THE RELATIONSHIP BETWEEN ELECTRICAL RESISTANCE AND DISPERSED PHASE CONCENTRATION IN OIL IN WATER EMULSIONS

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The electrical resistance of a series of oil-in-water emulsions has been measured, and used to test the validity of four equations relating resistance with the concentration of dispersed phase. A modification of one of the equations was found to give the best relationship.

ALTHOUGH the electrical conductivity (or its reciprocal, the resistance) of emulsions has been used qualitatively as a means of determining emulsion type since about 1920 (Clayton, 1918, Bhatnagar, 1920), little work has been published on the factors which influence the quantitative results.

Maxwell (1904) calculated that when a medium of specific resistance (R') contains a volume fraction (ϕ) of spheres of specific resistance (R''), then the specific resistance of the complete system (R) can be calculated from the equation:

$$R = \frac{2R'' + R' + \phi\,(R'' - R')\,R'}{2R'' + R' - 2\phi\,(R'' - R')} \qquad \qquad \qquad \qquad \text{(i)}$$

Oils have a much greater specific resistance than most aqueous solutions so that for oil-in-water emulsions R'' approaches infinity, and equation (i) can be simplified to:

$$\frac{R'}{R} = \frac{2\,(1 - \phi)}{2 + \phi} \qquad \qquad \qquad \qquad \qquad \qquad \qquad \text{(ii)}$$

Maxwell placed two limitations on his equation, (a) the spheres must not be too close together, and (b) R'' must not be considerably greater than R'. These limitations imply that equation (ii) is not valid for oil-in-water emulsions, particularly those containing large amounts of oil. However, Fricke and Morse (1925), who separated cream from milk, and determined the specific resistance of the cream, the skimmed milk, and mixtures of the two, obtained agreement within ± 0.5 per cent for emulsions containing a volume fraction of oil of up to 0.62, when using this equation.

More recently Mashovets (1951) studied the conductance of electrolyte solutions containing glass spheres, and found that for any arrangement, and all volume concentrations up to closest packing (0.7405), the results agreed with the empirical equation:

$$\frac{R'}{R} = 1 - 1.78\phi + \phi^2 \qquad \qquad \qquad \qquad \qquad \qquad \text{(iii)}$$

Equations (ii) and (iii) apply to systems containing spheres of uniform size. Bruggeman (1935) derived the equation:

$$1 - \phi = \frac{R'/R - R/R''}{(R'/R)^{\frac{1}{3}}\,(1 - R/R'')} \qquad \qquad \qquad \qquad \qquad \text{(iv)}$$

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for systems containing spheres of an infinite variety of diameters. When the disperse phase is non-conducting, this reduces to:

$$\frac{R'}{R} = \sqrt{(1 - \phi)^3} \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad \text{(v)}$$

De la Rue and Tobias (1959) applied this equation to dispersions of glass spheres in an aqueous solution of zinc bromide, and found that better agreement was obtained with dispersions consisting of a variety of sizes of spheres, than with uniform dispersions. Meredith and Tobias (1961) modified Bruggeman's equation to allow for equal volumes of spheres of two different diameters. For a non-conducting disperse phase this reduced to:

$$\frac{R'}{R} = \frac{8 (2 - \phi) (1 - \phi)}{(4 + \phi) (4 - \phi)} \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad \text{(vi)}$$

Meredith and Tobias recommended this equation for systems containing a volume fraction of over 0·2 of disperse phase, and equation (ii) for weaker emulsions.

The literature thus contains four equations which appear to be applicable to the electrical resistances of oil-in-water emulsions, and three of these have been derived from theoretical considerations. Three of the four equations have been utilised in studies of ideal systems. The purpose of the present work was to determine which of these equations best fitted the data obtained from a number of emulsions of possible pharmaceutical interest.

EXPERIMENTAL

Materials. Analar potassium chloride was used to prepare the 0·1 Demal solution used in the determination of cell constants. The polyvinyl alcohol was a commercial sample, Gelvatol 20–30 (Shawinigan Ltd.). All the other materials used in this preliminary investigation were of B.P. quality.

Apparatus. The resistances were measured using a Cambridge Conductivity Bridge, in conjunction with Mullard dip cells. Platinum black was removed from the electrodes because it would be difficult to clean them adequately after immersion in the emulsions. The cells were cleaned by rinsing with tap, and then purified water, before immersion in acetone. Cell constants were determined periodically and showed that the cleaning process was effective. The cell was always air dried before immersion in the emulsion to avoid dilution effects and to ensure good contact between the emulsion and the electrodes. All weighings and measurements were made at 25 ± 0·1°.

Methods

(a) *Preparation of emulsions.* In order that R' and ϕ could be most accurately ascertained the following procedure was adopted to prepare the emulsions. A solution of the emulgent was prepared in purified water and, if necessary, strained to remove foreign matter. The weight per ml.

