J. Pharm. Pharmac., 1967, 19, 78–86 Received July 18, 1966

A new method for the determination of globule size distribution of emulsions by dielectric constant measurement

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A new method for the determination of globule size distribution of emulsions prepared with non-ionic surfactants by ascent rate analysis is described. The proportion of dispersed phase in a narrow layer of dilute emulsion situated at a known height in a capacitance cell is determined at suitable time intervals and by the application of Stokes' Law, the droplet size distribution is calculated.

ALTHOUGH a great deal of attention has been paid to the determination of particle size of finely divided solids, comparatively little interest has been shown in the determination of the droplet sizes of emulsions. The principles of incremental sedimentation analysis used for the size-grading of solid powders (see for example Rose, 1958; Orr & Dallavalle, 1960; British Standards No. 3406: Part 2, 1963) could be applied to the determination of droplet sizes in emulsions, but this seems to have been neglected because of the difficulty of determining oil concentrations in withdrawn samples or in narrow layers of emulsions.

Recently, Kaye & Seager (1965) described a method for the detection of composition changes which occur in the upper layers of creaming emulsions. In this method, a glass cell provided with a pair of capacitor plates at its upper end is filled with emulsion. As the emulsion gradually separates and the concentration of oil in the upper layers increases, the dielectric constant of the emulsion in this region decreases. The change in dielectric value results in a decrease of cell capacitance which is measured by the heterodyne beat method.

Since the relation between dielectric constant and oil concentration in dilute emulsions is known, it seemed likely that an incremental method of sedimentational analysis could be based on dielectric constant measurement.

We now describe the accurate determination of the proportion of dispersed phase in a narrow zone of emulsion situated at a known height in a capacitance cell. The proportion of dispersed phase in this zone is obtained at suitable time intervals, and by the application of Stokes' law the droplet size distribution of the emulsion is calculated.

Experimental

APPARATUS FOR MEASUREMENT OF DIELECTRIC CONSTANT

Capacitance cell. The capacitance cell (Fig. 1) is a long glass vessel having two concentric walls (1 and 2) defining an annular space (3) between them. The vessel is filled with emulsion through an opening (4) provided near one end. The capacitor plates near the top of the cell are two conducting layers (5 and 6) formed by the deposition of silver

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onto the glass surface. The inner conducting plate (7) is electrically connected to the outer earthed plate (6) and acts as a guard ring which reduces the effect of fringe capacitance between plate (6) and the upper edge of plate (5). Electrical connection to the plates is made through a coaxial plug (8) which is used to connect the cell to the heterodyne beat oscillator.

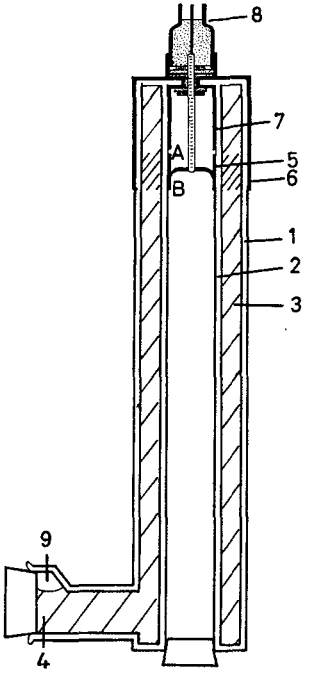

FIG. 1. Capacitance cell. For explanation see text.

Heterodyne beat oscillator. The capacitance of the emulsion-filled cell was measured by the heterodyne beat method. A block diagram of the apparatus is shown in Fig. 2. Radio-frequency signals, f_v and f_c, are generated by a variable frequency and a fixed frequency (crystal controlled at 7 Mc/sec) oscillator respectively. Both signals are fed into a mixer circuit, the output of which, $(f_v - f_c)$ or $(f_c - f_v)$, is monitored on a

