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A new method for the determination of emulsion stability by dielectric constant measurement: a preliminary report

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The creaming of emulsions of liquid paraffin in water stabilised by cetomacrogol 1000 has been studied in a specially designed capacitance cell. Before visual separation of the emulsion is detectable, changes in emulsion composition in the upper part of the cell result in a measurable decrease of dielectric constant. Differences in the creaming rates of a number of emulsions are easily detected and the rate of change of dielectric constant with time is dependent on globule size.

EMULSIONS are thermodynamically unstable systems which reach stability only when demulsification has occurred. The fundamental measurement of the instability therefore is the rate at which the globules of the emulsion coalesce. Creaming, or phase separation without coalescence, is quite a different phenomenon from demulsification but one that is often used as an indication of instability because the resulting closer association of the globules greatly facilitates their coalescence.

Creaming is difficult to detect visually in the early stages (except in very unstable emulsions) and there is no simple and rapid method for its quantitative determination. Andreasen's method (Andreasen, 1928) is feasible but tedious and methods which depend on changes in optical density, for example photoelectric sedimentometry, are not applicable because pharmaceutical emulsions are too opaque.

Since water has a high, and oil a low, dielectric constant the ascent of oil globules into the upper layers of the emulsion, and their replacement in the lower layers by the aqueous phase, should cause dielectric changes in these two regions of the emulsion. Such changes have been investigated using a specially designed capacitance cell.

Experimental

APPARATUS FOR THE MEASUREMENT OF DIELECTRIC CONSTANT

The dielectric constants of the emulsions were measured by the heterodyne beat method. In agreement with theoretical considerations [see equation (1) below], composition changes are more readily detected in the upper regions of the emulsion and hence a capacitance cell of the type shown in Fig. 1 was used. The cell responds to changes in dielectric because its capacitance is related to the dielectric constant by the following equation (Blaedel & Petitjean, 1956):

$$C = \frac{[(2\pi f)^2 C_0\epsilon(C_0\epsilon + C_g) + K^2]C_g}{(2\pi f)^2(C_0\epsilon + C_g)^2 + K^2} \quad .. \quad .. \quad .. \quad (1)$$

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where C = capacitance of cell when filled with emulsion
C_0 = capacitance due to air in the empty cell
C_g = capacitance due to the glass walls of the cell
ϵ = dielectric constant of emulsion
K = conductance of emulsion
f = frequency of electrical field.

The equation shows that the cell capacitance is sensitive to dielectric changes only in emulsions of low conductivity. In highly conducting emulsions such as those prepared with ionic surfactants, the terms $(2\pi f)^2 C_0\epsilon(C_0\epsilon + C_g)$ and $(2\pi f)^2(C_0\epsilon + C_g)^2$ may be neglected in comparison with K^2 when the equation reduces to

$$C = C_g \quad .. \quad .. \quad .. \quad .. \quad (2)$$

The cell capacitance is now independent of the dielectric constant of the emulsion and is determined only by the capacitance due to its glass walls. Thus the measurement of emulsion creaming by the dielectric method is limited to those emulsions of low conductivity prepared with non-ionic surfactants.

The cell (Fig. 1) consists of a glass vessel (1) having two concentric walls (2) and (3) defining an annular space (4) between them. The vessel is filled with emulsion through an opening (5) provided near one end of the vessel. The capacitor plates consist of two conducting layers (6) and (7) formed by the deposition of silver on the surface of the glass. An electrical connection to the inner plate is made by the threaded terminal

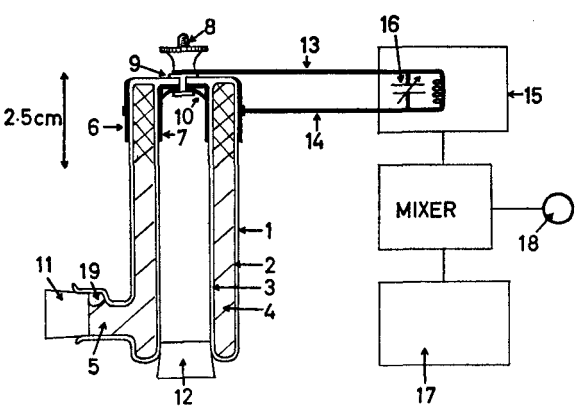

FIG. 1. Capacitance cell and block diagram of heterodyne beat circuit. For explanation see text.

(8) inserted through the end of the glass wall of the vessel. The terminal is secured by means of a nut (9), fibre washers being inserted between the metal and glass surfaces to prevent cracking of the glass. The terminal can be made more secure by using a suitable bonding compound. Electrical connection from the terminal to the inner silver coating is provided by means of a thin springy copper washer (10) inserted under

the head of the terminal. Electrical contact with the outer capacitor plates is made by wrapping three turns of wire around the silver coating and soldering the wire to it.