(at 25°) and the specific resistance of this solution were determined. The weight per ml. of the oil was similarly found. Known weights of the oil and continuous phase were triturated together in a mortar and pestle. With emulsions stabilised either by acacia or polyvinyl alcohol this treatment produced emulsions of suitable stability, but emulsions containing either cetrimide or sodium lauryl sulphate were coarse, and were passed through a hand-operated homogeniser to obtain stable preparations. In each instance, the orifice was set at the same distance. The completed emulsion was usually divided into two portions, each of which was transferred to a dry tube, capped, and placed in the water bath. The volumes of oil and aqueous phase were calculated, and the volume of oil divided by the total volume of the emulsion to obtain ϕ.

(b) *Measurement of resistance.* The dry dip cell was placed in the emulsion, care being taken to avoid the introduction of air bubbles, and the resistance measured at about 5 min. intervals. The resistance usually decreased gradually, becoming constant after about 20 min. This decrease was attributed to temperature changes brought about by the introduction of the cell. Duplicate measurements were made on each emulsion. Emulsions which showed a tendency to cream were stirred gently with the cell between measurements. The ratio R'/R found experimentally for each emulsion was compared with the values obtained by solving the various equations using the known values of ϕ.

Systems Studied

Unless otherwise stated olive oil was used as dispersed phase.

(i) *Acacia emulsions.* A total of 57 emulsions were made using 40 per cent w/v acacia solution as continuous phase. Oil contents varied between 0·09 and 0·60. Stronger emulsions could not be prepared. The more dilute systems ($\phi < 0.2$) tended to cream slowly.

Similar series of emulsions containing either castor oil or liquid paraffin dispersed in 40 per cent w/v acacia solution were prepared and measured, to determine whether the results were affected by the oil used. A series of emulsions containing olive oil dispersed in 30 per cent acacia solution, and another in 50 per cent acacia solution were also prepared.

(ii) *Polyvinyl alcohol emulsions.* Polyvinyl alcohol was chosen as an emulgent because it is non-ionic and forms an aqueous solution of fairly high resistance and also because of its reported protective colloid properties (Capitani and Pirrone, 1956) it was expected to behave in a similar way to acacia. A 10 per cent solution of polyvinyl alcohol in purified water was prepared and used as continuous phase in the preparation of olive oil emulsions. Although the emulsions were finely dispersed, they creamed visibly over several hours and were stirred gently at intervals between measurements of the resistances.

(iii) *Ionic emulgents.* Cetrimide and sodium lauryl sulphate were examined. In both cases a 5 per cent solution was used as continuous phase. All these emulsions tended to cream, and were stirred gently between measurements.

The results obtained with sodium lauryl sulphate are given in Table I and are typical of the whole series.

TABLE I

CALCULATED VALUES OF R'/R FOR SODIUM LAURYL SULPHATE STABILISED EMULSIONS OF OLIVE OIL

Equation	(ii)		(iii)		(v)		(vii)	
ϕ	R'/R Experimental	R'/R Calculated	Percentage error	R'/R Calculated	Percentage error	R'/R Calculated	Percentage error	R'/R Calculated	Percentage error
0·0959	0·8425	0·8627	+2·4	0·8385	−0·5	0·8597	+2·0	0·8521	+1·1
0·1395	0·7761	0·8044	+3·5	0·7712	−0·6	0·7982	+2·8	0·7885	+1·6
0·1439	0·7663	0·7986	+4·1	0·7646	−0·2	0·7921	+3·3	0·7822	+2·8
0·2053	0·6894	0·7207	+4·4	0·6767	−1·9	0·7084	+2·7	0·6968	+1·1
0·2213	0·6552	0·7011	+6·6	0·6551	−0·0	0·6872	+4·7	0·6753	+3·0
0·2274	0·6699	0·6937	+3·4	0·6469	−3·6	0·6791	+1·4	0·6672	−0·4
0·2987	0·5513	0·6102	+9·7	0·5575	+1·1	0·5873	+6·1	0·5756	+4·2
0·3078	0·5403	0·5999	+9·9	0·5469	+1·2	0·5759	+6·2	0·5643	+4·3
0·3344	0·5097	0·5703	+10·6	0·5166	+1·3	0·5430	+6·1	0·5321	+4·2
0·3813	0·4411	0·5196	+15·1	0·4667	+5·5	0·4867	+9·4	0·4771	+7·5
0·3900	0·4521	0·5105	+11·4	0·4579	+1·3	0·4764	+5·1	0·4673	+3·3
0·3994	0·4411	0·5006	+11·9	0·4486	+1·7	0·4655	+5·2	0·4567	+3·4
0·4448	0·3671	0·4542	+19·2	0·4061	+9·6	0·4137	+11·3	0·4071	+9·8
0·4816	0·3482	0·4178	+16·7	0·3747	+7·1	0·3732	+6·7	0·3688	+5·6
0·5091	0·3188	0·3913	+18·5	0·3530	+9·7	0·3439	+7·3	0·3410	+6·5
0·5410	0·3014	0·3613	+16·6	0·3297	+8·6	0·3110	+3·1	0·3100	+2·8
0·5972	0·2488	0·3102	+19·8	0·2936	+15·3	0·2556	+2·0	0·2588	+3·9
0·6696	0·1986	0·2475	+19·8	0·2565	+22·6	0·1899	−4·6	0·1985	0·0
0·6716	0·1907	0·2458	+22·4	0·2556	+25·4	0·1882	−1·3	0·1967	+3·1
0·7476	0·1411	0·1837	+23·2	0·2282	+38·2	0·1268	−11·3	0·1395	−1·2
0·7765	0·1173	0·1610	+27·1	0·2208	+46·9	0·1057	−11·0	0·1189	+1·3

DISCUSSION

Since the pattern of the results varied only slightly on changing the emulgent or the disperse phase, all the systems are considered together.

