the case in which a small amount of micron-range solid particles are added to an emulsion stabilized by a surfactant. This is a typical case in oil production where clay or sand particles are dragged away by the oil/water flow and are likely to interfere with the physico-chemical treatments, particularly crude oil dehydration, a process which is extremely sensitive to formulation. It is also the case of some drilling fluid, and the case of asphaltenic crude oils in which the asphaltenes can be viewed either as surfactants or colloid particles depending upon their degree of aggregation [13].

The present study analyzes how the properties of an anionic or nonionic surfactant-oil-water emulsion is altered by the addition of a small amount of hydrophobated clay used in drilling fluids.

1.2. Physico-Chemical Formulation

The properties of surfactant-oil-water systems either at equilibrium or in dispersed state depend upon a large number of formulation variables that include not only the nature of the three components, but also electrolytes, alcohols and other additives (type and concentration), as well as temperature and pressure.

These variables contribute to an overall affinity balance at interface, a fact that was recognized in Winsor's pioneering work [14] as an attempt to theoretically interpret the experimental results which were known to follow empirical or experimental formulation concepts such as Banckoft rule, Griffin's HLB [15] or Shinoda's PIT [16].

In the seventies, the Enhanced Oil Recovery research drive resulted in an extensive amount of experimental work dedicated to the development of multivariate empirical correlations for the attainment of three-phase behavior, a very well defined physico-chemical situation. The correlations contain a numerical contribution of the effect of each formulation variable, that was later on identified as an energy contribution to the surfactant affinity difference (SAD) [17] or its dimensionless equivalent the Hydrophilic-Lipophilic deviation (HLD), a generalized formulation variable which is discussed elsewhere [18].

Whenever HLD is negative or positive the surfactant has a stronger affinity for the water or the oil phase. The case $HLD = 0$ correspond to an exact balance of affinity of the surfactant for both oil and water, a physico-chemical situation which has been called optimum formulation because it is associated with an extremely low minimum of interfacial tension, which is the best case to recover petroleum.

HLD is in most cases changed by varying the aqueous phase salinity of ionic surfactant systems, and the degree of ethoxylation of polyethoxylated nonionics. The optimum formulation for $HLD = 0$ is noted as S^* in a salinity scan and EON^* in a EON scan.

1.3. Influence of Formulation on Emulsion Properties

The formulation has been associated with emulsion properties since Bancroft enounced his famous rule, which states that surfactants with hydrophilic affinity tend to stabilize O/W emulsions and conversely.

This is true for many systems, provided that some conditions are met, among them a water/oil ratio not too far from unity and an oil/water viscosity ratio close to unity. It can be said that the emulsion morphology inverts at optimum formulation, and that it is of the O/W (respectively W/O) type at $S < S^*$ and $EON > EON^*$ (respectively $S > S^*$ and $EON < EON^*$). Generally the aqueous phase contains some electrolyte which make it conductor of electrical current. Thus measuring the emulsion conductivity is a simple way to find out the morphology, i. e. high conductivity corresponds to O/W and low conductivity to W/O.

Emulsion stability is known to undergoes through a very low minimum at optimum formulation, and to increases quickly whenever the formulation departs from optimum [19].

These properties exhibit the said trend whatever the variable used to change the formulation. Other properties are affected by the formulation as well as by the water/oil ratio as discussed elsewhere [20]. It is worth remarking that an effect similar to the HLD variation has been found by changing the wettability of particles or mixing hydrophilic and hydrophobic particles. In other words it can be said that the mapping found for emulsions stabilized by surfactants [20] also applies when the emulsion is stabilized by particles. In that case the particle wettability is used instead of the physico-chemical formulation [11, 12, 21] although these authors did not use the same region symbolism than in the original mapping, which could produce some confusion at first sight.

2. EXPERIMENTAL CONDITIONS

Ionic surfactant systems contain sodium dodecyl sulfate whereas nonionic ones contain mixtures of ethoxylated nonylphenol oligomers characterized by their ethylene oxide number (EON) which is the average number of ethylene oxide group per surfactant molecules. Ethoxylated nonylphenols with EON = 4, 6 and 8 are commercially available. Intermediate EONs are attained by mixing neighboring products on a molar basis.

