

Review Article

The flow properties of emulsions*

P. SHERMAN, M.Sc., F.R.I.C.

EMULSIFICATION is essentially a process for diluting oils so as to facilitate their use in several ways. For example, in the field of pharmacy a medicinal oil may not only be more acceptable orally when administered as an oil-in-water (o/w) emulsion but it may also be absorbed more readily. Similarly, the application of an oil to the skin in emulsion form promotes easier spreading and absorption. The performance of such products depends very much on their flow properties. Unfortunately, most emulsions, apart from very dilute ones, do not exhibit simple Newtonian flow, that is, their viscosity is not independent of the applied rate of shear, so that the interpretation of flow data is often difficult.

The flow of Newtonian liquids can best be illustrated by the following model. Imagine the space between two parallel planes separated by a distance x to be filled with liquid. If a force F is applied to the upper plane A (Fig. 1), while the lower plane B remains stationary, A will move at a constant velocity u . All the liquid between the two planes does not move at the same speed. Instead the rate varies with the distance from A, being a maximum (u) in the layer adjacent to A and zero in the layer adjacent to B. The rate of change in fluid velocity is given by du/dx . This represents the rate of shear (v) of the liquid, whilst the force per unit area applied to A represents the shearing stress (S). The viscosity of the liquid (η) is given by the ratio S/v , and since this remains constant, η can be determined by a single measurement irrespective of the magnitude of S or v .

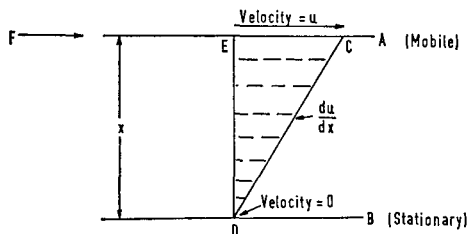


FIG. 1. Model for Newtonian flow.

Many liquids, emulsions, or suspensions which do not show this behaviour fall within the category exhibiting non-Newtonian behaviour (Fig. 2). This category includes both plastic and pseudoplastic flow. In pseudoplastic flow viscosity decreases curvilinearly with increasing rate of shear from the initial application of a shearing stress, whilst in plastic flow a minimum shearing stress (S_0) is required before flow begins.

* Based on three lectures given at the Post-Graduate School for Pharmacists, School of Pharmacy, University of London, April, 1963.

T. Walls & Sons (Ice Cream) Ltd., Acton, London, W.3.

Above S_0 viscosity decreases curvilinearly with increasing rate of shear. Ultimately, at infinitely high shear, the viscosity of either system does not alter with further increase in the shear rate.

Two other shear stress values are often quoted when reporting plastic flow data. These are the extrapolated yield value, the intercept on the shear stress axis obtained by extrapolation from the linear part of the curve, and the upper yield value, which refers to the applied shearing stress at which linear flow is first established. In dilatant flow the viscosity increases as the rate of shear increases, that is, the flow characteristics are the reverse to those encountered in pseudoplastic flow.

Since the viscosities of pseudoplastic, plastic, and dilatant emulsions vary with the rate of shear, measurements made at a single rate of shear have little significance, particularly when comparing the flow behaviour of two different emulsions. A reliable analysis involves detailed measurements over a wide range of shear rates.

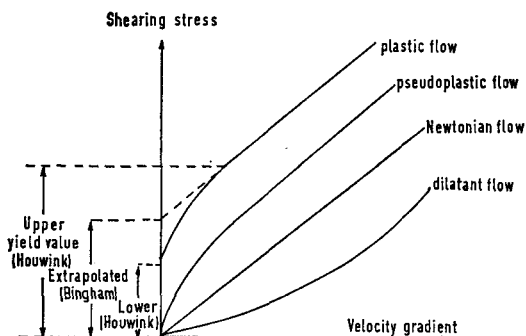


FIG. 2. Examples of flow behaviour.

Measurement of viscosity

TYPES OF VISCOMETER

Many commercial instruments are available for measuring viscosity. The principal kinds, and some typical examples of each type are enumerated in Table 1. Not all of these viscometers are designed to study the variation of viscosity with rate of shear. This applies particularly to the falling sphere and ultrasonic viscometers. Of the other three types, the cone-plate viscometer is the only one which provides uniform shearing conditions throughout the sample. In the capillary viscometer the rate of shear varies from zero at the capillary axis to a maximum at the wall surface. The measurement of viscosity in a coaxial cylinder instrument usually involves rotation of one of the cylinders, leading to a torque being transmitted through the test sample to the other cylinder. In this example the rate of shear varies from a maximum value at the rotating cylinder surface to a minimum at the surface of the other cylinder. By a suitable design, so that the thickness of the sample layer is small, the rate of shear gradient can be minimised.

