Properties of emulsion mixtures

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Abstract Emulsions are systems which exhibit some memory of their manufacturing process; thus, the same surfactant-oil-water system can result in different emulsions. This paper deals with the mixing of emulsions with the same formulation, but different drop-size distributions.

The two base emulsions are prepared in different vessels according to a standard procedure to attain fine or coarsely dispersed systems, with wider or narrower size distribution. Then, they are poured together and blended with a gentle stirring.

Experimental evidence indicates that the characteristics of the drop-size distribution of the emulsion mixture has a strong influence on the properties of the emulsion mixture, such as its viscosity and its stability. A considerable viscosity reduction can be attained by mixing two emulsions with identical formulation but different size distributions. The features which are found to promote the viscosity reduction are a strong bimodality of the combined distribution, a deep gap between modes, and a certain degree of polydispersity.

Key words Emulsion – mixture – inversion – bimodal – distribution

Introduction

The viscosity of a dispersed system, and particularly of an emulsion, is known to depend on its external phase viscosity, its internal phase ratio, and its drop size [1, 2]. The effect of the drop size is twofold: on the one hand, the smaller the average diameter, the higher the viscosity. On the other hand, the more polydispersed the drop size distribution, the lower the viscosity. This paper deals with the second effect, when the drop-size distribution exhibits two modes, i.e., two maxima, as found when different drop-size emulsions are mixed [3]. Most previous publications on the size distribution of mixed dispersions dealt with solid suspensions [4–6]; however, they can be taken as a guideline.

Experimental procedures

The surfactant-oil-water systems are pre-equilibrated at room temperature (21–24°C) for at least 48 h prior to emulsification. Used surfactants are a detergent grade dodecylbenzene sulfonate sodium salt symbolized as DDBS, and a commercial alpha-olefin sulfonate (Stepanflow 30) manufactured by Stepan Chemicals. All systems contain 1 wt.% hydrophilic surfactant, so that all emulsions are of the O/W type; the aqueous phase contains 1 wt.% NaCl; the oil phase is either an adjusted viscosity mixture of a low viscosity kerosene cut (1.3 cP) and a 4000 cP lubricating oil base, or a viscous (>10000 cP) heavy crude oil from the Hamaca field.
The emulsion viscosity is measured with a Contraves Rheomat 30 apparatus equipped with a Couette cell, at 25 °C.

The internal phase proportion is 70 vol.% oil in all cases, that is a high internal phase ratio, for which the effect of the size distribution is enhanced [6].

Mixed emulsions always correspond to the same original formulation and composition, and they only differ by their drop-size distribution.

Different average drop sizes are attained by changing the stirring energy input (time, rpm) with an Ultraturrax T4558 turbine blender; drop-size distribution can be altered also by spacial and time programming techniques reported elsewhere [7-10].

The drop-size distribution is determined with a Malvern Master Sizer laser diffraction apparatus with a 0.1–500 μm range and 2% accuracy. O/W emulsions are diluted in two steps to the required water-to-oil ratio (oil content about 1/1000) with a 0.5 wt% sodium pyrophosphate solution. The average drop size is the so-called D(V, 0.5), i.e., the diameter corresponding to 50% of the drop-size distribution in volume. Note that in a Gaussian distribution, this average diameter matches the mode.

Figure 1 shows the drop-size distribution of two 70/30 O/W emulsions which happen to exhibit essentially the same viscosity (220 and 230 cP at 25 °C). These two emulsions are prepared by very different methods, and it is worth noting that the difference in average drop size is almost tenfold; as a consequence, the smaller drop size emulsion might be expected to be much more viscous than the coarse one; however, this is not the case, and the lower than expected viscosity of the fine emulsion is attributed to two features exhibited by the drop-size distribution: polydispersity and bimodality.

Let's now look at these characteristics in detail.

**Viscosity of emulsion mixtures**

The simplest way to produce a bimodal emulsion is to mix two emulsions that are prepared separately. The resulting emulsion mixture size characteristics depend upon the characteristics of the two base emulsion distributions and the relative amount of each emulsion.

Figure 2, leftside, shows the variation of the viscosity of emulsion mixtures containing different proportions of two base emulsions; the size distributions of these two base emulsions are plotted in Fig. 2, rightside. The fine emulsion is the more viscous, both because it has smaller drops and because its distribution is more monodispersed; note that the opposite occurs for the coarse emulsion. Figure 2, rightside, indicates that the two distributions are overlapping only slightly in the 10–20 μm range.

Figure 2, leftside, shows the viscosity of emulsion mixtures as a function of the volume proportion (φ) of the fine emulsion. The data show that mixtures containing up to 50% of the fine emulsion exhibit a viscosity that is equal or even slightly lower than the viscosity of the coarse emulsion. In this case, the viscosity minimum seems to occur for a mixture containing about 25% of the fine emulsion.

Figure 3 shows the same type of data for emulsions made with a heavy crude oil. In this case, both the fine and coarse emulsions are very polydispersed (see Fig. 3, rightside), with log-normal characteristics that come from the stirring process. Because of this polydispersity, the two base emulsion distributions overlap over a wide range, e.g., 10 to 60 μm. Nevertheless, the viscosity of the emulsion mixture still goes through a minimum (Fig. 3, leftside) that this time occurs for a composition at about 50–60% of fine emulsion.

Other results (not shown) indicate that the overlapping of the two distributions tends to reduce and even

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**Fig. 1** Drop-size distributions of two emulsions exhibiting the same viscosity, but produced from a same formulation by different stirring methods.

**Fig. 2** Left: variation of the viscosity of emulsion mixtures as a function of the vol. proportion (φ) of the fine emulsion. Right: drop-size distribution of the two base emulsions.