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Formation and stability of miniemulsions produced by dispersion of water/oil/surfactants concentrates in a large amount of water

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Abstract

Phase diagrams of the pseudo-ternary (water, NaCl)/(paraffininc oil or tetradecane)/(TTAB, *N*-tallow amine) systems have been determined. Some of these systems, so-called concentrates, have been dispersed in water, at the concentrate to water weight ratio of 5/95. We have investigated the effect of composition variables and parameters of dispersion on the quality (mean size, standard deviation) of the miniemulsions formed. The droplet size distribution of the miniemulsions has been determined by using dynamic light scattering of samples submitted to further dilution. According to the dynamic light scattering results the composition, surfactant concentration, location in the phase diagram and temperature of the concentrate, and also the salinity and temperature of the water used for dispersion have an effect on the quality of the miniemulsions formed. However, this quality increases (smaller droplets and narrower droplet size distribution) when both the composition of concentrate favours the flexibility of the surfactant film and the physico-chemical conditions of the water used for dispersion increases the affinity of the surfactant film for water, and then favours the spontaneous emulsification of the concentrate. Ostwald ripening was responsible for the destabilisation of the miniemulsions.

Keywords: Formation; Stability; Miniemulsions; Concentrates; Dispersion in water

1. Introduction

Miniemulsions are finely dispersed emulsions with long-term stability due in part to sub-micrometric size of the droplets, which provides an increased stability against sedimentation or creaming and, generally, against flocculation and coalescence. Because miniemulsions are much more stable than common macroemulsions, they are of great interest for industrial applications. For basic studies, the presence of small droplets makes it possible to study one of the mechanisms, known as Ostwald ripening and due to the diffusion of the dispersed phase from the small droplets to the large droplets, for emulsion evolution towards equilibrium.

Several methods for preparing miniemulsions by using low energy techniques exit. The main methods are known as self-emulsification [1–3], which refers to situations in which a small amount of agitation is supplied to disperse the droplets formed spontaneously when the concentrates and the water phase are brought into contact, and PIT-method applies to systems containing nonionic surfactants, which consists in increasing/lowering the temperature quickly when the systems pass through an extremely unstable emulsion region, which corresponds to the HLB temperature or phase inversion temperature (PIT) [4–8].

We showed in a previous study that it was possible to obtain miniemulsions by dispersing microemulsions, containing a nonionic/cationic surfactant mixture, quickly in a brine [9]. The process involved in this miniemulsion formation was identified as self-emulsification. Many parameters of dispersion, such as salinity and temperature of the water used, may affect the quality of the miniemulsions formed. However, we did not investigated the influence of these parameters on the miniemulsion formation because the microemulsions dispersed in water contained nine chemicals and it would have been difficult to understand the interactions responsible for the modification of the miniemulsions formed.

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In the present study, we have worked on pseudo-ternary brine/oil/surfactants systems. Two types of oil were used: a paraffinic oil and tetradecane. The surfactants were a mixture of a cationic surfactant and a *N*-tallow amine. The phase diagrams of the pseudo-ternary systems were determined and some of these systems, so-called concentrates, located in the zone referred as NE in the phase diagram were dispersed in water. The size of the droplets of the emulsions obtained by this process was determined by dynamic light scattering. The influence of the salinity, pH and temperature of the water used to disperse the concentrates on the droplet size distribution (DSD) of the miniemulsions was investigated. From the results, we tried to understand the influence of the parameters of dispersion on the quality (mean size, standard deviation) of the miniemulsions formed. The stability of the miniemulsions formed from the dispersion of the concentrates containing tetradecane was investigated by analysing their DSD in function of time.

2. Experimental

2.1. Materials

- The oily phase:
  paraffinic oil (trade name: Marcol 52) manufactured by EXXON;
  tetradecane purchased from Sigma–Aldrich (purity > 99%).
- The aqueous phase:
  Mixture of water purified by a Millipore Milli-Q 185 E system (conductivity less than 10^{-1} μS/cm) and sodium chloride (Sigma–Aldrich, 98+%). The weight ratio of NaCl to the aqueous phase was written as X_{NaCl}:

$$X_{\mathrm{NaCl}} = \frac{m_{\mathrm{NaCl}}}{m_{\mathrm{NaCl}} + m_{\mathrm{water}}}$$

- The surfactant mixture:
  Mixture of a quaternary ammonium surfactant (tetradecyltrimethyl ammonium bromide (TTAB) purchased from Aldrich, purity > 99%) and an ethoxylated *N*-tallow amine (trade name: Noramox S2 (NS2)) manufactured by CECA. NS2 has some polydispersity in the EO-chain length distribution with an average of 2. The length of the chain is distributed as follows: 3 wt% of C_{14}, 30 wt% of C_{16}, 40 wt% of C_{18}=, 26 wt% of C_{18}, 1 wt% of C_{20}. The weight ratio of TTAB to the surfactant mixture was written as X_{TTAB}:

$$X_{\mathrm{TTAB}} = \frac{\mathrm{TTAB}}{\mathrm{TTAB} + \mathrm{NS2}}$$

The weight ratio of the aqueous phase to the oily phase was written as WOR:

$$\mathrm{WOR} = \frac{\text{aqueous phase}}{\text{oily phase}}$$

The weight ratio of the surfactant mixture to the system was written as X_{S}:

$$X_{\mathrm{S}} = \frac{\mathrm{TTAB} + \mathrm{NS2}}{\mathrm{TTAB} + \mathrm{NS2} + \text{aqueous phase} + \text{oily phase}}$$

2.2. Methods

2.2.1. Phase diagrams

For all systems X_{TTAB} was 0.40 and WOR was 1. The screening parameters were X_{NaCl} and X_{S}. The phase diagrams were obtained as follows: the samples were prepared in test tubes by mixing together and in the following order: NaCl, water, TTAB, oil and NS2. The samples were shaken for homogenisation and stored in a thermostat regulated water bath at a given temperature for 2 days, after which time the phase behaviour was determined visually.

2.2.2. Emulsion formation

The emulsions were prepared in small containers by adding, quickly and in one step, 1 g of concentrate to 19 g of water with different salinity, pH and temperatures. The samples were gently homogenised by a magnetic stirrer for a few seconds. Under these conditions the content of dispersed phase (oil + surfactants) in the emulsions varied from 2.65 to 2.78 wt% depending on X_{S}.

2.2.3. Droplet size

The size of the droplets of the emulsions was determined by dynamic light scattering. The apparatus was made up of a 15 mW He–Ne laser ($\lambda = 632.8$ nm) and a Malvern 7032 Multi-8 Correlator. All experiments were performed at the scattering angle $\theta = 90°$, and the sample temperature was maintained at 25 ± 1 °C. In order to limit the problems of data analysis linked to the multiple particle light diffusion of concentrated systems [10], the emulsions underwent a new dispersion with the same water as that used for the dispersion of the concentrates. The content of disperse phase (oil + surfactants) of the systems analysed by dynamic light scattering was equal to 0.136 wt%, which made it possible to assume that the measurements was carried out under "infinite" dilution [11]. The droplet size distributions were calculated using the CONTIN algorithm [12]. The time elapsed between the dispersion of the concentrate and the determination of the droplet size distribution of the emulsions was about 10 min.

3. Results and discussion

3.1. Phase diagrams

Fig. 1 shows the phase behaviour of (water, NaCl)/Marcol 52/(TTAB, NS2) in the diagram (X_{NaCl}, X_{S}) at $T = 25$ °C.

Four different phase behaviours can be distinguished in this phase diagram. For low enough values of X_{NaCl}, systems