Opening (5) is closed with a rubber stopper (11). The central space within the inner wall is also closed with a rubber stopper (12) to prevent the entry of dust and fumes which might impair the electrical contact to the inner conducting plate.

The two electrical leads (13) and (14) of the cell are taken to a variable frequency valve oscillator (15). The cell acts as a capacitance in the frequency-determining circuit of the oscillator (15). This circuit is tuned by means of a precision variable condenser (16). The output from the oscillator circuit is mixed with the output from a fixed frequency oscillator (17) (crystal controlled at 1·79 M cycles/sec) and the resultant beat frequency is monitored aurally on a loud speaker and visually on an indicator tube of the "magic eye" type (18).

In operation, the cell is filled with the emulsion under test and inverted. Initially the variable condenser in parallel with the cell is adjusted so that the frequency of the variable frequency oscillator is equal to that of the crystal reference oscillator. This is indicated by the absence of a note from the loudspeaker and of a sign on the indicator tube. As the emulsion gradually separates and oil globules float to the top, the electrical capacitance of the cell decreases causing a frequency shift in the output of the variable frequency oscillator and an audible note of increasing frequency from the loudspeaker. The amount by which the variable condenser must be adjusted to return the frequency to that of the reference crystal oscillator is a direct measure of the capacitance change brought about by creaming.

METHOD OF MEASURING CREAMING RATES

Emulsions containing 50% w/w of liquid paraffin B.P. in a 3% w/w aqueous solution of cetomacrogol 1000 B.P.C. were prepared in an Ato-mix M.S.E. Emulsifier. Details of the emulsions used are given in Table 1.

TABLE 1. DETAILS OF EMULSIONS USED

Emulsion	1	2	3	4	5	6
Homogenisation time min.	10	3	2	1·5	1	0·5
Average of log of globule diameter	0·46±0·01	0·49±0·01	0·50±0·01	0·56±0·01	0·60±0·01	0·65±0·01
Standard deviation of log of globule diameter	0·19	0·19	0·21	0·22	0·27	0·29
Number of oil globules measured for statistical analysis	501	582	509	509	546	476
Observed amounts of creaming (i.e. depth of translucent liquid at bottom of cell)	None after 7·24 hr	1·5 mm After 8·06 hr	2 mm After 8·24 hr	—	3·5 mm After 6·12 hr (Creaming line was diffuse)	4 mm After 2·21 hr (Creaming line was very diffuse)

50 ml of the emulsion was withdrawn from the emulsifier, gentle agitation of the latter being maintained to ensure uniform distribution of the globules. Air was removed from the sample by gentle rotation for 10 min in a flask under vacuum. Gentle shaking was continued as the emulsion was then warmed to 25°.

The cell, maintained at 25° in a small Perspex air chamber, was disconnected from the oscillator and filled with part of the emulsion. The rubber stopper was inserted and the cell was inverted so that the remaining air bubble was trapped in the small space provided (19) (Fig. 1). The gap between the capacitor plates was thus entirely filled with emulsion free from air bubbles.

A clock was immediately started, the cell was quickly reconnected to the oscillator and the thermostat box was replaced. The frequency of the variable oscillator was returned at suitable time intervals to that of the reference oscillator. The readings of the variable condenser were converted to dielectric constant units, the value at zero time being estimated by extrapolation.

MEASUREMENT OF GLOBULE SIZE

The remainder of the emulsion sample was used for the determination of globule size. One drop was diluted with a few drops of water and a little placed on a haemocytometer slide. Photomicrographs of randomly chosen fields were taken during the determination of creaming rate. The magnification of all finished photographs was the same and the diameters of all globules in each photomicrograph were measured to $\pm 0{\cdot}1\ \mu$. A total of about 500 globules was recorded for each emulsion.

Histograms in which the frequency of globule size was plotted against the logarithm of the globule diameters, showed the globule size distributions to be logarithmically normal. The means and standard deviations of the logarithms of the globule diameters were therefore used to characterise the emulsions.

Results and discussion

Many of the factors affecting the dielectric constant of emulsions have been discussed previously (e.g. Piekara, 1929, 1932; Heymann, 1934; Kruyt, 1952; Smyth, 1955; Hanai, Koizumi & Gotoh, 1962). It is apparent that the dielectric constants of liquid paraffin in water emulsions prepared with non-ionic surfactants, and measured in the way described, depend chiefly upon the relative concentrations of liquid paraffin and water between the capacitor plates. An increase in the liquid paraffin concentration results in a decrease of dielectric constant. In the present work therefore, the decrease in the dielectric constant of emulsions with time (see Fig. 2) is due to an increase in the concentration of liquid paraffin between the capacitor plates.

Comparison of Table 1 with Fig. 2 shows that whereas the dielectric change is quite marked, visual inspection of the emulsion in the lower part of the cell is a relatively insensitive method of detecting phase

separation. It has been found that stable emulsions in which no visible creaming can be detected for several days will provide a readily measurable change of dielectric constant after only a few minutes or at most a few hours. Detection of phase separation by the dielectric method is therefore rapid and precise.