The results obtained with the various equations are analysed in Table II, which shows that only 30 per cent of the 143 values of R'/R are within

TABLE II

ANALYSIS OF RESULTS

ϕ	Number of results	Number of results within 95 to 105 per cent of calculated value			
		Equation (ii)	Equation (iii)	Equation (v)	Equation (vii)
0·0000 to 0·1999	22	22	21	22	22
0·2000 to 0·2999	26	14	21	20	25
0·3000 to 0·3999	28	6	24	22	27
0·4000 to 0·4999	32	1	26	27	26
0·5000 to 0·5999	23	0	16	13	12
0·6000 to 0·8100	12	0	0	3	9
	143	43	108	107	121

±5·0 per cent of the results calculated from equation (ii). Best agreement occurred when ϕ was less than 0·3, and at all concentrations the results tended to be low. As the concentration of oil phase increased, the differences between true and calculated results increased also.

Since the experimental work reported in this paper was completed, Hanai (1960) published results on the conductivities of emulsions stabilised

with non-ionic emulgents. Results were compared with the theoretical values obtained using equations (ii) and (v), and showed that with equation (ii) poor agreement was obtained when ϕ exceeded 0·3.

Equation (v) fits the results for emulsions in which ϕ is less than 0·6, but for more concentrated emulsions the agreement is less impressive. Thus, Table II shows that although 79 per cent of those emulsions below $\phi = 0·6$ fell within $\pm5·0$ per cent of the calculated results, only 25 per cent of those above $\phi = 0·6$ fell within these limits. This agrees with Hanai's results in which 100 per cent fell within $\pm5·0$ per cent when ϕ was less than 0·6, and 17 per cent when ϕ exceeded 0·6. Equation (vi) would not be expected to be applicable since it applies to systems containing two globule sizes only. This was actually the case, since although it gave better agreement than equation (ii), it was inferior to equations (iii) and (v).

Although it has been stated that the value of equation (iii) is questionable because it was obtained empirically from a few results from an ideal system (De la Rue, 1959), it was used in the present work because it had not previously been applied to emulsions. The equation has been found to fit the experimental results reasonably well, 76 per cent of the results being within $\pm5·0$ per cent. Poor agreement was obtained, however, when ϕ was greater than 0·6. The emulgent used seemed to affect the results, for example in acacia emulsions the equation fitted the results when ϕ was less than 0·6 (88 per cent of the values fell within the limits), but for cetrimide and sodium lauryl sulphate emulsions the results only fitted the equation up to values of $\phi = 0·5$ and 0·4 respectively.

Equation (iii) could be the first three terms of a power series. The best coefficients for ϕ up to the fourth power to fit the results in each series were calculated using a Stantec Zebra electronic computer, but a better fit could not be obtained. (The whole 143 results could not be examined together since the programme could not cater for more than 100 terms.) Constants calculated by the computer for a quadratic equation were as follows:

Acacia	$R'/R = 1·00 - 1·66\phi + 0·75\phi^2$
Polyvinyl alcohol	$= 0·97 - 1·32\phi + 0·24\phi^2$
Cetrimide	$= 0·98 - 1·53\phi + 0·55\phi^2$
Sodium lauryl sulphate ..	$= 1·00 - 1·74\phi + 0·78\phi^2$

These gave good results within their own series but, as is evident from the considerable variation in the coefficients from series to series, none was any better than equation (iii) when applied to all 143 emulsions. An equation using the weighted means of each coefficient was no more successful; this was due to the fact that the system providing the greatest contribution to the mean coefficients (90 acacia emulsions) was not represented by any emulsions in which ϕ exceeded 0·62, the concentration at which equation (iii) breaks down.

The equation:

$$R'/R = 1·0 - 1·60\phi + 0·6\phi^2 \quad .. \quad .. \quad .. \quad .. \quad .. \quad \text{(vii)}$$

was derived by trial and error, and fitted our results better than any equations considered so far. Thus, Table II shows that 121 of the 143 results were within ± 5.0 per cent: these included 9 of the 12 results for emulsions in which ϕ was greater than 0.6. The results quoted by Hanai also fitted equation (vii) more favourably than the other equations. The fact that this equation fits the results better than equation (iii) does not suggest that the coefficients derived by Mashovets (1951) are incorrect, since his equation was derived from the study of an ideal system in which the interface was much simpler than that between an oil and an aqueous solution of a surface-active agent.

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