THE FLOW PROPERTIES OF EMULSIONS

TABLE 1. PRINCIPAL TYPES OF VISCOMETER FOR USE WITH EMULSIONS

	Application	
	Newtonian flow	Non-Newtonian flow
A. <i>Capillary</i> —		
U-tube; single or multi-bulb	X	X (multi-bulb only)
Variable pressure	X	X
Techné vibrating piston	X	X
B. <i>Coaxial Cylinder</i> —		
Ferranti Portable	X	X
Epprecht Rheomat	X	X
B.F.M.R.A. (Gaydon & Co.)	X	X
Rotovisko (Gebrüder Haake)	X	X
C. <i>Cone-plate</i> —		
Ferranti-Shirley	X	X
Rotovisko (Gebrüder Haake)	X	X
Weissenberg Rheogoniometer	X	X
D. <i>Falling sphere</i> —		
Höppler	X	—
E. <i>Ultrasonic</i> —		
Bendix Ultra-Viscoson	X	—

The principal practical disadvantage of capillary instruments is their unsuitability for studying the effect of time of shear on viscosity at any given rate of shear, and hysteresis effects, since the sample in the capillary is changing all the time. On the other hand, when time effects are shown, instantaneous viscosity data are obtained more easily with this instrument than with the coaxial or cone-plate instruments, unless an automatic recording device is connected up to the latter. The capillary instrument does not give rise to end effects, the Weissenberg effect, temperature fluctuation due to heat development, and to the danger of sample structure being altered due to homogenisation when sheared. All these phenomena may arise when using a coaxial instrument and a further source of error may result from incorrect alignment of the cylinders. Possibly the main advantage of a capillary instrument over a coaxial instrument is that higher rates of shear can be achieved with the former, thus extending its application to a wider range of flow behaviour.

When interpreting viscosity data obtained with a capillary viscometer the following points should be borne in mind.

(i) As the test sample moves from the wide tube in which it is initially deposited into the much smaller diameter capillary, the sample is deformed around the shoulder of the wider tube. The correction which has to be applied for this “end effect” (or more correctly, the “entrance effect”) can be minimised if the capillary has suitable dimensions.

(ii) Entry of a dispersion, or an emulsion, into a capillary may be accompanied by axial migration of the disperse phase. This gives rise to concentration fluctuations across the capillary width, the principal concentration reduction occurring in the sample layers nearest the capillary wall.

(iii) Part of the applied pressure is used to impart kinetic energy to the sample when it enters the capillary. All the pressure is not used, therefore,

in shearing the sample. This "kinetic energy correction" is more important than (i).

(iv) The shearing stress (S_0) required at any point in a capillary to produce flow is given by

$$S_0 = PR/2L \quad \dots \quad (1)$$

where P is the applied pressure, R is the capillary radius at that point, and L is the capillary length. Near the capillary axis R is very small, so that P would need to be infinitely large to exceed S_0 . This is not possible under practical conditions. Consequently, near the axis there is always a thin layer of sample which moves through the capillary as a solid plug ("plug flow"). From this we may infer that the $S-v$ curve for capillary viscometer data never becomes absolutely linear at high rates of shear.

Newtonian viscosity data obtained with a falling sphere viscometer are interpreted on the basis of Stokes's law for a sphere falling through a liquid at a constant speed. If the sphere is relatively large in comparison to the diameter of the tube through which it falls a more complex equation has to be used (Ladenburg, 1907; Flowers, 1914; Faxen, 1922). Recently it has been shown that using very small nylon spheres several tests can be made on a single sample (Scott-Blair & Oosthuizen, 1960). By rotating the tube between tests unsheared material becomes available for further determinations.

The ultrasonic viscometer operates very simply. It consists essentially of a probe and an electronic computer. At the end of the probe is a thin alloy steel blade, which is excited by a short electrical impulse, so producing ultrasonic shear waves in the medium around the probe. The computer translates the energy requirement for this motion into viscosity. Whilst this method lends itself to automatic control of viscosity, its range of application is very limited at present. The single available impulse permits viscosity measurement at only one rate of shear, so that it cannot be used for non-Newtonian systems.

Table 2 (after McKennell, 1956) summarises the equations required to calculate rate of shear, shear stress, yield value, and viscosity from the data obtained using the main types of viscometers discussed in this section. In capillary instruments both shearing stress and rate of shear vary from zero at the axis to a maximum at the capillary wall. When determining non-Newtonian viscosity it is customary to base the calculation on the conditions prevailing at the capillary wall.

