

Non-spherical emulsion particles

In recent years two explanations have been proposed to account for the occurrence of non-spherical disperse phase particles in oil-in-water emulsions stabilized by an ionic emulsifier combined with a long-chain alcohol. Such emulsions are usually prepared by dissolving the emulsifying agents at 60–70° in the phase in which they are soluble, and mixing whilst hot. When such a mixture is stirred until cold, a stable emulsion results. It has been proposed that emulsions of liquid paraffin in water stabilized by cetrimide and cetostearyl alcohol contain non-spherical particles due to localized close-packing of the particles during preparation of the emulsion (Groves & Scarlett, 1965, Groves & Freshwater, 1967). It was considered that this would lead to deformation of the particles which would be retained on cooling, due to the rigidity of the interfacial film. Where the cetostearyl alcohol content was high, it was thought that these polyhedral emulsion particles were formed by solidification of the disperse phase.

An alternative explanation is that the alcohol is deposited as discrete crystals in the oil phase as the emulsion cools, and that these crystals deform the particles (Axon, 1957, Barry, 1968a, b, Talman & Rowan, 1968). This phenomenon has been observed with emulsions stabilized by cetyl alcohol and sodium lauryl sulphate, and cetostearyl alcohol and cetrimide. The extent of crystallization has been reported to be affected by the diluent used in mounting the emulsion for microscopy (Barry, 1968a).

Schulman & Cockbain (1940) have reported non-spherical particles in water-in-oil emulsions, prepared using emulsifiers such as calcium oleate, calcium elaidate, heptadecylamine in the presence of sodium sulphate, and digitonin with cholesterol. Except for the last, all the above emulsions were prepared by phase inversion. Those containing calcium oleate or elaidate were first formulated as oil-in-water emulsions stabilized by the sodium soap, and inverted by addition of a calcium salt solution. The resulting calcium soap acted as a water-in-oil emulsifier. It was proposed that addition of the calcium salt solution would allow the oil particles to flocculate and coalesce, entrapping continuous phase as discrete irregular 'sacks', which would retain their shape due to the rigidity of the interfacial film.

Several water-in-oil emulsions have been examined in this laboratory, including Oily Cream B.P., White Liniment B.P.C., dispersions of distilled water in liquid paraffin stabilized with sorbitan esters, and also formulations similar to those of Schulman & Cockbain, containing calcium oleate or elaidate. The emulsions stabilized by the calcium soaps were prepared by inversion, and also directly, that is, by dispersing the calcium oleate or elaidate in liquid paraffin at 50°, adding distilled water at 50°, and stirring vigorously until cold.

Each emulsion was examined microscopically after dilution with liquid paraffin. When the dilution was mounted, it was found that disperse phase particles adhered to the slide and coverslip, and in the process became non-spherical. When the microscope was focused into the bulk of the liquid, spherical particles were seen. The method of preparation of emulsions stabilized by calcium soaps was found not to influence the phenomenon of adhesion and wetting.

When the slides and coverslips were siliconized to prevent wetting, using a 2% v/v solution of dimethyldichlorosilane in carbon tetrachloride (Repelcote, Hopkin and Williams Ltd.), the disperse phase particles were spherical in every case.

Typical results are shown in Fig. 1a and b, which are photomicrographs of a directly prepared water-in-oil emulsion stabilized with calcium elaidate. The preparation was diluted as described, and photographed at a magnification of 600×, using a Wild M20 microscope fitted with a phase contrast optical system. Deformation of the particles on the non-siliconized slide is plainly visible, whereas particles on the siliconized slide are spherical.

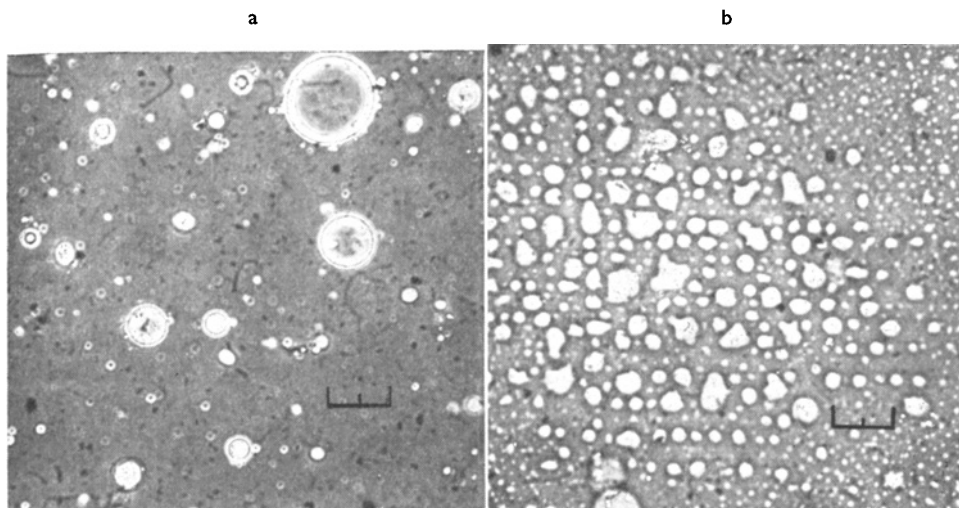


FIG. 1. Photomicrographs, in phase contrast, of a directly prepared water-in-oil emulsion stabilized with calcium elaidate. (a) Siliconized slide; (b) Non-siliconized slide. One division = 10 μm .

We propose, therefore, that when non-spherical globules are seen in a microscopic mount of a sample selected from the bulk of a freshly prepared water-in-oil emulsion, this is probably due to adhesion of the particles to the microscope slide and coverslip. This causes rupture of the interfacial film, with consequent wetting of the glass surfaces by the water. This adhesion and wetting is thought to be due to the slightly polar nature of the glass, which is a preferable environment for the water than the non-polar continuous phase. This phenomenon could affect the stability of water-in-oil emulsions stored in glass containers, as it would tend to promote coalescence of the disperse phase at the container surface. In special circumstances, for example when the emulsion has been aged, or subjected to large stresses such as those imposed during transportation or large range temperature cycling, it is possible that some globules may deform in the bulk of the emulsion. If the emulsifier forms a solid, condensed film (particularly if this is a multilayer), then these particles may be stabilized in the deformed state.

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