PARTICLE SIZE DISTRIBUTIONS IN ULTRASONIC EMULSIFICATION

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1. Introduction

The particle size distribution in emulsions is one of the important factors which influence all their physical properties. In the past numerous empirical studies have been made on this subject, but the only previous study on emulsions prepared by ultrasonic methods is that of Bondy and Sollner (1936) which indicated that the particle sizes are comparable to those in emulsions prepared with colloid mills, etc. But as Bondy and Sollner themselves pointed out, the small number of particles studies in each specimen (≈ 300) allows only a semiquantitative discussion. The present studies were made to correlate the particle sizes in emulsions prepared by ultrasonic irradiation and by handshaking, and to investigate the effect of increasing the time of irradiation of the emulsion.

2. Experimental Details

Among the many techniques available for the determination of the particle sizes (Hahn, 1928; Dallavalla, 1948; Fischer, 1953; Cadle, 1955), the photomicrography has several advantages for the present work. It is direct and complete though somewhat tedious. The emulsion chosen was the kerosene-in-water system with sodium oleate emulsifier. The details of the emulsification set up has been described by Krishnan *et al.* (1959). The fresh emulsions were photographed at $\times 400$ and further enlarged to give an overall magnification of 2,000. The various experimental techniques of photomicrography are given in detail by Green (1921) and by Shillaber (1944).

Several errors exist in this type of work which are often overlooked. The various types of errors are (*a*) errors of magnification, like the calibration of the stage and the scales used, distortion of the images, etc., (*b*) errors in size measurements due to the diffraction effects, distortion of the photographic emulsion and rounding off the observations and (*c*) statistical errors. The major experimental difficulties are poor focussing, oblique illumination, improper exposure and developing. With some care many of these troubles

are overcome, though some are of instrumental origin. But the statistical errors require some consideration. Errors of this category are (1) finite number of particles and (ii) poor selection of the field. In order to have a statistical basis for the analysis of the data, at least 1,000 particles must be counted and preferably many more. As most of the particles are very small, there is a tendency to photograph only such fields containing small particles, and so the bigger particles do not get fair justice. Also, in many cases, local clusterings occur. A good sampling of the emulsion is very difficult to achieve (Cadle, 1955). This, as well as the truncation error (*Kolloid. Z.*, in press), may account for the many discordant experimental results in the literature.

3. Results and Discussion

Some experiments were made to compare the particle size distributions in emulsions produced by different methods. As an example, emulsion I is prepared by the intermittent handshaking method (Berkman and Egloff, 1941, p. 162), and emulsion II is a D.D.T. emulsion produced ultrasonically at $\bar{E} = 100$ ergs/c.c. The D.D.T. is included as a 1 per cent. kerosene solution. The fractile diagrams of the two samples, drawn according to the usual statistical procedure (Hald, 1954; Rajagopal, 1959), are given in Fig. 1. The 15–85 per cent. range of the ordinates (y between $\pm$ 1) is quite linear; the apparent derivations beyond the 85 per cent. level are due to the distortions inherent in the fractile plots, as discussed by Hald and Rajagopal. In fact, all the emulsions studied by us followed the lognormal distribution quite well. The parameters $ln\xi$ and σ of the lognormal frequency distribution

$$f(x)\,dx = \frac{dx}{x\sigma\sqrt{2\pi}} \exp.\left\{-\frac{(lnx - ln\xi)^2}{2\sigma^2}\right\}$$

are evaluated from these fractile plots as:

Emulsion I: $ln\xi = 1{\cdot}27$; $\sigma = 0{\cdot}44$.

Emulsion II: $ln\xi = 0{\cdot}61$; $\sigma = 0{\cdot}66$.

The lognormal frequency functions for these values are given in Fig. 2, together with the corresponding experimental histograms.

It is seen that the handshaken emulsion has a broad maximum at a large size ($a_m \approx 2{\cdot}9\,\mu$), while Emulsion II has a sharp maximum at a small particle size ($a_m \approx 1{\cdot}2\,\mu$). The colloid mills also produce such fine particles. The ultrasonically prepared emulsions are quite similar to those produced in such homogenisers as far as the particle sizes are concerned.

