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Polyhedral emulsion particles

SIR,-In 1965, irregular polyhedral particles were reported in a semi-solid emulsion system (Groves & Scarlett, 1965) and it was suggested that they may have arisen in areas of localized close packing within the system which produced distortion of the molten oil phase droplets at elevated temperatures, the shape being retained when the droplets cooled and solidified. However, the fact that close packing could occur in a system with a disperse ratio of 0.225 was of interest since this would not be anticipated until the concentration approached a value of approximately 0.74, the theoretical limit for a system consisting of equal diameter spheres.

We have now examined systems similar to the emulsion system previously investigated and consisting of an oil phase of equal parts by weight of cetostearyl alcohol and liquid paraffin dispersed in 0.5% w/w aqueous cetrimide solutions. A series of dispersions containing different amounts of the oil phase were prepared under standardized conditions. The molten oil phase at 70° was added to the aqueous phase at the same temperature and stirred with a high speed laboratory stirrer (Silverson, fitted with homogenizer head) until the mixture had cooled to 30°, when the stirrer was switched off and cooling allowed to proceed undisturbed to room temperature.

Samples were withdrawn and particle size distributions measured with a Coulter Counter Model A (Industrial) fitted with a 70 μ orifice tube. Results are summarized in Table 1.

TABLE 1. PARTICLE SIZE DISTRIBUTIONS OF THE DISPERSIONS PREPARED WITH DIFFERENT DISPERSE PHASE RATIOS. MEASURED WITH A COULTER COUNTER MODEL A (INDUSTRIAL) FITTED WITH A 70 μ ORIFICE TUBE (GROVES, 1966)

Dispersion phase ratio (weight)	Particle size distribution parameters ¹	
	D50 (μ)	Standard deviation
0.012	2.75	3.20
0.05	3.40	2.03
0.10	5.30	1.89
0.15	5.00	1.90
0.20	4.65	1.87
0.30	4 ⋅85	2.06
0.40	8.30	1.92
0.20	8.50	2.00
0.223	8.00	2.21

¹ From a logarithmic probability plot of the cumulative weight percent distribution. ² The data on this sample is unreliable since microscope examination showed that most particles were below the limit of detection of the Counter under the conditions of measurement. ³ Attempts to prepare systems more concentrated than 0.55 were not supervised. Attempts to prepare systems more concentrated than 0.55 were not successful.

Using a photomicrographic technique, at least 1,000 particles from each sample were classified visually as either spherical or non-spherical and the results are shown in Fig. 1.



Disperse phase ratio by weight

FIG. 1. The relative number of non-spherical particles in dispersions of different disperse phase ratio.

Although the particle size analysis of the most dilute system is not reliable since most of the particles appear to be below the discrimination of the Coulter Counter under the conditions of measurement, it will be seen from Table 1 that there is a general tendency for the particles to increase in size as the systems become more concentrated. This was also observed visually. In addition, the standard deviations of the size distributions remain relatively constant. However, the relative number of non-spherical particles shows a considerable increase above a disperse phase ratio of about 0.1. This latter effect supports the earlier contention that the polyhedral particles are unlikely to be due to crystallization of the high-melting point cetostearyl alcohol (Axon, 1957).

Viscosity measurements using a Ferranti-Shirley cone-plate viscometer indicate that the dilute systems behave as Newtonian fluids. Systems with disperse phase ratios in excess of 0.1 exhibit pseudoplastic flow and hysteresis, the amount of hysteresis increasing with increasing concentration. This also suggests that interparticulate interactions are occurring. One tentative explanation for the presence of irregular polyhedra may be that flocculation is occuring in the systems whilst the particles are liquid droplets. Droplets in the centre of a floccule may then be sufficiently close to be distorted and this shape could be retained on cooling.

Research Department, Boots Pure Drug Company Ltd., Station Street, Nottingham. M. J. GROVES

D. C. FRESHWATER

Chemical Engineering Department, Loughborough University of Technology, Loughborough, Leics. December 21, 1966

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