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The use of the Coulter Counter for the particle size analysis of some emulsion systems

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The Coulter Counter is suitable for the particle size analysis of emulsions containing insoluble oils. All the emulsions obey the log normal distribution of particle size if allowance is made for particles below the lower limits of the apparatus. The variation of particle size with emulsifier concentration and volume fraction has been studied for liquid paraffin emulsions stabilized by potassium laurate and potassium arabate.

IN an investigation to examine the effect of emulsifier concentration on the rheology of liquid paraffin emulsions stabilized by potassium laurate and potassium arabate (Davis, 1967), it was necessary to measure the particle size distribution.

The Coulter Counter has been used to study a wide variety of particulate systems, including emulsions, since its introduction in 1956. Comparisons with other size analysis methods have been made by Irani (1960) for glass beads, Batch (1964) for coal dust and by Marshall & Taylor (1965) and Groves, Scarlett & Freshwater (1966) for emulsions. Schrenzel (1966) has discussed the errors inherent in the microscopic methods of analysis of emulsions and has concluded that the Coulter Counter, with its high statistical accuracy, is the preferable instrument. However there are still a number of problems that are raised by the literature.

Higuchi, Okada & Lemberger (1962), Samyn & McGee (1965) and Groves (1966) found that initial dilution of an emulsion with saline had no detectable effect on particle size distribution, whereas Marshall & Taylor (1965) and Schrenzel (1966) reported that direct saline dilution was detrimental. This may be due to differences in the emulsifying agents and disperse phases employed.

The use of electrolyte containing emulsifier, at concentrations below the critical micelle concentration (CMC) has been described by Rowe (1965) and Samyn & McGee (1965) although no explanation was given for its addition. Groves (1966) advocated the use of surfactant at concentrations above the CMC to prevent aggregation of the emulsion by saline.

Nash (1965) considered that the Coulter Counter was unsuitable for aggregated systems as these would be broken down on dilution. Higuchi & others (1962), however, used the instrument as a direct means of studying the aggregation and disaggregation of hexadecane emulsions stabilized by Aerosol O.T. (Cyanamid Ltd). Swift & Friedlander (1964) used the instrument to study the coagulation of hydrosols.

Emulsion systems that have been studied have all had insoluble oils as disperse phase. It is a matter of conjecture whether emulsions of soluble oils stabilized by thick interfacial films of the hydrophilic colloid type (Shotton & White, 1963) can be counted.

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The representation of the size distributions of emulsions by smooth continuous mathematical functions has been advocated by Becher (1965). The distribution can then be easily defined and an estimate made of those particles that are outside the limits of the sizing apparatus. Empirical distribution functions have been suggested by Rossi (1933) and Jellinek (1950) among others. The theoretical work of Rajagopal (1959a) and the observations of Epstein (1947, 1948) indicate that the particle size distribution of an emulsion formed by disrupture processes should be log normal. Many workers have since found that the log normal distribution (eqn 1) is a valid mathematical model for describing the size distributions of particulate materials (Rajagopal, 1959b; Batch, 1964; Talman, Davies & Rowan, 1967)

$$y = \frac{1}{\ln \sigma\sqrt{2\pi}} \exp\left[-\frac{(\ln x - \ln M)^2}{2\ln^2 \sigma}\right] \quad .. \quad .. \quad (1)$$

where y is the probability function, x the particle diameter, σ the standard deviation and M the geometric mean particle size.

Other modifications of the normal distribution have also been used (Schwarz & Bezemer, 1956; Mugele & Evans, 1951; Sprow, 1967). The log normal distribution has been described in detail by Kottler (1950) and Smith & Jordan (1964). Truncated log normal distributions may be converted to their original distributions by algebraic and statistical methods (Kottler, 1950; Rajagopal, 1959b) or by graphical methods (Irani & Callis, 1963).

Using the Coulter Counter, Rowe (1965), Marshall & Taylor (1965) and Schrenzel (1966) reported a poor fit to the log normal distribution. However, these workers may not have considered particles outside the limits of the apparatus (Batch, 1964) or the inherent statistical errors of the distribution (Smith & Jordan, 1964; Gwyn, Crosby & Marshall, 1965).

These problems have been investigated in the present work so as to enable the determination of particle size distributions for potassium laurate and potassium arabate emulsions of liquid paraffin.

Experimental

Materials. Liquid paraffin of British Pharmacopoeia quality. Benzene of Analar quality. Lauric acid of 99% purity was checked by gas chromatography and potassium arabate prepared according to Shotton (1955).