General interpretation of non-Newtonian viscosity

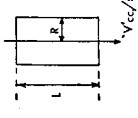
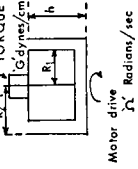
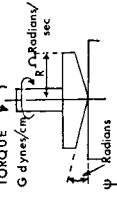
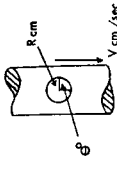
Many attempts have been made to define mathematically the shape of the $S-v$ curve for plastic flow. Bingham (1922) proposed an equation for an idealised system in which the $S-v$ relationship is linear overall provided the critical shearing stress at which flow begins (S_0) has been exceeded.

$$v = u(S - S_0) \quad \dots \quad (2)$$

where u is the mobility, or $1/\eta_\infty$.

THE FLOW PROPERTIES OF EMULSIONS

TABLE 2. EQUATIONS REQUIRED TO CALCULATE RATE OF SHEAR, SHEAR STRESS, YIELD VALUE AND VISCOSITY FROM DATA OBTAINED USING THE MAIN TYPES OF VISCOMETER DISCUSSED

Viscometer	Capillary	Coaxial cylinder	Cone-plate	Falling sphere
				
Newtonian Viscosity η	$\eta = \pi PR^4/8LV$	$\eta = \frac{G \left(\frac{1}{R_1^2} - \frac{1}{R_2^2} \right)}{4\pi h \Omega}$	$\eta = \frac{3G}{2\pi R^3 / \psi}$	$\eta = \left(\frac{2}{9} \frac{d_1 - d_2}{v} \right) \frac{g R^2}{\text{uncorrected}}$
Non-Newtonian viscosity η_{∞}	$\eta_{\infty} = \frac{\pi R^4 g \sigma}{8 L e} \left(\frac{dQ}{dP} + \frac{P}{4} \frac{d^2 Q}{dP^2} \right)$	$\eta_{\infty} = \frac{M}{4h\Omega} \left(\frac{1}{R_1^3} - \frac{1}{R_2^3} \right) - \frac{v}{\Omega} \ln \frac{R_2}{R_1}$		
Rate of shear v	$v_{\text{capillary wall}} = \frac{4Q}{\pi R^3}$ $v_{\text{axis}} = 0$	$v_{\text{max}} = \frac{2\Omega}{R_1^2} \left(\frac{1}{R_1^2} - \frac{1}{R_2^2} \right)$ $v_{\text{min}} = \frac{2\Omega}{R_2^2} \left(\frac{1}{R_1^2} - \frac{1}{R_2^2} \right)$	$v = \frac{\Omega}{\psi}$	$v_{\text{max}} = \frac{3V}{2R} (\theta = 90^\circ)$ $v_{\text{min}} = 0 (\theta = 0^\circ)$
Shear stress S	$\frac{PR}{2L}$	$\left(\frac{1}{R_1^2} - \frac{1}{R_2^2} \right) \frac{G}{4\pi h}$	$\frac{3G}{2\pi R^2}$	
Yield value f	$\frac{P_0 g \sigma R}{2L}$ $P_0 = P_v \sim \infty$	$\frac{S G_2}{\ln(R_2/R_1)}$	SG_2	

G_2 = extrapolated value of torque for $\Omega = 0$. σ = density of Hg. e = constant for converting flowmeter readings into c.c./sec efflux.

P. SHERMAN

Ostwald (1925), and de Waele (1925), independently modified Poisseuille's equation, and both arrived at the same result.

$$v = \frac{1}{\eta^*} S^n$$

or in more detailed form

$$V^n = \frac{\pi R^4 (P - a e^{-PR/2}}{8L\eta^*} \dots \dots \dots (3)$$

where n is a measure of the structure developed within the test material, having a value of 1 for a Newtonian fluid, 'a' is some form of yield value, and η^* is the viscosity. Several objections have been raised against eqn 3. In some systems η^* does not have a steady value; instead it fluctuates with variation in n, which may arise from change in S. Furthermore η^* does not have the correct dimensions for viscosity.

Herschel & Bulkley (1926), and Scott (1931), developed power equations resembling eqn 3.

$$v = u (S - a)^n \dots \dots \dots (4)$$

In general, power equations have no theoretical significance because they will fit any viscosity data provided the constants are suitably adjusted.

Krieger & Dougherty (1959) assumed that temporary pairing of particles occurred during flow, due to localised concentration fluctuations, and that the viscosity of such a system is related to S by

$$\frac{\eta_s - \eta_\infty}{\eta - \eta_\infty} = \left[1 + \left(\frac{S}{S_c} \right) \right]^{-1} \dots \dots (5)$$

where η_s , η_∞ , and η are the limiting viscosities at shear stress S, at infinite shear, and at zero shear respectively. S_c depends on particle size and temperature.