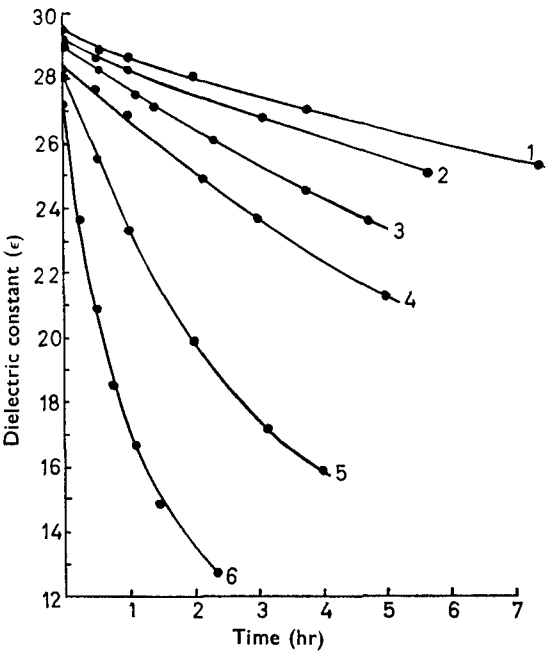

FIG. 2. Relation between dielectric constant and time for emulsions.

An important factor governing the rate of emulsion creaming is the globule size. Comparison of the dielectric constant changes for emulsions 1 and 5 in Fig. 2 and the photomicrographs of these same emulsions (Fig. 3) illustrates the greater creaming rate of the coarser emulsion. A quantitative relation between globule size and creaming rate of the systems studied is given in Fig. 4. The logarithm of the rate of change of dielectric constant $d\epsilon/dt$, 30 min after the commencement of the experiment, has been plotted against the mean of the logarithms of the diameters and also against the standard deviations of the logarithms of the diameters. This shows that the rate of change of dielectric constant with time is markedly dependent on globule size, small changes of which lead to large changes in the gradient of the dielectric curve. Dielectric measurements therefore may provide a simple method for determining differences in the globule size of two emulsions.

The initial readings of dielectric constant for emulsions of a given concentration vary with globule size. This effect is much greater than can be explained by the $\pm 0{\cdot}1\%$ experimental error in dielectric constant measurement and the phenomenon is not yet fully understood.

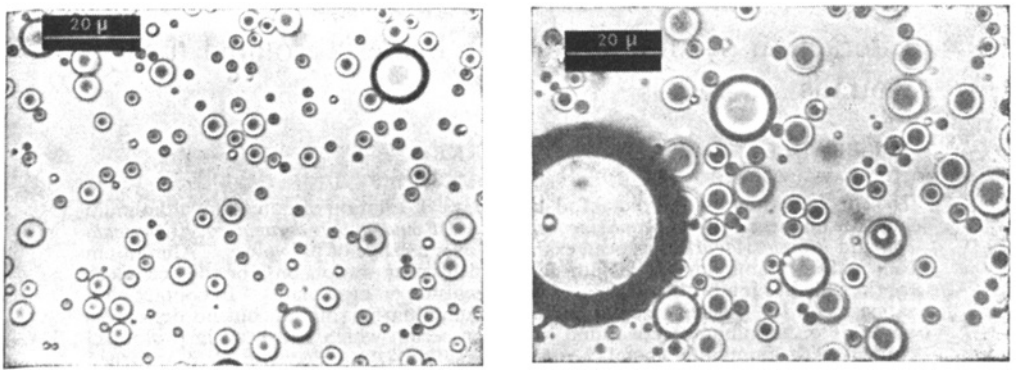

FIG. 3. Photomicrographs of emulsions 1 and 5.

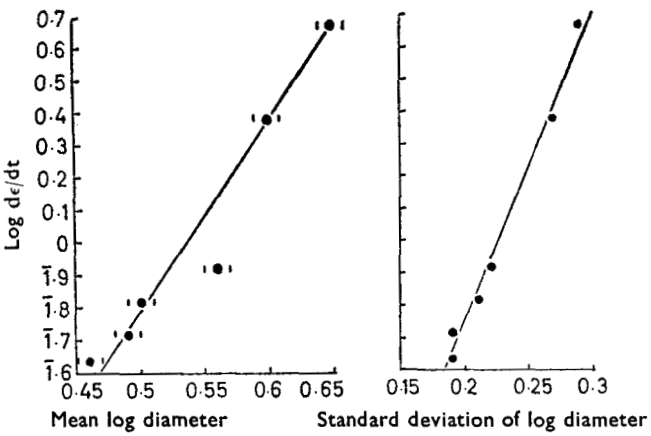

FIG. 4. Relation between log rate of change of dielectric constant dε/dt and mean of log diameter and standard deviation of log diameter.

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

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