Surfactant-oil-water systems contain 25 ml of aqueous phase and 25 ml of a kerosene cut and a certain amount of surfactant. They first are equilibrated for 24 h at ambient temperature ($23 \pm 2^\circ\text{C}$). The powdered solid is a hydrophobated clay (amine treated bentonite) with particle size smaller than $2 \mu\text{m}$, when dispersed in a oil phase. Just before emulsification, the corresponding amount of powdered solid is poured in the equilibrated system which is gently stirred with a rod. Emulsification is then carried out with a 6000 rpm turbine blender for 30 seconds. The electrolytical conductivity is measured under magnetic stirring. 20 ml of the emulsion sample is poured in an elongated graduated test tube, which is then closed with a plastic cap and left to rest in a vertical position in a rack. The coalesced phase volume is measured versus elapsed time. The stability is taken as the time at which 30% of the emulsion internal phase has coalesced.

3. INFLUENCE OF HYDROPHOBIC CLAY

3.1. Ionic Systems

Figure 1 represents the variation of conductivity of emulsions stabilized by an ionic surfactant and containing different amounts of solids. The diamond data points correspond to the system with no solid. The conductivity is found to follow the typical variation along a salinity scan [22].

In this case the change in conductivity that indicates the emulsion inversion (from O/W to W/O) takes place around 3.8 wt.% NaCl.

When solid particles are added, the conductivity variation retains the same aspect, but it is shifted somehow to the left, i. e. towards a lower salinity. This means that the solid contribution is equivalent to reduce the hydrophilicity in a way than can be quantified through basic SAD equations [17].

The solid behaves as if it were a hydrophobic co-surfactant whose effect can be taken into account, at least in the studied amounts, through a mixing rule [23] between surfactant and solid.

Figure 2 shows the variation of the stability of the same emulsified systems. In all cases the general phenomenology is exhibited, i.e., a minimum stability is found at optimum formulation which corresponds to the inversion of the emulsion according to the previous figure. This confirms that the presence of solid particles essentially produces a formulation shift. Moreover, it is seen that the stability is systematically increased by the presence of solid particles at a salinity superior to optimum, i. e., for W/O emulsions. This effect is consistent with the known role of hydrophobic particles.

