An examination of some oil-in-water emulsions by electron microscopy

Various methods have been used to obtain information about the structures responsible for the semi-solid consistency of oil-in-water emulsions containing self-bodying waxes (Axon, 1957; Barry, 1968, 1969; Talman, Davies & Rowan, 1967, 1968; Talman & Rowan, 1968). The mean globule size of products made and analysed as described previously (Talman & others, 1967) was about 1 μm; this approaches the limit of resolution of the optical microscope, which therefore could not be used for detailed examination. We have now examined some typical emulsions by electron microscopy. The preparations selected contained 50% w/w liquid paraffin, 0·5% w/w cetrimide or cetomacrogol 1000 and (A) 10·0% w/w oleyl alcohol, (B) 0·5% w/w cetostearyl alcohol or (C) 7·0% w/w cetostearyl alcohol. Emulsions (A) and (B) were fluids whereas (C) was a cream. The products were diluted with bovine plasma fraction V (Armour) and a drop of the diluted material placed on a carbon film supported by a 200 mesh copper grid 3 mm in diameter. The liquid was evenly dispersed over the carbon film and then as much liquid as possible drained off. The specimens were dried in a dessicator over silica gel and then examined in a Philips EM100B electron microscope.

Nothing was visible in specimens prepared from the fluid emulsions (A) and (B). The fate of the liquid paraffin globules can not be stated with any certainty but several explanations are possible. Using a technique similar to that described above, Groves & Scarlett (1965) observed numerous globules but the carbon film they employed was treated with Formvar before deposition of the sample. It is possible that the untreated carbon film which we used absorbed the oil. Alternatively, the globules may have collapsed during the course of specimen drying to give a thin layer of oil over the carbon surface. A further possibility is that the electron density of the oil was not sufficiently different to that of the carbon film for the former to show up by electron microscopy. Finally the oil may have evaporated at the pressure (about 10^{-5} torr) in the specimen chamber of the electron microscope. At pressures of this order the evaporation rate is independent of the external pressure and the rate was conveniently determined at 10^{-6} torr and at 20° in an apparatus similar to that described by Holland, Laurenson & Deville (1965). The liquid paraffin was contained in a small beaker, its free surface being 3·5 cm below a quartz crystal microbalance cooled to −78° by solid carbon dioxide. As the vapour pressure of ice at this temperature is much greater than that of the system, error due to condensation of the residual water in the apparatus onto the microbalance was avoided. The observed evaporation rate of the liquid paraffin ($2{\cdot}43 \times 10^{-8}$ g cm^{-2} s^{-1}) corresponded to a loss of 1×10^{-7} g of this material per minute from a grid in the specimen chamber of the electron microscope. The amount of the oil deposited on the grid during specimen preparation was estimated to be 10^{-6} to 10^{-5} g and would require 10 to 100 min for complete removal. Furthermore, it is likely that the bovine plasma film used to "fix" the specimen to the grid would retard the evaporation of the oil and also prevent the enhanced evaporation of liquids from droplets as compared with a bulk liquid surface observed by Shapiro & Hanyok (1968). Since globules were not present initially or any time during examination we consider this explanation to be the least likely of the four possibilities.

Figs 1a, b and c were obtained when specimens prepared with emulsion (C) were examined by electron microscopy. The objects had one or more projections which in some cases formed links between them. They did not give an electron diffraction pattern which indicates the absence of an ordered crystal lattice. Shadowing

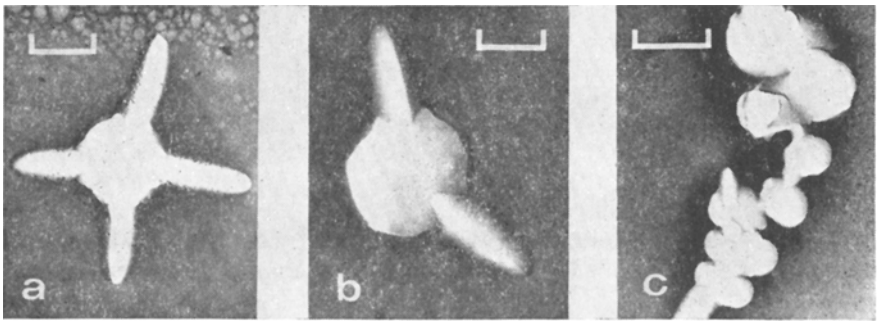

FIG. 1. Electronmicrographs of an emulsion containing 50% w/w liquid paraffin, 7·0% w/w cetostearyl alcohol and 0·5% w/w cetomacrogol 1000. (a) One division = 1 μm, (b) one division = 0·5 μm, (c) one division = 1 μm.

with gold and manganin showed that they were concave and not convex. These objects were examined over a period of hours and the grids were introduced into the specimen chamber more than once and no change was observed. In view of our failure to find emulsion globules when observing specimens prepared from emulsions (A) and (B) we suggest that the objects shown in Figs 1a, b and c are the structuring elements which impart to emulsion (C) its semi-solid consistency. They would be comprised largely of cetostearyl alcohol transferred from the oil to the aqueous phase but it is likely that some water, surfactant and perhaps liquid paraffin may also be present. These materials would "plasticize" the fatty alcohol and allow the structure to collapse when water was removed during the preparation of the specimens, to the shape revealed by shadowing. Fig. 1c is one of a stereoscopic pair which together show a three dimensional network which survived the disruptive effect of the mixing required for specimen preparation.

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