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A method for the characterization of emulsions, thermogranulometry: Application to water-in-crude oil emulsion

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Abstract

Emulsions are used in a wide range of applications and industries. Their size distribution is an important parameter because it influences most of the emulsion properties of emulsions. Several techniques of characterization are used to determine the granulometric distribution of emulsions, but they are generally limited to dilute samples and are based on complex algorithms. We describe a method that allows characterization of the droplet size distribution of emulsions using thermal analysis (thermogranulometry). This method permits the use of very concentrated samples without any dilution or perturbation of the system. We first define our method by a thermodynamic and kinetic approach. We studied a real system, i.e., crude oil emulsions, which form very concentrated, viscous, and opaque emulsions with water. We present a correlation between the size of droplets and their freezing temperature, corresponding to our system. Then we compare the size distributions obtained by our method with those derived by direct microscopy observations. The results obtained show that thermogranulometry may be an interesting method of characterization of emulsions, even for concentrated systems.

Keywords: Emulsion; Granulometry; Thermal analysis; Crude oil

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1. Introduction

Emulsions are systems made of liquid droplets dispersed in another nonmiscible liquid. They are referred to as either w/o emulsions, water droplets dispersed in an oil medium, or o/w emulsions, oil droplets dispersed in an aqueous medium. They are either the desired result of a mechanical process or the spontaneous result of favorable conditions of formation. For instance, food emulsions belong in the first category, and water-in-crude oil emulsions in the petroleum industry in the second category. Generally speaking, manufactured emulsions are expected to keep their structure as long as possible and natural emulsions are submitted to destabilization processes to separate the two phases to recover pure oil and pure water. Therefore, the problem to solve is to limit the instability or to enhance it. But, for both cases, it is necessary to control the coalescence of the droplets. One way to do so is to determine droplet size versus time. Various experimental techniques have been proposed, but few are suitable for studying concentrated water-in-crude oil emulsions with heavy opacity. Most of these techniques are easily applicable to dilute oil-in-water emulsions (light scattering, Coulter counter, microscopy, etc.), but they are unfortunately not adaptable to opaque and concentrated water-in-oil emulsions. Even optical microscopy is very complicated to use in the case of systems containing different types of solids [1]. This technique is also very time consuming and does not permit the study of large samples (only a few droplets are analyzed). A rapid way to assess the stability of complex emulsions is the "bottle test," which consists of monitoring the extent of phase separation with time. This test provides a significant amount of information relating to both emul-

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sion stability and clarity of the separated water, but it is very empirical [2]. It is well known that dilution may create perturbation in surface properties of droplets and in interactions between droplets. For instance, matter transfers due to osmotic chocks may occur, causing droplet size changes [3,4]. In fact, very few techniques avoid dilution, namely, dielectric or hertzian spectroscopy [5–7]; rheology [8]; conductometry [4,5]; and more recent techniques based on acoustical methods [9]), focused beam reflectance [10,11], or microwave attenuation [12]. All these techniques are, of course, complementary.

So, characterization of emulsions is difficult, especially when they are concentrated, opaque, highly viscous, or nonconductive. In this context, we suggest a new method based on a thermodynamic and kinetic approach to emulsion properties. Each droplet is individually considered in the calculations. This allows direct access to emulsion properties from the measured parameter without complex deconvolution algorithms.

In this article, a technique that has shown efficiency in characterizing qualitatively such emulsions is thoroughly described [13]. By use of this technique, it is possible to determine [14]:

- the emulsion type among the different ones possible (w/o, o/w, w/o/w, o/w/o),
- the total amount of water,
- the ratio of dispersed water,
- the presence of additives in water.

The technique proposed is based on a correlation between the most probable freezing temperatures T^* of droplets and their radii R. As it has been described in [14], it is not necessary to know the quantitative correlation between T^* and R to obtain the named data. But to further characterize the emulsion, namely, its evolution versus time at a fixed temperature or the effect of accelerated aging by heating or performing freezing–melting cycles or centrifugation, it is necessary to know the exact correlation between T^* and R. As is shown in the next section, T^* is dependent not only on R but also on other parameters that have to be clearly identified to define the conditions of application of the calibration curve obtained.

Therefore, in this article, the theory is first developed, emphasis being placed on the parameters to consider for obtaining the calibration $T^*(R)$. Second, the technique for determining T^* of the droplets dispersed within the emulsions is discussed. It is through the energy released during freezing that this has been done, and therefore differential scanning calorimetry (DSC) appeared to be a suitable technique. The radii R are determined by microscopy. It must be noted that microscopy is used only to determine the calibration curve. It is done on a limited number of droplets representative of the emulsion under study. When the correlation is known, only a DSC test is used to determine T^*, and R is deduced from the calibration curve. Third, experimental results obtained by studying water-in-crude oil emulsions by calorimetry and microscopy are presented to illustrate the possibilities of thermal analysis in the study of emulsions.

2. Physical model

This model describes the way the solidification of liquid droplets dispersed within emulsions occurs and how it is possible to obtain information about droplet sizes.

A great number of articles deal with the nucleation of a new condensed phase from a vapor phase; fewer are devoted to the nucleation from a liquid phase and even fewer to nucleation of a solid phase in a liquid dispersed as tiny droplets. To obtain the latest information, different steps have to be understood. First, it is the nucleation of a solid phase in a single liquid sample that has to be considered. Afterward, considering that droplets within an emulsion constitute a statistically representative population of single samples, a statistical analysis has to be done. The main points of these developments are given thereafter; more details can be found in more specialized literature [15,16].

2.1. *Ice nucleation in a liquid sample*

To form a solid phase, molecules exhibiting only short-range order have to gather to make the structure of the solid phase, which has long-range order. This cannot be done instantaneously for the whole liquid when the liquid–solid equilibrium temperature is reached, namely, 273.15 K for water under atmospheric pressure. Due to local fluctuations of density, some molecules can gather to form a very tiny solid particle that will grow or disappear depending on its size. The particle that reaches the critical size required to grow is called a *germ*. It is not difficult to understand that this germ contains a very small number of molecules and, by the way, is very small in size. Therefore, it belongs to what are called "colloidal particles," the diameters of which are between 10 nm and 0.1 µm. Therefore, capillary phenomena have to be taken into account.

As is shown later, the birth of germs requires cooling of the sample below the bulk ice–liquid water equilibrium temperature, namely, 0 °C. Therefore, as liquid water still exists below 0 °C, it can be described as undercooled water.

To obtain, at any temperature, the radius R^* of the germ supposed to be spherical and in equilibrium with the surrounded undercooled water, it is necessary to consider the pressure difference ΔP between the inside and the outside of the germ, namely,

$$\Delta P = \frac{2\gamma}{R^*}, \qquad (1)$$

γ being the surface energy of the interface separating the ice germ from the undercooled water.

It can be shown [17] that R^* is linked to T according to the relation