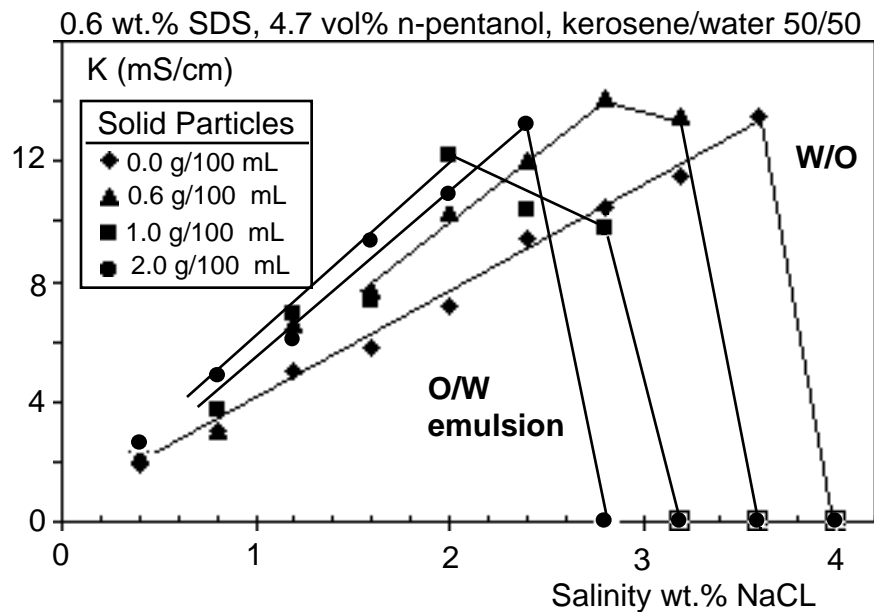


Figure 1 : Conductivity variations for emulsified ionic systems

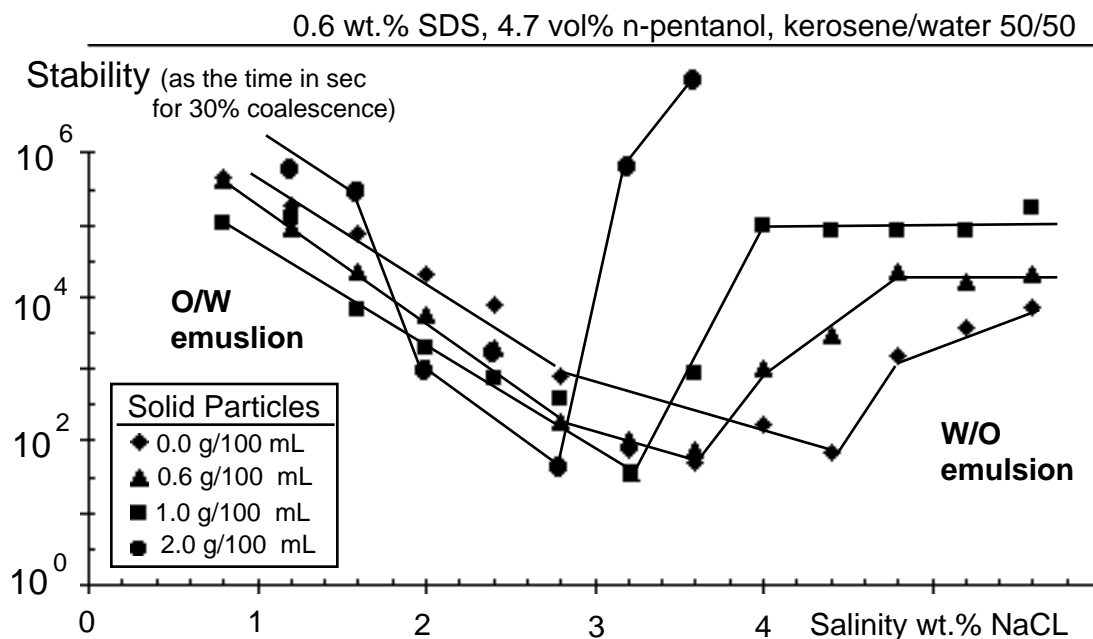


Figure 2. Emulsion stability variation for ionic systems

3.2. Nonionic Systems

Figure 3 and 4 indicate the same kind of data for a nonionic surfactant system. In this case, the hydrophilicity of the surfactant increases from left to right, i. e., opposite to the previous case. It is seen that the addition of solid particles shifts the emulsion inversion and stability minimum towards a higher EON.

This also means that the powdered solid effect is what is expected from a hydrophobic co-surfactant. In this case the increase in stability on the W/O side is considerable, e.g., 2 orders of magnitude at least as soon as some solid is added.

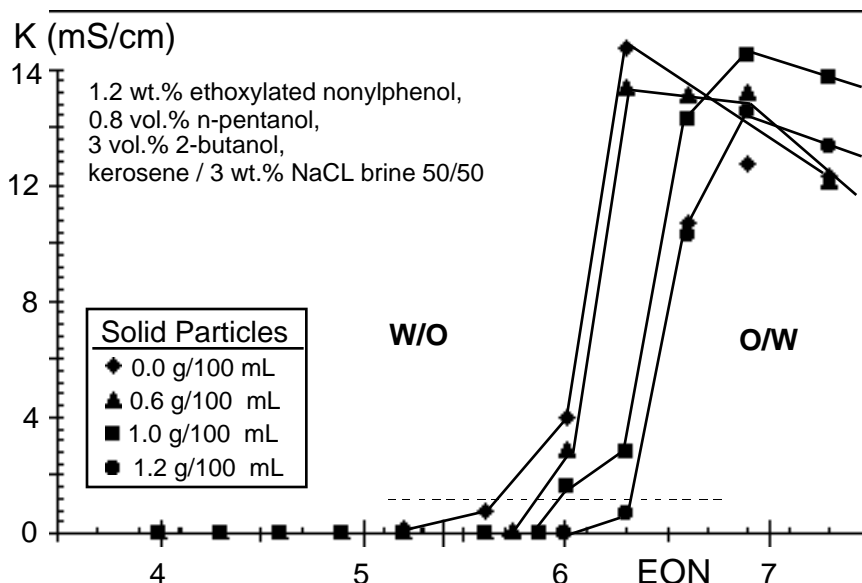


Figure 1 : Conductivity variations for emulsified nonionic systems

1.2 wt.% ethoxylated nonylphenol, 0.8 vol.% n-pentanol,
3 vol.% 2-butanol, kerosene/3w wt.% NaCl brine 50/50

