# **343.** *The Phase Volume Theory and the Homogenisation of Concentrated Emulsions.*

By Joseph Beatty Parke.

If into a given space spheres of *equal* diameter are packed as closely as possible, the space occupied by the material of the spheres is 74·048% of the total available volume. Pickering (J., 1907, **91**, 2001) has referred to this fact in connection with emulsions, and pointed out that in an emulsion containing uniform spherical globules the volume of oil would be less than this theoretical value, as the spheres are not in actual contact, the separating film of medium being of appreciable thickness. He succeeded in emulsifying 99% by volume of ordinary lighting oil in a 1% soap solution to give a very viscous emulsion, and stated that, since in an emulsion the spheres are not uniform, there is no reason why the ratio of the volume of the oil to the total volume of the emulsion should be of any particular magnitude.

Pickering prepared a series of three emulsions containing varying amounts of paraffin oil as the disperse phase. After the emulsions had been allowed to stand for 12 weeks, the " cream " which had risen to the surface in each case was analysed at intervals from top to bottom. The results were as follows :

| | | | |
|---|---|---|---|
| Percentage of oil in original emulsion ......................... | 67 | 50 | 33 |
| Average percentage of oil in cream ............................ | 81·0 | 81·9 | 77·7 |

As will be seen, the average oil contents of the three " creams," which presumably contained the globules in close packing, did not vary very greatly.

Ostwald (*Kolloid-Z.*, 1910, **6**, 103; **7**, 46), in what is now known as the phase volume theory of emulsions, suggested that it should be impossible to obtain an emulsion containing more than 74·048% by volume of the disperse phase for the reason given above. On an attempt being made to increase the oil content of, say, an oil-in-water type of emulsion by the addition of more oil, Ostwald's theory pictures a change of type which, it suggests, should be brought about by the contact and subsequent coalescence of the oil globules.

Bancroft (*J. Physical Chem.*, 1912, **16**, 179) points out that both the assumptions underlying the phase volume theory of emulsions are far from correct. First, owing to the properties of the enveloping film of emulsifier, deformation of shape, rather than coalescence, would take place when two or more globules are brought into contact, and, secondly, the fact that the globules of an emulsion are not of uniform diameter is sufficient to explain why the 74·048% limit of packing can be exceeded.

The following experiments were carried out in order to examine this matter.

225 C.c. of benzene containing 2·319 g. of oleic acid and 25 c.c. of water containing 0·329 g. of sodium hydroxide were placed together in a glass-stoppered bottle of 8-oz. capacity. The mixture was shaken by hand, using Briggs's intermittent method (*J. Physical Chem.*, **1915**, **19**, **233**). The rest interval adopted was one minute, and emulsification was found to be complete after 14 minutes. A very stable emulsion of the oil-in-water type containing 2·5 g. of sodium oleate as emulsifier was thus produced. Microscopic examination of this emulsion revealed that the globules of the disperse phase were not of uniform diameter and that smaller globules were packed into the interstices between the larger. Plate I shows a photomicrograph of this " 90% emulsion."

The emulsion was passed through a small homogeniser and it was found that partial decomposition resulted. The mixture delivered by the homogeniser consisted of clots of an oil-in-water type of emulsion distributed throughout a considerable excess of benzene. These clots quickly coalesced to form a layer at the bottom of the mixture. Plate II shows an emulsion containing 90% of benzene (right) before homogenisation and (left) after having been passed through the homogeniser.

The lower layer of emulsion was separated from the free benzene and the percentage of benzene in this emulsion was determined by " breaking " a known quantity, generally 25 c.c., with dilute hydrochloric acid in a burette, and found to be 72% by volume. The results obtained from this and three other emulsions stabilised by sodium oleate are shown in the following table :

PLATE I.