This method of analysing the particle size distributions is applied to investigate the variation of the particle sizes with the time of irradiation. As usual 2 c.c. of kerosene and 2 c.c. of a 1 per cent. aqueous sodium oleate solution are irradiated at $\bar{E} = 120$ ergs/c.c. for various lengths of time. The

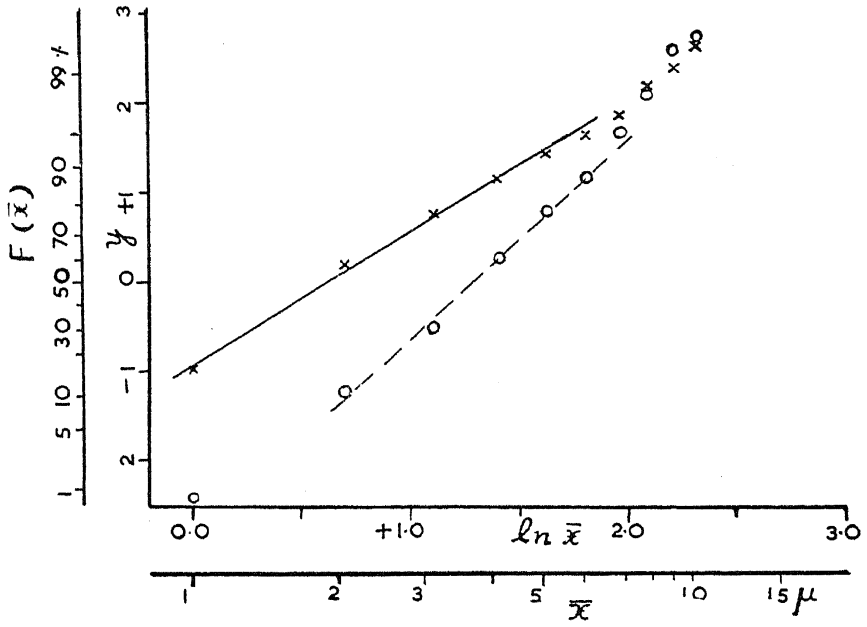

FIG. 1. Fractile Diagram for Emulsion I (handshaken; broken line) and for Emulsion II (ultrasonic irradiation of D.D.T. solution; continuous line).

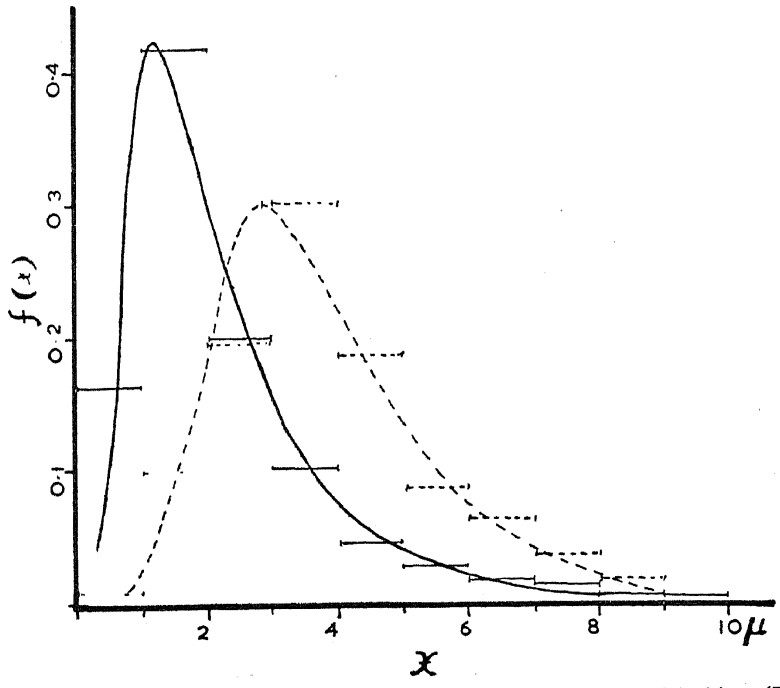

FIG. 2. Particle size distribution for emulsion prepared by handshaking (I: broken line) and by ultrasonic irradiation (II: continuous line).

TABLE I

Variation of particle size with the time of ultrasonic irradiation

Class interval / Time minutes	10	15	20	30	40	75	Hand-shaken	D.D.T.
μ	%							
0– 1	33·48	41·00	32·89	21·78	17·59	5·34	0·80	16·31
1– 2	32·49	27·82	26·12	33·64	31·48	22·05	9·95	41·71
2– 3	20·74	14·62	17·10	18·93	25·80	27·06	19·76	19·86
3– 4	5·50	6·75	9·87	12·56	14·54	19·62	30·10	10·08
4– 5	2·65	4·29	6·30	7·47	5·51	13·33	18·68	4·55
5– 6	1·38	2·25	2·73	2·77	2·38	6·09	8·60	2·77
6– 7	0·95	1·33	1·41	1·15	1·15	2·98	6·32	1·78
7– 8	0·74	0·82	1·03	0·69	0·49	1·69	3·63	1·50
8– 9	0·63	0·51	0·85	0·38	0·41	0·88	1·75	0·59
9–10	0·53	0·31	0·75	0·23	0·32	0·47	0·13	0·38
10–15	0·74	0·29	0·75	0·31	0·32	0·41	0·26	0·38
>15	0·11	..	0·19	0·08	..	0·14	..	..
Total No.	945	978	1,064	1,299	1,217	1,478	744	1,012
$ln\xi$	0·35	0·25	0·46	0·55	0·64	1·00	1·27	0·61
σ	0·74	0·87	0·88	0·76	0·64	0·55	0·44	0·66
a_m	0·82	0·60	0·73	0·97	1·26	2·01	2·93	1·19