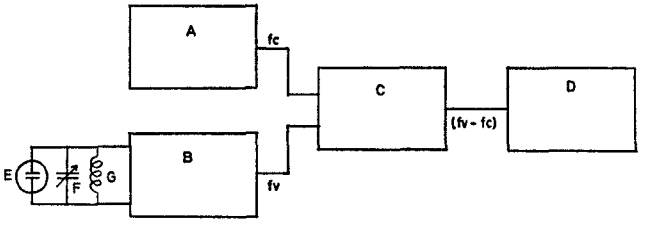

FIG. 2. Block diagram of the heterodyne beat apparatus. A, crystal oscillator. B, variable frequency oscillator. C, mixer. D, beat detector. E, capacitance cell. F, precision condenser. G, inductance.

loudspeaker and on a "magic eye" indicator tube. When the frequencies of the R.F. outputs from each oscillator are the same, i.e. $f_v = f_c$, there is no note from the loudspeaker and no flickering on the "magic eye" tube.

The frequency of the variable oscillator R.F. output is given approximately by the equation

$$f = \frac{1}{2\pi\sqrt{LC}} \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where L and C are respectively the inductance and capacitance of its tuned circuit. The capacitance in the frequency determining circuit is made up of the capacitance cell (the dielectric of which is formed by the emulsion under investigation) and a precision variable condenser, both connected in parallel with the inductance (of constant value). With the emulsion-filled cell in position, the variable frequency oscillator is tuned by the precision variable condenser to the same frequency as that of the crystal controlled oscillator. Any composition change in the emulsion shifts the frequency of the R.F. output of the variable frequency oscillator and gives rise to a note in the loudspeaker and flickering of the indicator tube. The amount by which the precision condenser must be adjusted to return the frequency to that of the crystal oscillator is a direct measure of the capacitance change brought about by the change of emulsion composition.

METHOD OF MEASURING CREAMING RATES

Emulsions containing up to 2% w/w of liquid paraffin B.P. in a 1% w/w aqueous solution of cetomacragol 1000 B.P.C. were prepared in an Atomix M.S.E. Emulsifier. A uniform sample of emulsion was taken and any air removed by gentle rotation for 10 min in a flask under vacuum. Gentle shaking was continued to ensure uniform globule distribution as the emulsion was warmed to 25°. The cell, maintained at 25° in a Perspex air chamber, was disconnected from the oscillator and filled with the emulsion. The rubber stopper was inserted and the cell inverted so that the remaining air bubble was trapped in the small space provided (Fig. 1, 9). The gap between the capacitor plates was thus filled with emulsion free from air bubbles.

A clock was immediately started, the cell quickly reconnected to the oscillator and the variable capacitor adjusted so that the frequency of the variable oscillator was equal to that of the crystal reference oscillator. As the emulsion gradually separated and the concentration of oil between the capacitor plates decreased, the dielectric changes caused a corresponding increase in cell capacitance. The frequency of the R.F. output of the variable frequency oscillator was returned at suitable time intervals to that of the reference oscillator by adjusting the variable capacitor.

CONVERSION OF CAPACITANCE READINGS INTO DIELECTRIC VALUES

The cell capacitance C_c is related to the dielectric constant of its contents by the following equation (Sherrick, Dawe, Karr & Ewen, 1954; Blaedel & Petitjean, 1956; Kaye & Seager, 1966).

$$C_c = \frac{[(2\pi f)^2 C_o\epsilon(C_o\epsilon + C_g) + K^2]C_g}{(2\pi f)^2(C_o\epsilon + C_g)^2 + K^2} \quad .. \quad .. \quad .. \quad (2)$$

where C_o = capacitance due to air in empty cell
C_g = capacitance due to glass walls of cell
ϵ = dielectric constant of emulsion
K = conductance of emulsion
f = frequency of electrical field

For the system studied, the conductance term K^2 may be neglected in comparison with the capacitance terms $(2\pi f)^2 C_o\epsilon(C_o\epsilon + C_g)$ and $(2\pi f)^2(C_o\epsilon + C_g)^2$ and the equation reduces to

$$C_c = \frac{C_o\epsilon C_g}{C_o\epsilon + C_g} \quad .. \quad .. \quad .. \quad .. \quad (3)$$