Apparatus. Particle size measurements were made using a Coulter Counter model A, industrial, with 30 and 100 μ orifice tubes previously calibrated with polyvinyl toluene lattices and pollens of known diameter. Details of the apparatus and its calibration have been given by Wachtel & LaMer (1962), Edmundson (1967) and Allen (1967).

PREPARATION OF EMULSIONS

The required quantities of oil and surfactant solution were weighed into a stainless steel beaker and an initial dispersion brought about by means of a high speed stirrer fitted with a "dispersator" head. Further homogenization was produced by an Omerod Q.P. hand homogenizer. A total of 4 passages was made with the homogenization pressure increased each time. To obtain a standardized homogenization procedure, the same series of arbitrary pressures were used for each emulsion system.

The emulsions were stored at 25° for four days before examination. Formulation details are given in Table 1.

PROCEDURE

The electrolyte was commercial normal saline, low in particulate contamination. The emulsions were diluted (1 : 250,000) with saline using a two step process to give a suitable concentration for counting (Samyn & McGee, 1965) and counted immediately. The effect of diluting the

TABLE 1. FORMULATION DETAILS AND PARTICLE SIZE RESULTS POTASSIUM LAURATE-LIQUID PARAFFIN EMULSIONS

Emulsifier conc. % w/w	ϕ	Particle size data			Conc. % w/w	ϕ	Particle size data		
		Mean vol. diam. μ	s.d. σ	Correl. coeff.			Mean vol. diam. μ	s.d. σ	Correl. coeff.
Laurate									
10·0	0·05	2·77	2·80	0·998	1·0	0·05	3·50	2·52	0·998
	0·11	2·56	2·57	0·991		0·11	3·98	2·45	0·997
	0·16	3·10	2·87	0·996		0·16	3·34	2·49	0·995
	0·22	2·20	2·28	0·997		0·22	3·92	2·19	0·995
	0·33	3·15	2·47	0·997		0·33	3·97	2·24	0·996
	0·43	2·09	2·37	0·991		0·43	4·26	2·27	0·988
	0·53	2·68	2·24	0·991		0·53	3·39	2·02	0·997
	0·63	2·40	2·19	0·997		0·63	3·69	2·23	0·995
5·0	0·05	2·95	2·55	0·987	0·75	0·05	4·10	2·34	0·995
	0·11	3·62	2·54	0·996		0·11	4·00	2·34	0·997
	0·16	2·88	2·88	0·995		0·16	3·44	2·05	0·992
	0·22	3·06	2·31	0·976		0·22	4·17	2·23	0·995
	0·33	3·35	2·11	0·995		0·33	3·29	1·95	0·996
	0·43	2·81	2·16	0·994		0·43	3·92	2·16	0·993
	0·53	3·01	2·09	0·998		0·53	3·83	2·13	0·997
	0·63	3·61	2·35	0·997		0·63	3·78	2·21	0·997
2·5	0·05	3·00	2·60	0·998	0·5	0·11	5·12	2·43	0·995
	0·11	3·98	2·45	0·997		0·22	5·08	2·22	0·996
	0·16	3·04	2·52	0·996		0·33	4·45	2·10	0·995
	0·22	4·07	2·31	0·997		0·43	5·31	2·18	0·997
	0·33	3·52	2·37	0·997		0·53	4·49	2·19	0·997
	0·43	3·41	1·99	0·991		0·63	5·06	2·09	0·997
	0·53	3·28	2·20	0·999					
	0·63	3·36	2·19	0·998					
Arabate									
0·75	0·11	4·66	2·12	0·992	8·0	0·12	3·78	2·28	0·989
	0·22	5·04	2·23	0·993		0·23	5·27	2·05	0·986
	0·33	3·57	3·76	0·976		0·33	9·91	2·28	0·985
	0·43	8·35	4·85	0·991		0·44	10·3	1·65	0·998
	0·53	21·5	2·01	0·991		0·54	13·6	1·62	0·998
	0·63	28·3	2·13	0·995		0·64	16·8	1·74	0·987
2·25	0·11	3·84	2·26	0·994	12·0	0·12	4·61	2·24	0·993
	0·22	4·84	2·26	0·989		0·23	4·88	2·10	0·988
	0·33	6·31	2·19	0·996		0·34	9·46	2·01	0·982
	0·43	13·8	1·54	0·951		0·44	11·0	1·72	0·996
	0·53	14·5	1·62	0·996					
	0·63	17·0	1·75	0·990					
4·5	0·11	4·02	2·38	0·981					
	0·22	6·04	2·18	0·994					
	0·33	5·89	2·19	0·991					
	0·43	13·5	1·60	0·991					
	0·53	12·3	1·63	0·990					
	0·63	13·6	1·70	0·998					

emulsion with saline was investigated by making initial dilutions with either saline or distilled water. No significant difference in particle size results was detected.