data are given in Table I and the nature of the variation of the frequency distribution is best understood from Fig. 3, based on the values of $ln\xi$ and σ. The distributions show the general feature that the mode a_m is shifted to the larger size of the particles and the distribution gets broader as t is increased. The peak value of the maxima decreases. This behaviour was

found by Bondy and Sollner (1936) also, and is easily understood on considering the mutual collisions of the emulsified droplets.

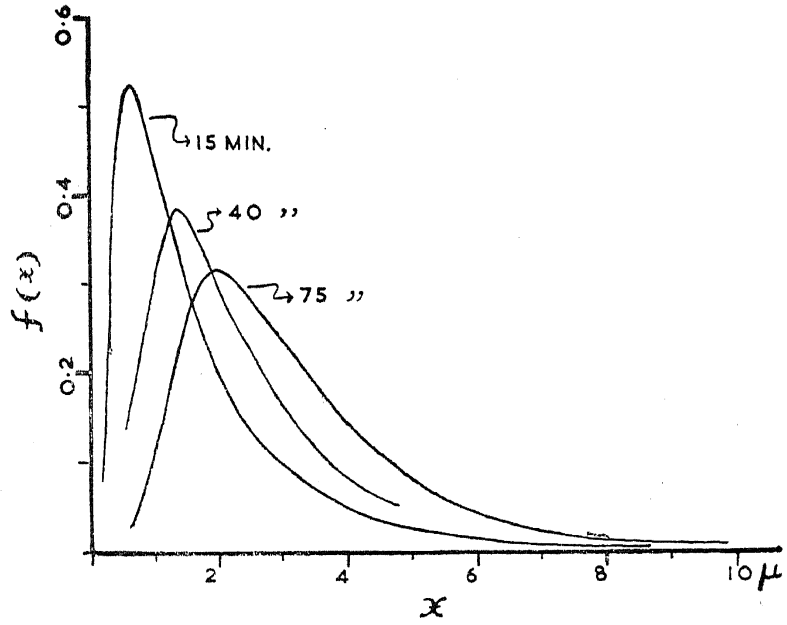

FIG. 3. Particle size distributions after 15, 40 and 75 minutes of irradiation.

The quantitative analysis of the data can be made by considering the variations of $ln\xi$ and σ as is done in Fig. 4. Apart from the usual statistical and experimental scatter in the data, the value of $ln\xi$ increases showing that

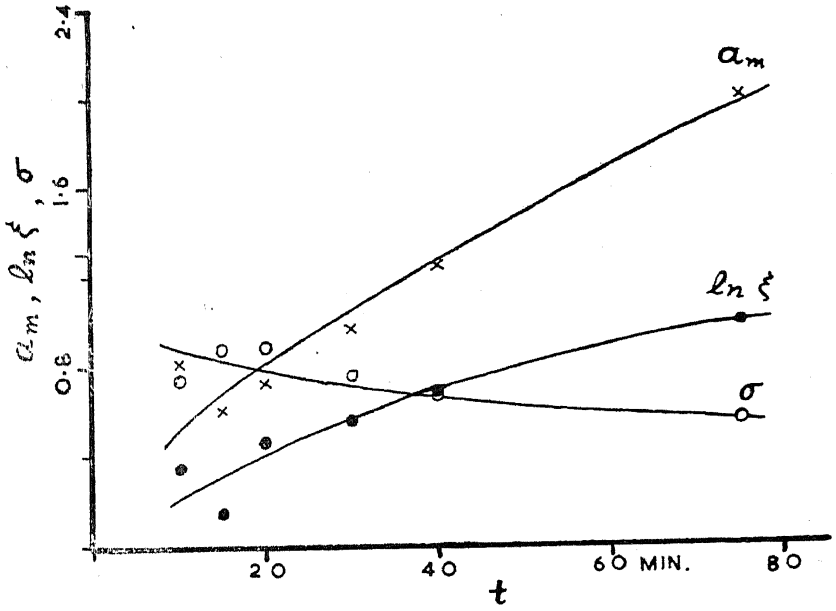

FIG. 4. Variation of a_m, $ln\xi$ and σ with the time of irradiation.

the particles are getting larger. σ decreases but still the distribution gets broader on account of the rapid increase of a_m. If one defines a width as the difference between two values of the sizes where the ordinate has a value $1/1 \cdot 6487$ ($= e^{-\frac{1}{2}}$) times that value at the mode, then this width is $2a_m \sinh \sigma$. The increase in a_m dominates over the small decrease in σ.