Since the capacitance of the cell when empty is given by

$$C_c = \frac{C_o C_g}{C_o + C_g} \quad .. \quad .. \quad .. \quad .. \quad (4)$$

the capacitance C due to the emulsion may be obtained by subtracting equation (4) from (3)

$$C = \frac{C_o\epsilon C_g}{C_o\epsilon + C_g} - \frac{C_o C_g}{C_o + C_g} \quad .. \quad .. \quad .. \quad (5)$$

and the dielectric constant of the emulsion may then be determined from capacitance measurements by employing the rearranged form of equation (5)

$$\epsilon = \frac{C_g + C(C_g/C_o + 1)}{C_g - C(C_o/C_g + 1)} \quad .. \quad .. \quad .. \quad (6)$$

CONVERSION OF DIELECTRIC DATA INTO EMULSION COMPOSITION

Many equations relating the dielectric constant of an emulsion to its composition have been proposed (Lorenz & Lorentz, 1880; Rayleigh, 1892; Wiener, 1912; Wagner, 1914; Lichtenecker, 1926; Piekara, 1932; Bruggeman, 1935; Fradkina, 1950; Kubo & Nakamura, 1953; Reynolds & Hough, 1957). Because of the unknown effect of the oil-water interface on the electrical field strength between the capacitor plates, no single equation is suitable for use over a wide range of concentrations (Piekara, 1929, 1930; Heymann, 1934; Kruyt, 1952; Smyth, 1955; Fradkina & Khmunin, 1956; Naiki, Fujita & Matsumura, 1959; Khmunin, 1959; Hanai, Koizumi & Gotoh, 1962).

Most authors agree that the experimental results, especially in the case of dilute emulsions, are best fitted by the Bruggeman equation

$$\frac{\epsilon - \epsilon_o}{\epsilon_w - \epsilon_o}\left(\frac{\epsilon_w}{\epsilon}\right)^{1/3} = 1 - \phi \quad .. \quad .. \quad .. \quad (7)$$

where ϵ = dielectric constant of emulsion; ϵ_o = dielectric constant of dispersed phase; ϵ_w = dielectric constant of continuous phase; ϕ = volume fraction of dispersed phase. A theoretical plot of this equation is shown in Fig. 3, along with the experimentally determined dielectric constants

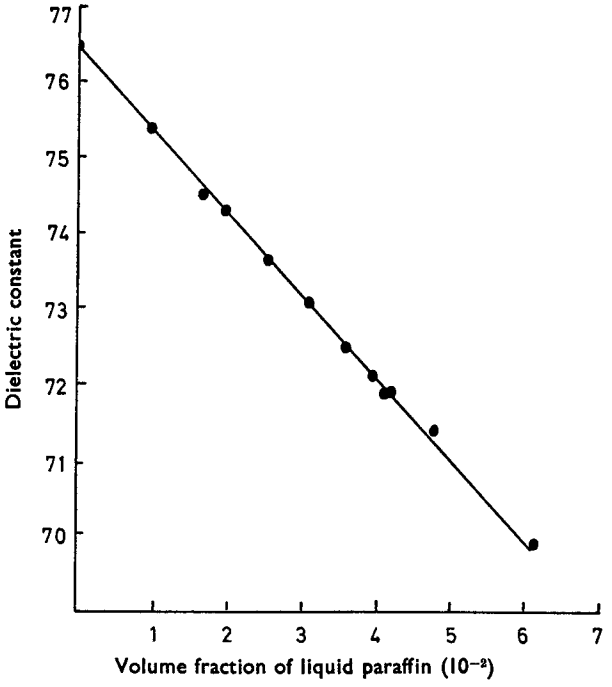

FIG. 3. Relation between volume fraction of dispersed phase and dielectric constant for liquid paraffin-in-water emulsions. — Theoretical curve calculated from the Bruggeman equation. ● Experimental points.

of a series of dilute liquid paraffin-in-water emulsions. The agreement between the theoretical and practical values is excellent. The Bruggeman equation was therefore used to calculate the composition of the emulsion lying between the capacitor plates from the dielectric values.