Particles actually form doublets, or triplets in the absence of shear due to inter-attraction forces, and statistical considerations indicate that such aggregates take the form of long chains. To deflocculate these aggregates S and v may be related by an equation of the form (Casson, 1959):

$$S^\ddagger = K_0 + K_1 v^\ddagger \dots \dots \dots (6)$$

where K_0 and K_1 are constants, their values depending on the properties of the solid and liquid phases respectively.

Williamson (1929) restricted his attention to pseudoplastic flow. He suggested a graphical procedure for calculating the total power required to achieve linear flow from the S—v curve.

$$Sv = S_p v + S_1 v \dots \dots \dots (7)$$

where $S_p = PR/2L$ (plastic resistance)

$S_1 = PR/2L$ (viscous flow)

The total power (Sv) is the sum of two independent contributions. The power required to overcome plastic resistance ($S_p v$) is used to break

THE FLOW PROPERTIES OF EMULSIONS

down the structure arising from particle aggregation when the system is at rest. When shear is applied the particles deflocculate; further increase in shear rate provides power ($S_1 v$) to overcome the viscous resistance of the deflocculated system.

Eqn 5 can be written as

$$S = \frac{S_\infty v}{\phi + v} + \eta_\infty v \quad \dots \quad \dots \quad \dots \quad \dots \quad (8)$$

where ϕ is a measure of the curvature of the graph showing the change in S required to overcome the plastic resistance with change in v . This graph is derived from the pseudoplastic flow curve. S_∞ is S_p at infinitely high rate of shear. When $S_\infty = 0$, the $S-v$ plot will be a straight line, and Poisseuille's equation is applicable. Flow is defined by eqn 2 when $\phi = 0$.

Williamson's treatment gives satisfactory results only when the curved and linear portions of the $S-v$ curve are well defined. Recently, (Gillespie, 1960) calculated the $S-v$ relationship for pseudoplastic flow by accounting for link formation between particles, and for link breakage due to shear and temperature. At high shear rates his equation approximates to eqn 6.

The assumption that pseudoplasticity can be represented by the sum of two independent effects is undoubtedly an oversimplification of the true conditions. Goodeve (1939), however, developed this theme further. He believed that a Newtonian effect, where the shearing force is proportional to the rate of shear, and a thixotropic effect, where the shearing force is constant irrespective of the rate of shear, contribute to flow behaviour of concentrated suspensions and emulsions.

$$F = Rv + E$$

$$\text{or } \eta_\infty = R + \frac{E}{v} \quad \dots \quad \dots \quad \dots \quad \dots \quad (9)$$

where R and E are constants, the former representing the residual viscosity, and the latter representing a coefficient of thixotropy. The thixotropic effect is attributed to particle interaction during flow, leading to link formation. When these links are stretched and broken momentum is transferred from a moving layer to the adjacent layer.

Interaction between particles results from the prevailing forces of repulsion and attraction. In an aqueous continuous phase the former are usually electrostatic in origin, depending among other things on the electrical charge on the particles, electrolyte concentration, particle size, and the distance separating the particles (Verwey & Overbeek, 1948). In oil continuous media, the repulsion is substantially reduced (Albers & Overbeek, 1960). The attraction forces, which operate over greater distances than the repulsion forces, are unaffected by the polar nature of the continuous phase. Fig. 3 shows the characteristic shapes of the attraction (V_A), repulsion (V_R) and net potential energy of interaction ($V = V_A + V_R$) curves for an o/w emulsion. The V curve shows a peak

at a certain distance between the particles. If the particles are to come closer together this potential energy barrier (V_{\max}) has to be overcome. When V_{\max} has a value not greater than a few kT , where k is the Boltzmann constant and T is the absolute temperature, a certain proportion of the particles are able to get over the barrier. At this very small distance of separation in the primary minimum the particles are held together by strong forces of attraction if the layer of emulsifier around the particles prevents spontaneous coalescence. On the other hand, if V_{\max} exceeds $20\text{--}25 kT$ the particles cannot surmount the potential energy barrier and they flocculate in the secondary minimum where the attraction forces are very weak, usually not exceeding a few kT .

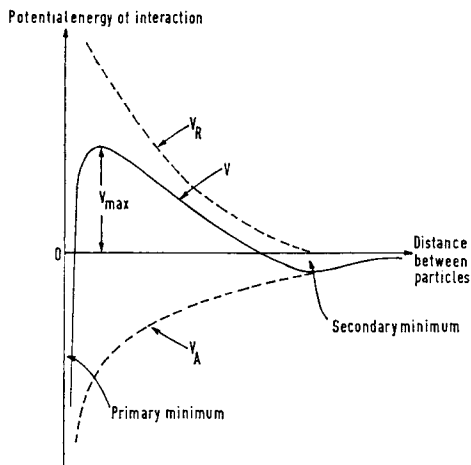


FIG. 3. Characteristic curve for the potential energy of interaction between particles in a suspension or in an emulsion.