The addition of surfactant (potassium laurate) at concentrations below the CMC appeared to have no effect on particle size distribution but did create counting and filtration difficulties due to the formation, by carbon dioxide, of small needle shaped crystals of acid soap. Concentrations above the CMC, as suggested by Groves (1966), were not employed for, besides filtration and calibration problems, such a small quantity of oil reaches the counting vessel that loss of the smaller particles may well occur due to solubilization (McBain & Richards, 1946).

RESULTS

These are in Table 1.

DATA ANALYSIS

The raw count, after correction for coincident passages, gives the number of particles, N_i, that have volumes greater than V_i, for the range $i = 1$ to $i = n$.

V_i is related to the threshold value, T_i, of the instrument and the particle diameter (d_i) may be calculated from

$$d_i = KT_i^{1/3} \quad \ldots \quad (2)$$

where K is the calibration constant.

For the size range d_i to d_{i+1} the mean volume is proportional to $\bar{T}_i$ where

$$\bar{T}_i = \tfrac{1}{2}(T_i + T_{i+1}) \quad \ldots \quad (3)$$

and the fraction of the total volume of particles (Q_i) within the interval is

$$Q_i = (N_i - N_{i+1})\bar{T}_i \quad \ldots \quad (4)$$

If d_n is the smallest size level of the instrument and d_z the size of the smallest particle, then in the analysis of the results two cases may arise.

(i) If d_n is *below* the size of the smallest particle (d_z) the complete distribution is obtained by calculating the percentage volume of the particles above a given size (% volume oversize) C_i

$$C_i = \frac{\sum_{1}^{i} Q_i \times 100}{\sum_{i}^{n} Q_i} \quad \ldots \quad (5)$$

(ii) In many cases the size of the smallest particle (d_z) is below the limit of the apparatus. For such systems the Coulter Counter handbook (1966) suggests a graphical extrapolation method to find N_z using a plot of log N_i against log T_i. This is an empirical and rather lengthy procedure only suitable for cases where the log N_i versus log T_i plot is curved. Extrapolation to a low value of log T_i, (log T_z) where log N_i is independent of log T_i, gives the log N_z value.

then

$$Q_z = (N_z - N_n)\frac{(T_z - T_n)}{2} \quad \ldots \quad (6)$$

and
$$C_i = \frac{\sum_{1}^{i} Q_i \times 100}{\sum_{1}^{z} Q_i} \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

A log probability plot of C_i against log d_i for a suitable emulsion (amenable to the Coulter handbook method) is shown in Fig. 1, curve A.

For many emulsion systems the plot of log N_i versus log T_i does not show curvature and no extrapolation is possible. If the particle size distribution is assumed to be log normal, as predicted by Rajagopal (1959a), a more rigorous procedure, amenable to computer analysis, can be developed for the present work. If the distribution is considered to have been truncated at the smallest measured size (0·9 μ for the 30 μ tube), i.e., no particles below d_n, then calculation of the C_i values using equation (5) gives the curve B, Fig. 1. This is typical of a truncated log normal distribution with an asymptote to the size at which truncation has occurred (0·9 μ). Truncated log normal distributions of this type may be corrected to their original distribution (Irani & Callis, 1963) by extrapolation of the straight line obtained at higher levels to the asymptote size (0·9 μ). The value of probability at this point P gives the percentage oversize obtained had there been no truncation. Multiplication of C_i values by P/100 gives a corrected log normal distribution that takes into account those particles below the limit of the apparatus. Using the same emulsion as before, a close agreement in C_i values is obtained with the Coulter handbook method, Fig. 1, curve C.

The values of percent oversize obtained at the largest sizes were subject to statistical scatter in some cases and for this reason the extrapolation considered those points lying between the limits of 20–80% probability (Kottler, 1950; Smith & Jordan, 1964).