CALCULATION OF GLOBULE SIZE DISTRIBUTION

Consider the behaviour of a dilute monodispersed emulsion in a cell having very narrow capacitor plates, i.e. the distance AB (Fig. 1) is similar to the size of the globules themselves. The globules cream at the same velocity and the concentration of oil in the zone between the capacitor plates remains constant for a time because all disappearing globules are replaced by others rising from the layers below. When all the globules which were in the lowest regions of the emulsion have risen beyond the zone, the oil concentration suddenly falls to zero.

If the emulsion is not monodispersed, the globules of different sizes cream at different rates and the concentration of oil within the zone does not change suddenly but decreases gradually with time due to the continual disappearance of globules of certain sizes. At zero time, the emulsion between the capacitor plates is made up of globules of all sizes but after time t, only globules with an ascent velocity less than x/t (where x is the distance from the base of the cell to the capacitance zone, and t is

the time of creaming) are still to be found in the zone. All globules with ascent velocities greater than x/t will have risen completely from the lowest region of the emulsion to a point above the zone leaving the zone with a reduced concentration of oil. Similarly, after time t_1, the concentration of oil within the zone is further reduced due to the complete disappearance of all globules with a velocity greater than x/t_1.

If the change in concentration within the zone is measured at suitable time intervals and the equation

$$d_{st} = \sqrt{\frac{18\eta x}{g(\rho_1 - \rho_2)t}} \quad .. \quad .. \quad .. \quad .. \quad (8)$$

where d_{st} = diameter of globules; η = viscosity of continuous phase (0·009621 poise); x = height of globule ascent 25·952 cm); ρ_1 = density of dispersed phase (0·8797 g/cc); ρ_2 = density of continuous phase (0·99602 g/cc); t = time of globule ascent; g = acceleration due to gravity, derived from Stokes' law is used to calculate the sizes of droplets which have risen above the capacitance zone at these times, a cumulative weight undersize curve may be constructed from the results; from this a weight distribution of globule sizes may be obtained.

In practice, a cell with such a narrow capacitance zone would be insensitive to small changes in emulsion composition. To increase the sensitivity therefore, a cell with a wider capacitance zone was employed. This does not affect the above argument except that since each droplet now spends a significant proportion of its total ascent time within the capacitance zone, its contribution to capacitances does not fall instantaneously but decreases rapidly to zero as it rises through the zone In the following experiments, the distance x was taken to be the distance from the bottom of the cell to a point midway between the capacitance zone AB, i.e. to the point in the zone where the globules spend their average time. The error introduced by this step was expected to be small (see Seager, 1966).

Examples of results obtained for an emulsion of liquid paraffin in water are given in Table 1. The cumulative weight undersize and weight distribution curves for the same emulsion are shown in Fig. 4.

TABLE 1. RESULTS FOR AN EMULSION OF LIQUID PARAFFIN IN WATER

Time		Zone capacitance (in μμf)	Dielectric constant of sample in zone	Composition of sample in zone			Diameter of globules leaving zone (μ)
min	sec			Volume fraction	Weight fraction	Weight undersize %	
0		29·84	74·44	0·0265	0·0233	100	—
4	35	29·84	74·44	0·0265	0·0233	100	120
8	8	29·85	74·55	0·0250	0·0220	94·3	90
13	27	29·89	75·01	0·0217	0·0191	81·9	70
18	18	29·92	75·41	0·0174	0·0153	65·7	60
26	22	29·96	76·02	0·0121	0·0106	45·1	50
41	11	30·01	76·62	0·00710	0·00625	26·8	40
73	14	30·03	77·00	0·0030	0·00264	11·3	30
166	26	30·05	77·27	0·00130	0·00114	4·91	20
292	55	30·06	77·31	0·00075	0·00066	2·83	15