In oil continuous media V_{\max} is very small, so that the emulsifier films around the particles make contact when the particles flocculate (Albers & Overbeek, 1960). O/w emulsions stabilised by commercial grade non-ionic emulsifiers show a V_{\max} which is somewhat larger than for w/o emulsions (Sherman, 1963).

Non-Newtonian flow behaviour can be interpreted on the basis of this attractive theory. The main difficulty lies in choosing the correct value for the Van der Waal's constant (A) when calculating V_A . If the value chosen is too large, V_{\max} becomes too small and the secondary minimum becomes too large. In some examples the general shape of the net interaction curve may be drastically altered. For suspensions of solid particles in liquid media A can be calculated from rate of flocculation data. In emulsions, coalescence follows flocculation so that this method for deriving A cannot be used.

When particles flocculate in a suspension, or in an emulsion, part of the continuous phase is immobilised within the aggregates. Each aggregate behaves as if it had a volume greater than the sum of the volumes of the individual globules from which it is constituted (Vand, 1948; Robinson,

THE FLOW PROPERTIES OF EMULSIONS

1948), and at very low shearing stress it rotates around its centre of mass like a single particle (Manley & Mason, 1954). In the absence of any shearing force the size of the aggregates would increase with time, and hence the viscosity at low shear rate would also increase. When shear is applied the aggregates break down along their weakest planes, and the viscosity decreases. The final stage of deflocculation involves the separation of residual particle pairs. Flow under shear not only makes them rotate, but it also sets up a tension which promotes the separation of the particles within each pair. When the tension exceeds the attraction forces between these particles they separate. The tension (v_{\min}) which effects the separation of non-deformable particles in emulsions is calculated (Albers & Overbeek, 1960) from

$$v_{\min} = \frac{A}{18 \pi \eta_0 D_m Z^2 \sin(2\alpha)} \quad \dots \quad (10)$$

where η_0 is the viscosity of the continuous phase, D_m is the mean particle size, Z is the distance between the particles and α has a value of 30° . This equation should also be applicable to small sized deformable particles.

The influence of flocculation under shear (Van den Tempel, 1963) on emulsion viscosity, and also of shear thickening (de Vries, 1963), have been recently interpreted using the Verwey-Overbeek theory. Casson (1959) considered that viscosity is controlled by the dimensions of the particle aggregates. During flow the aggregates are subjected to disruptive stresses, their magnitude depending on the size of the aggregates and the rate of shear. At any rate of shear there is an equilibrium size for the aggregates.

The viscosity of very dilute systems arises from hydrodynamic interference between particles, and their associated zones of continuous medium, during flow. In concentrated systems the interference is much greater since the particles are now closer together. Simha (1952) pointed out that particles have a finite size with respect to their distance of separation, so that the interaction between two particles on either side of a central particle will be reduced due to a "shielding effect" exerted by the latter. In the mathematical development of this theory a particle with a diameter D is enclosed within a concentric sphere of diameter M . This sphere diameter represents the maximum distance over which other particles interact with the central particle. The interaction factor λ depends on the ratio D/M .

$$\lambda = \frac{1 - D/M}{D/M} \quad \dots \quad (11)$$

for D/M values greater than 0.5. Small increases in this ratio then produce larger increases in viscosity.

Ree & Eyring (1955), and Kim, Hirai, Ree & Eyring (1960), interpreted non-Newtonian flow in terms of the theory of rate processes (Glasstone, Laidler & Eyring, 1941) which assumes that before a particle can move past its neighbour it must surmount a potential energy barrier. Once

again two kinds of flow units are believed to be involved, one Newtonian and the other non-Newtonian. Several such flow units are present in every non-Newtonian system. Each unit has its own characteristic mean relaxation time β_n , and its own characteristic shear volume $a_n \times kT$. Each unit occupies a fraction x_n of the total shear surface. If all units on the same shear plane have the same rate of shear, then the viscosity (η) of the whole system is given by

$$\eta = \sum_{n=1}^n \frac{x_n \beta_n \sinh^{-1} \beta_n v}{a_n \beta_n v} \quad \dots \quad (12)$$

The values of the parameters in the equation are calculated from given $\beta-v$ relationships which are valid at the inflexion points in the $\eta-\log v$ curve. Unfortunately, the inflexion points are usually very difficult to identify on emulsion flow curves.

