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Crystallization in polyhedral emulsion particles

SIR,—During an investigation of the properties of emulsions, preparations were made by adding a mixture of cetyl alcohol in liquid paraffin at 65° to an aqueous solution of sodium dodecyl sulphate at the same temperature and stirring with a Silverson mixer until cold. The systems used were liquid paraffin 100 g, water 300 g and:

	A	B	C	D	E	F	G	H	I
Sodium dodecyl sulphate ..	0·8	1·2	1·6	2·0	2·4	2·8	3·2	3·6	4·0 g
Cetyl alcohol ..	7·2	10·8	14·4	18·0	21·6	25·2	28·8	32·4	36·0 g

Non-spherical particles were observed microscopically in each cooled emulsion, even though the concentration of alcohol in liquid paraffin was sufficiently low to ensure that the globules were essentially liquid. These deformed globules varied in shape from flattened spheres to polyhedra, and contained anisotropic crystals which lay along the straight sides of the globules. Crystals were formed even though the alcohol to liquid paraffin ratio was much less than 8:5, which has been quoted as the minimum ratio for crystallization in similar systems by Groves & Scarlett (1965). The crystals I observed were usually acicular but occasionally flat and hexagonal. They were not easily visible in ordinary light but showed up clearly when a specimen was mounted between crossed polars. The system of lowest emulsifier concentration (A) contained some large globules

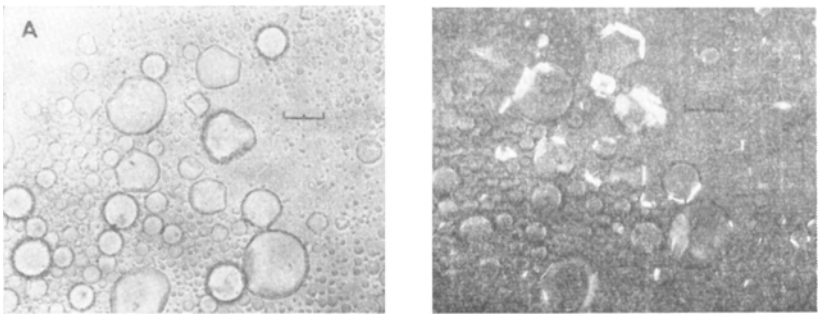

FIG. 1. Photomicrographs of System A mounted in 50% v/v glycerol in water. (a) Ordinary light (b) crossed polars. One division = 10 μ.

which showed this phenomenon well (Fig. 1). Thus it would appear that in these systems the formation of polyhedral particles is a result of crystallization.

Recently, there have been reports of irregular polyhedral particles in semi-solid emulsions consisting of equal parts by weight of cetostearyl alcohol and liquid paraffin dispersed in 0·5% w/w aqueous cetrimide solution and prepared in a similar manner to the above (Groves & Scarlett, 1965, Groves & Freshwater, 1967). It was concluded that during the emulsification process localized close-packing existed, droplets were distorted and polyhedral particles were formed. As these were solid at room temperature, their shapes were maintained on cooling and on dilution for microscopic examination. In other cases, it was suggested that liquid particles may retain their shapes because of the rigidity of the interfacial film. In both papers it was concluded that the polyhedral particles were unlikely to be due to crystallization of the alcohol. However, cetrimide emulsions prepared to the above formula have been examined in this laboratory and crystals have been detected in deformed globules. Thus, crystallization as a cause of polyhedral emulsion particles in these systems cannot be discounted.

Preparation for microscopy may also affect the behaviour. The examination of emulsions for polyhedral particles usually requires a dilution which in the first instance should be made with a surfactant solution of the same strength as that used in the preparation of the emulsion. This avoids a change in the nature of the continuous phase which may increase crystallization. Thus, with systems A to I and the cetrimide emulsions, dilution with 50% v/v glycerol in water caused a small increase in the fraction of globules containing crystals; when mounted in undiluted glycerol, crystals were precipitated in most of the larger globules. It may be convenient to mount specimens in aqueous glycerol solutions for photomicroscopy as in Fig. 1, so as to reduce Brownian movement, but if the fraction of globules which are polyhedral or contain crystals is to be estimated, it is necessary to confirm that the mounting technique does not increase the proportion.

With time, systems A to I changed in appearance as they became more mobile and formed silvery crystalline deposits in the external phase. The lower the concentrations of the mixed emulsifiers the more readily deposits were formed. These anisotropic, hexagonal, flat crystals melted *in situ* at temperatures varying between 28° and 39° (determined using a Kofler Micro Hot Stage). Similar crystals have been reported for the sodium dodecyl sulphate—cetyl alcohol—water system (Barry & Shotton, 1967). They should not be confused with polyhedral emulsion droplets.

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