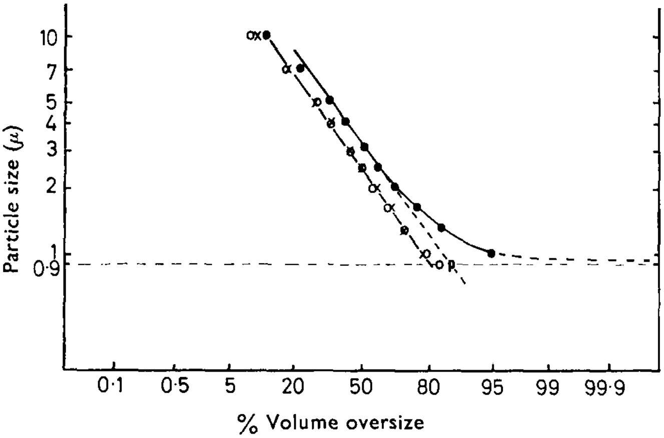

FIG. 1. The log normal distribution and its correction for instrumental truncation. Abscissa: Percentage volume oversize (on probability scale) (C_i). Ordinate: Particle size (μ) (log scale) (d_i). × Curve A, Coulter handbook extrapolation. ● Curve B, original uncorrected curve. ○ Curve C, original curve corrected for instrumental truncation.

Complete data analysis was carried out using the University of London Atlas computer and the resultant corrected log normal curve analysed statistically. The following were evaluated: (i) the correlation coefficient for a linear regression analysis on the corrected log probability plot; (ii) the mean volume diameter; (iii) the standard deviation. Once (ii) and (iii) have been evaluated other parameters such as mean weight diameter, mean number diameter, specific surface area, polydispersity, etc., can be determined if required (Irani & Callis, 1963; Rowe, 1965).

POTASSIUM LAURATE–LIQUID PARAFFIN EMULSIONS

These emulsions provided suitable systems for counting. Above 1·0% soap the emulsions were aggregated (Shotton & Davis, 1967) but microscopic examination showed that the aggregates were broken down by the two-step dilution for counting and the individual particles sized. The three typical results in Fig. 2 demonstrate the very good fit to the

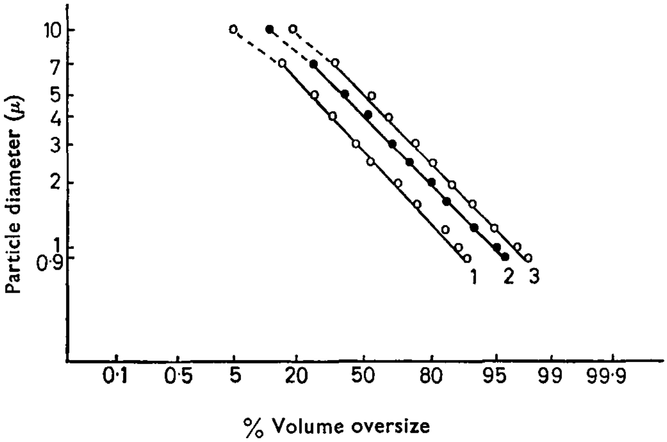

FIG. 2. The particle size distributions for three liquid paraffin, potassium laurate emulsions (log probability plot). Soap concentration 1, 10%; 2, 2·5%; 3, 0·5%; volume fraction 0·22.

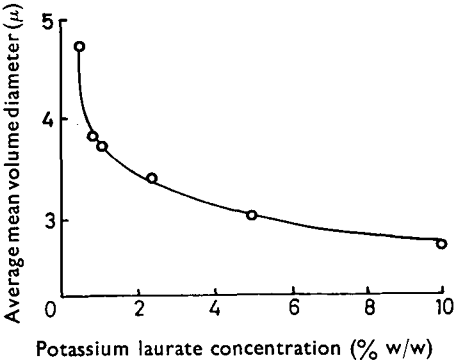

FIG. 3. The change in mean volume diameter with soap concentration for liquid paraffin, potassium laurate emulsions (average results for volume fractions 0·05–0·63).

log normal obtained after correction for instrumental truncation. In Table 1 only three of the potassium laurate, liquid paraffin emulsions give a linear regression coefficient of less than 0·990.

The mean volume diameter appears to be almost independent of volume fraction (ϕ), although in some cases a slight fall in size with increased ϕ is indicated. The average mean volume diameter (volume fractions 0·05 to 0·63) varies in an approximately exponential manner with soap concentration (Fig. 3).

POTASSIUM ARABATE–LIQUID PARAFFIN EMULSIONS

Microscopic examination showed that these emulsions were aggregated at high volume fraction (Davis, 1967) but the aggregates were *not* broken down on dilution. Both the aggregated and non-aggregated emulsions could be described by the log normal distribution, but with a generally lower value for the correlation coefficient than the laurate emulsions. A plot of average mean volume diameter (arabate concentrations 2·25 to 12·0%) against volume fraction demonstrates the aggregation of the emulsions when the *volume fraction* is in the region of 0·33 (Fig. 4).