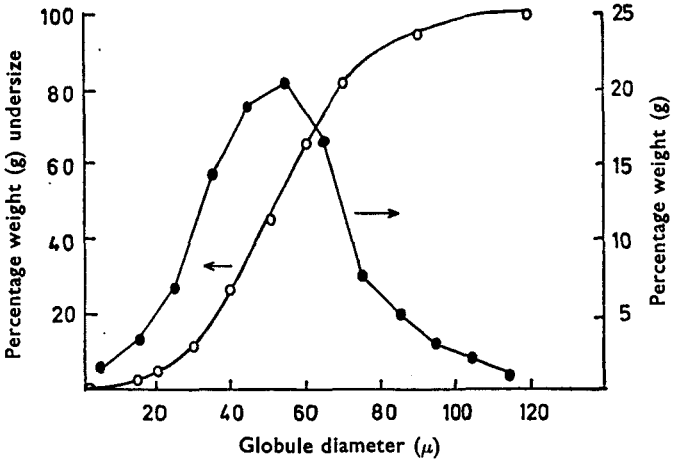

FIG. 4. Cumulative weight undersize curve (-○-) and weight distribution curve (-●-) for an emulsion of liquid paraffin in water stabilized by cetomacrogol 1000.

MICROSCOPIC MEASUREMENT OF GLOBULE SIZE

Size analysis by microscopy has been used for many years and while it is laborious, the results are often among the more satisfactory. It was therefore decided to compare the results obtained by the dielectric method with weight distribution curves obtained by microscopic measurement.

A sample of each emulsion was placed in a haemocytometer and photomicrographs of randomly chosen fields were taken concurrently with the determination of creaming rates. The magnification of all finished photographs was the same and the diameters of all globules were measured to 0·5 μ. In order to minimize the error which often occurs in the calculation of weight distribution curves from microscopic measurements (i.e. due to the accentuated effect of larger globules), at least 2000 globules were recorded for each emulsion.

Results and discussion

Six emulsions of different globule size distribution were prepared and the droplet size distributions obtained as described. The size distributions, expressed by weight, are shown in Fig. 5 along with the distributions obtained by microscopy. The agreement between the results from these two methods is excellent, showing that the dielectric method offers a simple and accurate alternative to microscopy for the droplet size grading of emulsions.

The systems used were coarser than many commercially produced emulsions. Coarse emulsions were used to avoid the complicating effects of Brownian motion and diffusion. Coarse emulsions also shortened the experimental time required to establish the correlation between the results obtained by dielectric constant measurement and those obtained by microscopy. With finer emulsions, much longer times would have been

