

pH controlled interfacial mechanisms and macroscopic O/W separation

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In a previous presentation^[1], we have shown how naphthenic acids, bases, and asphaltenes interplay to control oil/water separation, depending on the final pH of the water : from simple tests, by varying the initial pH of the water phase, it is possible to determine a classification of "acidic" crude oils and to rank their potential issues, in particular concerning separation.

In this paper, we study how kinetic mechanisms taking place at oil/water interfaces are governed by the pH of the water phase, itself influenced by the contact with the crude oil, and control the macroscopic rate of oil/water separation.

We have realized bottle tests using water, with initial pH varying from 2 to 12, and crude oils. We monitor the separated water over time at 50°C, and measure the final pH of the water (pHf).

When pHf is very high, an O/W emulsion is obtained in the water phase; separation is usually slow.

Up to pHf that can be as high as 11, a W/O emulsion is observed. Over time, the emulsion is composed of big water droplets stabilized by organic films. The stability of the emulsion varies as a function of pHf : The emulsion for acidic pHf is very stable. A strong optimum of separation rate is observed at intermediate pHf (from 7 up to 11 sometimes).

In order to understand the phenomena governing the macroscopic separation, we have used a pendant drop tensiometer to determine the interfacial tension, and to perform dynamic interfacial rheology.

At very basic pHf, there is no interfacial film, the level of the interfacial tension is very low : naphthenates control the interface.

The difference between the acid stable emulsions and the intermediate optimum range is not related to the level of interfacial tension : in both case, at acidic pH, or at the optimum, the interfacial tension is close.

The use of dilatational rheology is necessary to understand the interfacial phenomena and their kinetics.

The determination of the level of elastic modulus, and of the viscoelastic behaviour of interfaces over time shows that rigid films are formed, similarly to what has already been observed (^[2] or ^[3] among many other examples).

There is a strong control of the pHf on the properties of these films, both on their formation, or rearrangements and their level of elasticity.

At acid pHf, the interfacial film is formed right after the formation of the droplet, and its properties vary only slowly with time. The slower water / oil separation is usually attributed to these interfacial films preventing coalescence.

Surprisingly, at intermediate pHf, there is also formation of a film. Initially, this film has even a higher modulus than at acidic pHf. Its evolution over time is not monotonic, and, if the elastic modulus finally gets close to the level of the acid film, it keeps a very specific signature, with a purely elastic behavior whereas the acid film is always viscoelastic.

The improved oil / water separation observed for the intermediate pH could in fact come from breakage of these very elastic interfacial oil films during the drainage of the organic films between water droplets, and not from the absence of solid films at the oil / water interface.

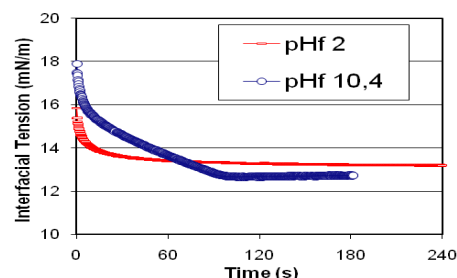


Fig. 1. Evolution of the interfacial tension versus time for pHf=2 (stable emulsion) and pHf=10.4 (unstable emulsions)

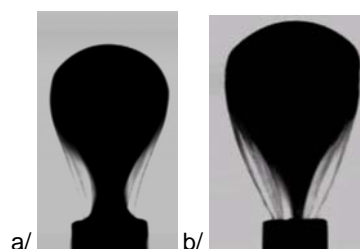


Fig. 2. Interfacial film after a/ 10s (pHf=2) b/ 180s (pHf=10.4)

References

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