In non-Newtonian flow some form of structural change occurs as v increases. Reaction kinetics have been used to define this change (Denny & Brodkey, 1962) leading to

$$\eta_1 - \eta_\infty = \sum_{i=1}^n \left(x\beta/a \right)_i \quad \dots \quad (13)$$

where η_1 is the Newtonian viscosity at $v = 0$. This theory makes no specific assumptions about the mechanism responsible for the structural change, and it therefore does not presuppose the presence of many flow units as in the Ree-Eyring treatment. It does assume, however, that no structural breakdown is possible at zero shear. When the theory, in its present state, is applied to emulsion viscosity data a different rate constant is derived for each volume concentration of disperse phase (ϕ). No attempt has been made to integrate the rate constants for the different values of ϕ so as to generalise the application of this theory.

Recipe ingredients and their effect on emulsion viscosity

Many factors contribute to the viscosity of an emulsion. They arise primarily from the chemical nature and properties of the materials used

TABLE 3. FACTORS WHICH INFLUENCE EMULSION VISCOSITY

1. *Internal phase*—
 - (a) Volume concentration (ϕ)
inter-particle interference; flocculation; aggregation.
 - (b) Viscosity (η_1).
 - (c) Particle size, and size distribution.
technique used to prepare the emulsion; interfacial tension; particle deformation.
 - (d) Chemical constitution.
2. *Continuous phase*—
 - (a) Viscosity (η_0).
 - (b) Chemical constitution, and polarity.
effect on the potential energy of interaction between particles.
3. *Emulsifying agent*—
 - (a) Chemical constitution, and concentration.
 - (b) Solubility in continuous and internal phases; pH of liquid phases.
 - (c) Physical properties of film around the particles; thickness of film; particle deformation; fluid circulation within the particles; influence on the attraction forces between particles.
 - (d) Electroviscous effect.
electrolyte concentration in aqueous continuous media.
4. *Additional stabilising agents*—
Pigments, hydrocolloids, hydrous oxides, etc.

THE FLOW PROPERTIES OF EMULSIONS

in its preparation. Table 3 lists the principal factors, and their associated phenomena, which have been reported in the literature. This form of representation is convenient but not wholly satisfactory since it suggests that each factor acts independently, whereas two, or more factors may act simultaneously. The net result is an effect which differs from the sum of their individual contributions. The following example may be used to illustrate this factor interaction. Two emulsions containing different concentrations of disperse phase are prepared using the same ingredients and the same method of pre-mixing and homogenisation. Their viscosities are then compared over a wide range of shear rates so as to determine the effect of ϕ on η . It is possible that the more concentrated emulsion will have a larger mean particle size, and broader particle size distribution than the other emulsion. Unless this is recognised, and accounted for, the wrong conclusions may be drawn from the data. Other examples of this interaction will appear in the subsequent discussion. In general, the listed factors exert a greater effect in concentrated emulsions, because the particles are packed closer together.

The interpretation of emulsion viscosity data is further aggravated by the possibility of particle deformation. This will depend, to some extent, on the physical properties of the film of emulsifier around the particles. If a particle is only slightly deformed when sheared, the deformation can be calculated (Taylor, 1934) from

$$\frac{L - B}{L + B} = \frac{vD_m \eta_o}{2\gamma} \left(\frac{\frac{19}{16}\eta_1 + \eta_o}{\eta_1 + \eta_o} \right) \quad \dots \quad (14)$$

where L and B are the dimensions of the major and minor axes, γ is the interfacial tension, and η_1 is the viscosity of the internal phase. Small particles of a few microns diameter will, therefore, undergo negligible deformation even at high shear rates. When particles in emulsions suffer little deformation under shear, conclusions regarding emulsion flow behaviour can be drawn, by analogy, from the much more detailed information which is available for suspensions of rigid spheres.

INTERNAL PHASE

Volume concentration. The viscosity of an extremely dilute ($\phi < 0.05$) suspension of rigid spherical particles in a fluid medium is given by (Einstein, 1906; 1911),

$$\eta = \eta_o(1 + a\phi) \quad \dots \quad (15)$$

provided there is no interaction between the particles, and their distance of separation greatly exceeds their diameter. The constant a has a value of 2.5.

Eqn 15 can be presented in another way

$$\frac{\eta}{\eta_o} - 1 = \eta_{sp} = 2.5\phi \quad \dots \quad (16)$$

So that if the specific increase in viscosity (η_{sp}) is plotted against ϕ ($\phi < 0.05$), one should obtain a straight line with a gradient of 2.5.