As stated earlier, the present note confirms quantitatively the conclusions that the ultrasonically prepared emulsions are similar in particle sizes to the emulsions produced in colloidal mills, and that the effect of prolonged ultrasonic irradiation is to coarsen the particle sizes. As has been pointed out by Sollner, the increase in the sizes of the particles is due to the mutual collisions among the particles, the presence of the dispersion factor at the high energies preventing complete coalescence and demulsification. It has been shown by Berkman and Egloff (1941, Chapter III) that the small rises in temperature of the order observed in the present measurements, namely, from $\sim 30°$ C. to ~ 40–$50°$ C., does not cause any significant change in the stabilization and coagulation mechanisms in oil/water type emulsions. The temperature effect becomes prominent when the temperature rises above ~ 60–$70°$ C. In ultrasonic irradiation, the temperature rises from $\sim 30°$ C. to $\sim 45°$ C. in about 10 minutes and remains steady thereafter due to the equilibrium with the heat loss from the surrounding oil-bath.

In any case, the resultant phenomenological variations in the particle sizes are similar to those given by the well-known Smoluchowsky theory (1917), especially when modified to take into account the distribution of sizes (Rajagopal *et al.*, to be published). But a quantitative comparison is not possible since the dispersion of the emulsified droplets is not envisaged there. For example, in the Smoluchowsky theory the average volume of a particle (proportional to $\langle x^3 \rangle_{Av}$) should increase linearly with time (Lawrence and Mills, 1953). But in the present case $\langle x^3 \rangle_{Av}$ shows only some fluctuations about a steady value. Since the concentration of the emulsion is also stationary, the number of particles per c.c. is maintained constant, unlike in the Smoluchowsky theory where it varies as

$$\frac{N_t}{N_0} = \frac{1}{(1 + kt)}.$$

4. SUMMARY

The sizes of the particles formed in ultrasonic emulsification are studied and are shown to be of the same order ($\sim 1\,\mu$) as those obtained in colloid mills. The effect of continued irradiation is to increase the mean size of the particles and to broaden the size distribution. The results are quantitatively analysed in terms of the lognormal particle size distribution.

5. Acknowledgements

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References

1. Berkman, S. and Egloff, G. *Emulsions and Foams*, Reinhold, New York, 1941.
2. Bondy, C. and Sollner, K. *Trans. Faraday Soc.*, 1936, **32**, 556.
3. Cadle, R. D. .. *Particle Size Determinations*, Interscience, New York, 1955.
4. Dallavalla, J. M. .. *Micromeritics*, Pitmans, New York, 1948.
5. Fischer, E. K. .. *Colloidal Dispersions*, Wiley, New York, 1953.
6. Green, H. .. *J. Franklin Inst.*, 1921, **192**, 637.
7. Hahn, F. V. .. *Dispersoidanalyses*, Steinkopf, Berlin, 1928.
8. Hald, A. .. *Statistical Methods with Engineering Applications*, Wiley, New York, 1954.
9. Krishnan, R. S. *et al.* .. *J. Colloid Sci.* (Under Publication).
10. Lawrence, A. S. C. and Mills, O. S. *Disc Faraday Soc.*, 1954, **18**, 98.
11. Rajagopal, E. S. .. *Kolloid. Z.*, 1959, **162**, 85.
12. Shillaber, C. P. .. *Photomicrography*, Wiley, New York, 1944.
13. Smoluchowsky, M. .. *Z. Physik. Chem.*, 1917, **72**, 129.
14. Sollner, K. .. *Alexander's Colloid Chemistry*, 1944, **5**, 337.

Note added in Proof

The following papers, which have become available to the author only now, treat some aspects of the present work. Levius *et al.* (1953) showed that below 60° C. temperature has little effect on the stability conditions of emulsions. Antonevich (1959) and Audouin *et al.* (1954) have studied the mean particle sizes for several emulsions under ultrasonic irradiation. Beal and Skauen (1955) have followed the change in the mean volume of the droplets under continued ultrasonic irradiation. They, too, have found little temperature effect. The quantitative conclusions of the present paper are supported by these observations.

References

15. Antonevich, J. N. .. *I.R.E. Trans. Ultrason. Eng.*, 1959, **7**, 6.
16. Audouin, A. and Levasseur *Mem. Ser. Chim. Etat. Franc.*, 1954, **39**, 313.
17. Beal, H. M. and Skauen, D. M. *J. Amer. Pharm. Assoc.*, 1955, **44**, 490.
18. Levius, H. P. and Drommond, F. G. *J. Pharm. Pharmacol.*, 1953, **5**, 743.