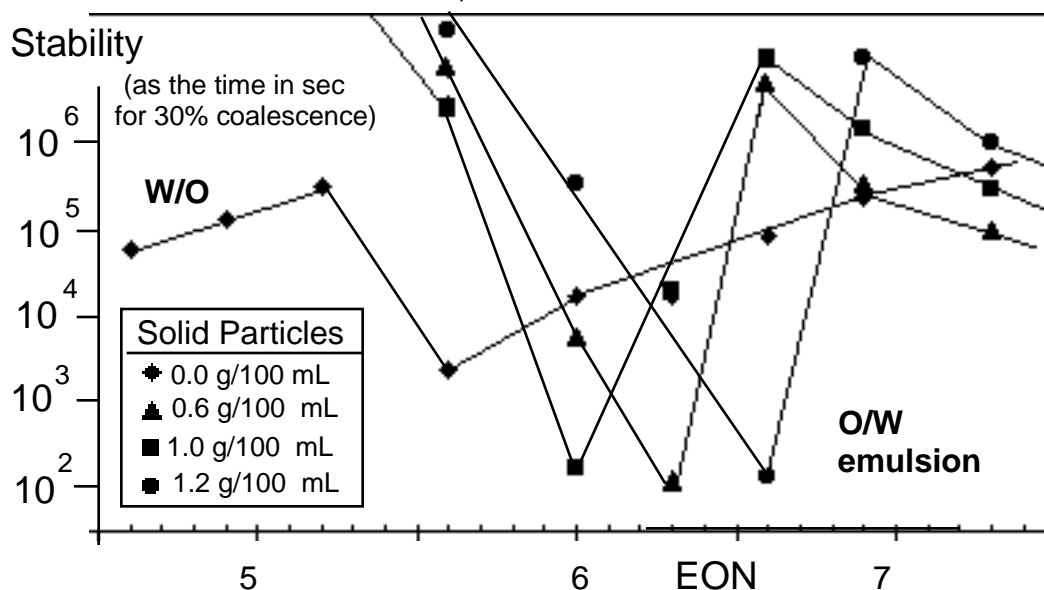


Figure 2. Emulsion stability variation for nonionic systems

3.3. Use of pre-washed Clay

Since the effect of the powdered solid is similar to the addition of a hydrophobic surfactant, it could be conjectured that it is produced by the desorption of the hydrophobating substance, which is presumably of the amine type. Powdered solid was left in contact for 6 h with kerosene in one case and with 1 wt.% NaCl brine in another case, in order to allow for any desorption to take place.

The pre-cleaned solid samples were filtered and dried, before being used as in the previous cases. Figure 5 indicates that the same results are attained with the unaltered clay and with the pre-cleaned samples in water or oil. Since the contact time (6 h) is far superior to the contact of the solid with the emulsion components prior to emulsification (a few minutes at most), the desorption of a hydrophobic surfactant was ruled out. A similar experiment ruled out a significant salt desorption.

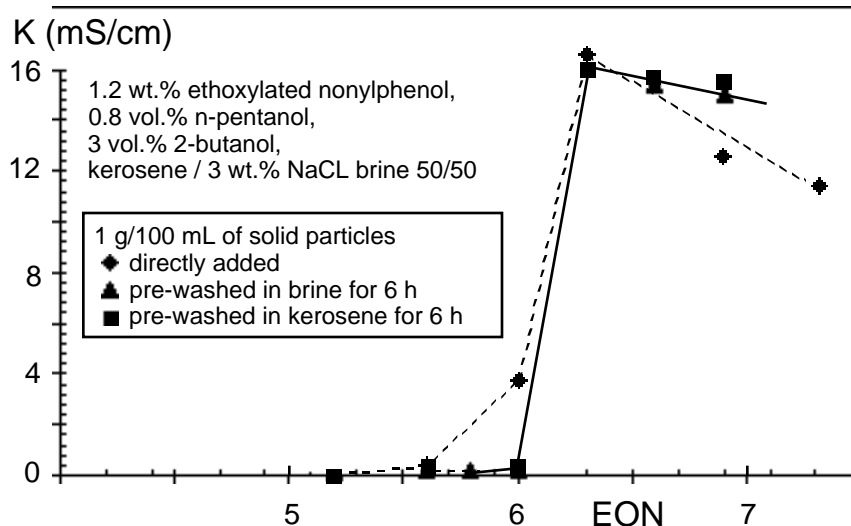


Figure 5 : Emulsion conductivity variation with directly applied solid or precleaned solid

4. CONCLUSIONS

Hydrophobated clay acts as a hydrophobic co-surfactant as far as the formulation of surfactant-solid-oil-water systems is concerned. Moreover, it tends to enhance the stability of W/O emulsions, with no significant effect on O/W emulsions.

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