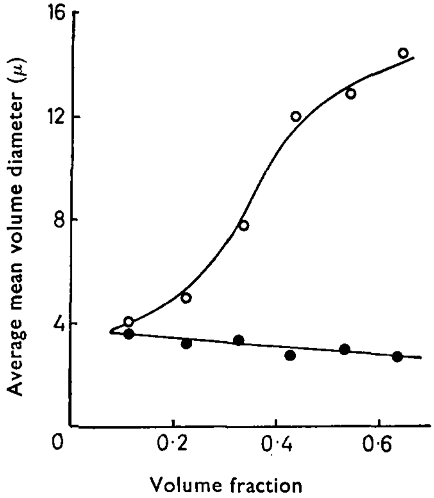

FIG. 4. The change in mean volume diameter with volume fraction for potassium arabate and potassium laurate emulsion of liquid paraffin (average results for arabate concentrations 2·25–12·0%, laurate concentration = 5%.) ○, Arabate, ●, Laurate.

Laurate and arabate emulsions stabilized by benzene could not be counted. At the high dilution used the benzene rapidly dissolved in the saline and only the background count for the saline was obtained. This effect was *not* prevented by the thick interfacial film produced by potassium arabate. Saturation of the saline with benzene enabled counts to be made but their accuracy was suspect due to a very high background count caused by small benzene droplets that were difficult to remove by filtration.

Discussion

Only emulsions with insoluble oils can be counted using the Coulter Counter. These include those emulsions stabilized by a thick interfacial film. Liquid paraffin emulsions aggregated by soap are completely broken down on dilution whereas arabate aggregates are not. Higuchi & others (1962), however, were able to count soap-stabilized hexadecane aggregates and it therefore appears that dilution breakdown depends both on the disperse phase and the emulsifier.

Volume fraction appears to have little effect on the mean particle diameter of liquid paraffin–potassium laurate emulsions. This is in contrast to Groves & Freshwater (1967) who found an increase in mean size with increased volume fraction. However their emulsions were stabilized by a cetrimide, cetostearyl alcohol complex which may explain the difference between the results. The mean volume diameter is related almost exponentially to the emulsifier concentration. Rowe (1965) suggested that the activity of the surfactant was the determining factor for particle size and that it was related to concentration by a log function. This is somewhat doubtful for Kolthoff & Johnson (1948) have shown that the activity of soaps is independent of concentration above the CMC, and an alternative explanation is therefore advanced.

THE EFFECT OF EMULSIFIER CONCENTRATION ON PARTICLE SIZE

Above the CMC the interfacial tension is almost constant (Powney & Wood, 1941) so that standardized homogenization of emulsions containing different soap concentrations will give, *initially*, globules of similar particle size distributions. The *resultant* globule sizes will depend on how quickly the surfactant reaches the interface and forms an interfacial layer sufficient to prevent coalescence. Ward & Tordai (1946) studied the diffusion of surfactants to the interface and obtained the equation

$$M = \int_0^t \left(\frac{dm}{dt}\right)_{x\to 0} dt = 2C \left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \quad \cdots \quad (8)$$

where M is the surface concentration at time t, C the constant bulk concentration, x the distance from the interface and D the diffusion coefficient.

Assuming that a given surface concentration is required to prevent droplet coalescence then the time for that excess to be obtained, i.e., the time available for coalescence, will be proportional to the square of the reciprocal of the emulsifier concentration $\left(\frac{1}{C^2}\right)$

i.e.,

$$t = \frac{\pi M^2}{4DC^2} \quad \cdots \quad (9)$$

If the resultant globule sizes are proportional to the time available for coalescence then the mean globule size $(\bar{d})$ is proportional to $^1/C^2$.

This type of relation gives a plot somewhat similar to an exponential plot and gives a far better explanation of the shape of the curve in Fig. 3 than that advanced by Rowe (1965).

The increased viscosity of the continuous phase with emulsifier concentration will reduce the rate of coalescence and will have a similar, but slight, effect on the shape of the mean volume diameter, emulsifier concentration relation.

The aggregation of potassium arabate emulsions with volume fraction has been investigated in detail (Davis, 1967) and is due to a macromolecular bridging mechanism of the type described by Smellie & LaMer (1958) and discussed recently by Overbeek (1966).

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