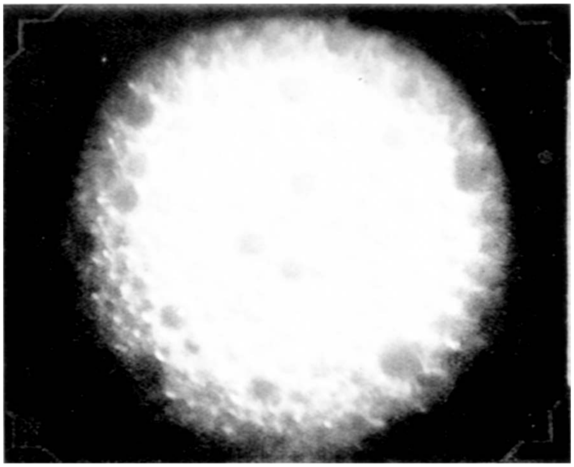
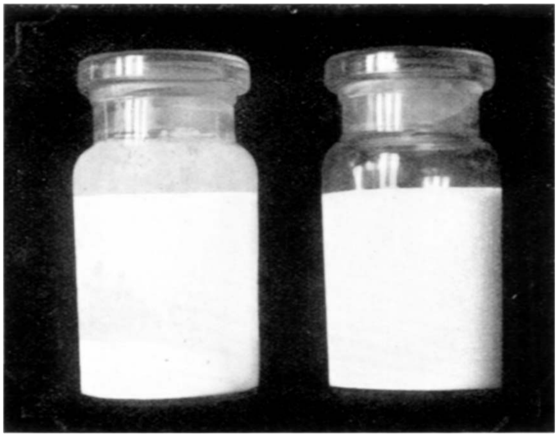


PLATE II.



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| Vol. of $C_6H_6$, c.c. | Vol. of $H_2O$, c.c. | Mass of oleate, g. | $C_6H_6$, %, in emulsion produced. | Vol. of $C_6H_6$, c.c. | Vol. of $H_2O$, c.c. | Mass of oleate, g. | $C_6H_6$, %, in emulsion produced. |
|---|---|---|---|---|---|---|---|
| 225 | 25 | 2·5 | 72·0 | 225 | 25 | 1·25 | 70·0 |
| 200 | 50 | 2·5 | 70·5 | 200 | 50 | 1·25 | 68·0 |

Potassium oleate was substituted for sodium oleate and the experiments were repeated as before :

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 225 | 25 | 2·5 | 78·0 | 225 | 25 | 1·25 | 68·0 |
| 200 | 50 | 2·5 | 76·5 | 200 | 50 | 1·25 | 70·0 |

The experiments were then repeated with purified toluene instead of benzene :

| Vol. of $C_7H_8$, c.c. | Vol. of $H_2O$, c.c. | Mass of oleate, g. | $C_7H_8$, %, in emulsion produced. | Vol. of $C_7H_8$, c.c. | Vol. of $H_2O$, c.c. | Mass of oleate, g. | $C_7H_8$, %, in emulsion produced. |
|---|---|---|---|---|---|---|---|
| Emulsifier : sodium oleate. | | | | | | | |
| 225 | 25 | 2·5 | 74·0 | 225 | 25 | 1·25 | 60·0 |
| 200 | 50 | 2·5 | 65·0 | 200 | 50 | 1·25 | 58·0 |
| Emulsifier : potassium oleate. | | | | | | | |
| 225 | 25 | 2·5 | 73·0 | 225 | 25 | 1·25 | 79·0 |
| 200 | 50 | 2·5 | 65·0 | 200 | 50 | 1·25 | 69·5 |

When the emulsions produced by homogenisation were examined under the microscope, they were seen to contain very small globules of practically uniform diameter. Attempts to obtain a photomicrograph of this type of emulsion were unsuccessful owing to extensive scattering of light by the tightly packed mass of small spheres.

Emulsions containing less than 72% by volume of benzene or 70% of toluene did not show any tendency to decompose on being passed through the homogeniser, but instead, in every case, an emulsion of greatly enhanced stability was produced.

It was observed that when an emulsion had been partially broken by homogenisation, the content of oil in the new emulsion could only be increased by adding the oil very slowly, about 1 c.c. at a time, and shaking after each addition.

## SUMMARY.

(1) Attempts to homogenise an emulsion containing more than 74% by volume of oil (the disperse phase) resulted in the production of a new emulsion containing approximately the volume of oil required for the globules to be in closest packing provided that they are of uniform diameter.

(2) Microscopic examination of the new emulsion produced by homogenisation revealed that the globules were small and of almost uniform diameter.

(3) It was found very difficult to increase the oil content of such an emulsion.

I wish to express my indebtedness to Professor A. W. Stewart and Dr. H. Graham for their interest in this work, and for the many helpful suggestions.

I also gratefully acknowledge the award of a Musgrave Studentship by the Queen's University, Belfast.

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[*Received, October 9th*, 1933.]