When the particles in dilute emulsions are deformable eqn 15 has to be modified to allow for the influence of η_1 . If the emulsifier film around the particles does not prevent the transmission of tangential stress from the continuous phase, and if there is no slippage at the oil-water interface (Taylor, 1932), the relative viscosity (η_{rel}) is given by

$$\frac{\eta}{\eta_0} = \eta_{rel} = 1 + 2.5 \left(\frac{\eta_1 + \frac{2}{3}\eta_0}{\eta_1 + \eta_0} \right) \phi \quad \dots \quad (17)$$

When η_1 is large, this equation reduces to eqn 15; in all other instances η_{rel} is lower than for a corresponding dispersion of solid particles. Eqn 17 was modified by Leviton and Leighton (1936) to extend its validity to more concentrated emulsions.

$$\ln \eta_{rel} = 2.5 \left(\frac{\eta_1 + \frac{2}{3}\eta_0}{\eta_1 + \eta_0} \right) \left(\phi + \phi^{\frac{5}{3}} + \phi^{\frac{11}{3}} \right) \quad \dots \quad (18)$$

At low values of ϕ eqns 17 and 18 are identical. Eqn 18 was found to agree with experimental data up to $\phi = 0.4$. The term $\phi^{\frac{5}{3}}$ was introduced following a suggestion by Smoluchowski (1916) that it approximates to the next term in the series expansion of eqn 15; the term $\phi^{\frac{11}{3}}$ was introduced to obtain closer agreement between theoretical and experimental values of η , and it has no theoretical significance.

Eqns 17 and 18 do not recognise the effect on shear flow which an emulsifier layer around the particles may exert.

If this layer has viscoelastic properties the particles will not deform when sheared, but when the emulsifier layer is viscous, particle flow resembles that of unstabilised dispersions of fluid particles (Oldroyd, 1953; 1955). The emulsifier layer also introduces the possibility of slippage at the interface (Rajagopal, 1960).

$$\eta_{rel} = 1 + \frac{2.5 [\eta_1 + \frac{2}{3}\eta_0 + (2V_s + 3V_B)/2.5r] \phi}{\eta_1 + \eta_0 + \frac{2}{3}(2V_s + 3V_B)/r} \quad \dots \quad (19)$$

where r is the particle radius, and V_s and V_B are the shear viscosity of the emulsifier layer and its area viscosity—the two dimensional analogue of bulk viscosity—respectively. This equation, therefore, provides an indirect way of differentiating between plastic solid and fluid emulsifier layers. The quantity $(2V_s + 3V_B)$ has been calculated for several dilute emulsions (Nawab & Mason, 1958) and found to be within the range 0.92×10^{-4} to 0.014×10^{-4} g sec⁻¹. These values are about the same as values of V_s reported for films of surface-active agents spread at an air-water interface (Joly, 1956), although the two sets of data are not strictly comparable. Other emulsions which did not obey eqn 19 were found to follow eqn 17 provided the emulsifier layer did not inhibit fluid circulation within the particles.

As ϕ increases so does η , and when ϕ exceeds about 0.4—0.5 the emulsion becomes pseudoplastic. If it contains pigments, gums, or

THE FLOW PROPERTIES OF EMULSIONS

hydrocolloids, the emulsion may eventually become plastic and develop a yield value. Small increases in ϕ now produce very large increases in η . When ϕ exceeds a critical value which is often, but not always, in the region of 0.74 the emulsion may invert. This will be accompanied by marked changes in η (Sherman, 1950a).

Richardson (1933) calculated the "compressibility" of an emulsion when ϕ is increased by $\delta\phi$, and from this he derived an expression for the viscosity of concentrated emulsions. At any given rate of shear

$$\ln \eta_{rel} = K\phi \dots \dots \dots (20)$$

where K is a constant. This equation was later amended empirically by Broughton & Squires (1938) to obtain better agreement with their experimental data

$$\ln \eta_{rel} = K\phi + Y \dots \dots \dots (21)$$

where Y is also a constant. Simpson (1949) found that the modified equation held for nitrocellulose lacquer emulsions. Neither eqns 20 nor 21 fitted viscosity data for w/o emulsions satisfactorily (Sherman, 1950a). The values of the supposed constants varied with ϕ , and with the emulsifier concentration. When ϕ exceeded 0.5 the discrepancies were exceedingly large.

Hatschek (1911) proposed that η_{∞} for non-Newtonian emulsions with ϕ exceeding 0.5 could be represented by

$$\frac{\eta_{\infty}}{\eta_0} = \frac{1}{1 - 3\sqrt{\phi}} \dots \dots \dots (22)$$

Sibree (1930, 1931) found that eqn 22 gave η_{∞} values lower than the experimental values. The discrepancy was attributed to an increase (h) in the effective volume of the particles due to hydration of the emulsifier layer around the particles. Accordingly

$$\frac{\eta_{\infty}}{\eta_0} = \frac{1}{1 - 3\sqrt{h\phi}} \dots \dots \dots (23)$$

Most of the emulsions examined gave a value of 1.3 for h . Other workers, however, have found large variations in h (Broughton and Squires, 1938; Toms, 1941).