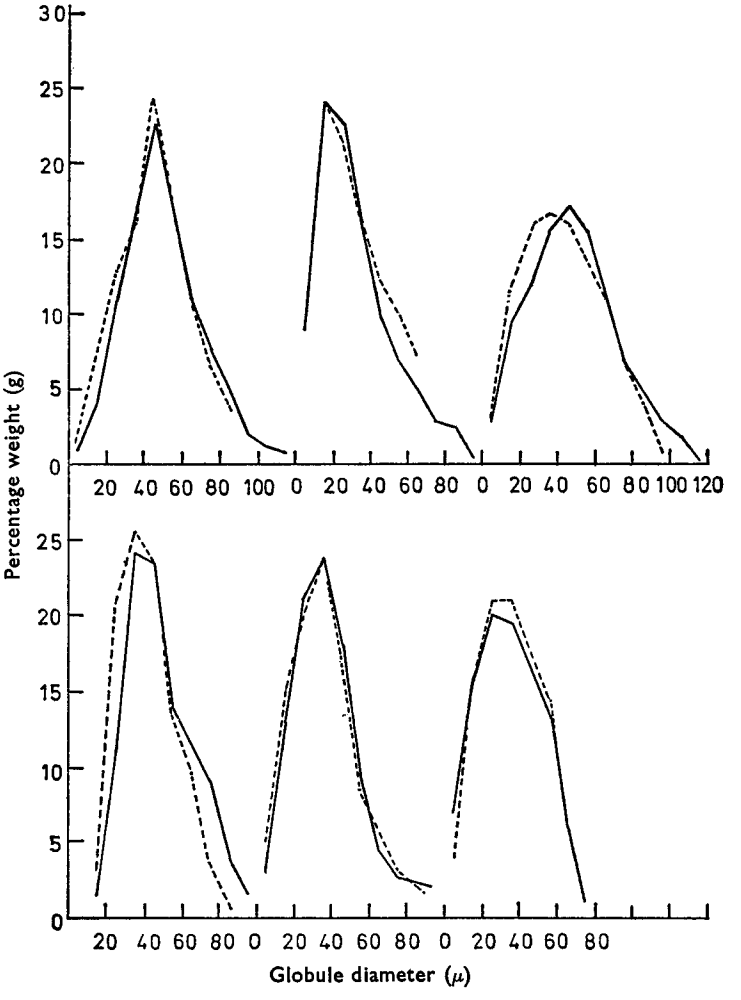

FIG. 5. Weight distribution curves for six different liquid paraffin-in-water emulsions. — Results by dielectric method. – – – Results by microscopy.

required to complete the experiments unless the time had been shortened by centrifugation.

One limitation of the method is that it is applicable only to emulsions of low electrical conductivity (Kaye & Seager, 1965).

The apparatus described is the subject of United Kingdom Patents Application No. 4885/64.

References

Blaedel, W. J. & Petitjean, D. L. (1956). *Physical Methods in Chemical Analysis*, editor, Berl, W. G. Vol. III, p. 107 *et seq.* London: Academic Press.

British Standard 3406: (1963). *Methods for the Determination of Particle Size in Powders.* Part 2. Liquid sedimentation methods.

Bruggeman, D. A. J. (1935). *Annls Phys.* **24**, 636–679.
Fradkina, E. M. (1950). *J. exp. theor. Phys.*, **20**, 1011.
Fradkina, E. M. & Khmunin, S. F. (1956). *Kolloid. Zh.*, **18**, 601–605.
Hanai, T., Koizumi, N. & Gotoh, R. (1962). *Bull. Inst. chem. Res. Kyoto Univ.*, **40**, 240–271.
Heymann, E. (1934). *Kolloidzeitschrift*, **66**, 229–235; 258–264.
Kaye, R. C. & Seager, H. (1965). *J. Pharm. Pharmac.*, **17**, *Suppl.*, 92S–97S.
Kaye, R. C. & Seager, H. (1966). *Inst. Pract.*, **20**, 733–738.
Khmunin, S. F. (1959). *Kolloid. Zh.*, **21**, 731–738.
Kruyt, H. R. (1952). *Colloid Sci.*, Vol. I. Amsterdam: Elsevier.
Kubo, K. & Nakamura, S. (1953). *Bull. chem. Soc. Japan*, **26**, 318–322.
Lichtenecker, K. (1926). *Phys. Z.*, **27**, 115–158.
Lorenz, L. & Lorentz, H. A. (1880). *Wied. Ann.*, **9**, 641; **11**, 70.
Naiki, T., Fujita, K. & Matsumura, S. (1959). *Mem. Fac. Ind. Arts Kyoto Tech. Univ. Sci. Technol.*, **8**, 1.
Orr, C. & Dallavalle, J. M. (1960). *Fine Particle Measurement.* New York: Macmillan.
Piekara, A. (1929). *Kolloidzeitschrift.*, **49**, 97–102.
Piekara, A. (1930). *Phys. Z.*, **31**, 579–584.
Piekara, A. (1932). *Kolloidzeitschrift.*, **58**, 283–285.
Rayleigh, J. W. (1892). *Phil. Mag.*, **34**, 481.
Reynolds, J. A. & Hough, J. M. (1957). *Proc. phys. Soc.*, **70***B*, 769–777.
Rose, H. E. (1958), *The Measurement of Particle Size in very fine Powders.* London: Constable.
Seager, H., Ph.D. thesis, 1966, University of Leeds.
Sherrick, H., Dawe, G. A., Karr, R. & Ewen, E. F. (1954). *Manual of Chemical Oscillometry.* Chicago: E. H. Sargent and Co.
Smyth, C. P. (1955). *Dielectric Behavior and Structure*, 1st edn. New York: McGraw Hill.
Wagner, K. W. (1914). *Arch. Elektrotech.*, **2**, 371.
Wiener, O. (1912). *Abh. sächs. Akad. Wiss.*, **32**, 509.