Another equation for concentrated emulsions has been derived by modifying eqn 15. The amended equation takes the form

$$\eta = \eta_0 (1 + a\phi + b\phi^3 + c\phi^3 \dots) \dots \dots (24)$$

where b and c are constants. Table 4 summarises some of the values given in the published literature for a , b , and c . In general a retains a value of 2.5, but the values of b are widely different. Few values of c have been reported. The variation in b probably arises from differences in the particle sizes of the various systems studied. When ϕ exceeds 0.05 hydrodynamic interference takes place between the particles, the magnitude of the effect depending on particle size (Saunders, 1961).

TABLE 4. VISCOSITY OF DILUTE EMULSIONS AND DISPERSIONS OF SOLID PARTICLES

Reference	<i>a</i>	<i>b</i>	<i>c</i>
1. <i>Suspensions of solid spherical particles</i> —			
Saito (1950)	2.5	2.5	—
de Buijn (1942; 1948)	2.5	4.7	—
Eilers (1941; 1948)	2.5	4.94	8.78
Eirich, Bunzl, & Margaretha (1936)	2.5	8.0	—
Simha (1952)	2.5	12.6	—
		(changes with ϕ)	
Guth & Simha (1936)	2.5	14.1	—
Roscoe (1952)	2.5	—	—
Kynch (1956)	2.5	6.75–10.0	—
		(changes with ϕ)	
Vand (1948)	2.5	7.35	—
Higginbotham, Oliver & Ward (1958)	2.33–2.46	—	—
Mooney (1951)	2.5	—	—
Robinson (1949)	3–5	—	—
2. <i>Emulsions</i> —			
Albers (1957)	4–5	—	—
Sherman (1950)	2.3–2.8	0.9–7	—
		(changes with ϕ)	
Nawab & Mason (1958)	1.5–2.3	—	—
van der Waarden (1954)	2.6–5.0	—	—
Leviton & Leighton (1936)	2.44	—	—
	(average)	—	—
Maron, Madow & Krieger (1951)	2.20	—	—
Saunders (1961)	2.504	6.29–7.64	26.9–36.3

Brinkman writes eqn 24 as

$$\eta_{rel} = \frac{1}{(1 - \phi)^a} \quad \dots \quad (25)$$

where *a* is 2.5. Gillespie (1963) suggests that *a* has this value only in systems where the particles are deflocculated. If partial aggregation occurs *a* will have a value greater than 2.5, particularly if liquid is held within the aggregates.

Part of the continuous phase is immobilised between particles in concentrated emulsions and dispersions. The “free volume” of this phase in which particles move past one another is then $1 - H\phi$, where *H* is a measure of the volume of fluid immobilised. Several viscosity equations take the general form.

$$\eta_{rel} - 1 = \eta_{sp} = \frac{a\phi}{1 - H\phi} \quad \dots \quad (26)$$

For dispersions of solid particles in liquid media *H* usually represents the volume occupied by the particles after flocculation. The constant *a* has been interpreted in several ways, although it has often fitted the experimental data satisfactorily by assuming a value of 2.5 as in eqns 15 and 24.

Eilers (1941, 1943) observed that emulsions in which ϕ did not exceed 0.65 obeyed the equation:

$$\eta_{rel} = 1 + \frac{2.5\phi}{6(1 - \phi)} \quad \dots \quad (27)$$

For those emulsions in which η_{rel} became infinite when $\phi = 0.74$

$$\eta_{rel} = 1 + \frac{2.5\phi}{2(1 - H\phi)} \quad \dots \quad (28)$$

where *H* has a value of 1.28–1.35.

THE FLOW PROPERTIES OF EMULSIONS

Robinson (1949, 1957) regarded the constant a in eqn 26 as a coefficient of friction, its value depending on the shape and surface roughness of the particles. According to Mooney (1951), and Maron & others (1951, 1953), H defines the crowding effect which arises when particles of more than one size are packed together. In the simple case of a dispersion with only two particle sizes present H will be a function of their size ratio.

Sweeney & Geckler (1954) found that H varied from 1.00 to 1.47, H increasing as the particle size decreased. Saunders (1961) also observed this dependence of H on particle size in monodisperse latexes with particle sizes less than 1μ . His values for H ranged between 1.118 and 1.357: the constant a was unaffected by particle size, retaining a value of 2.504 provided the thickness of the emulsifier layer was allowed for when calculating ϕ . These two publications are probably the first to point out in semi-quantitative fashion the influence of particle size on viscosity data. Since eqn 26 on expansion gives a series of the form of eqn 24 this observation is of some importance. The relevance of particle size to viscosity will be discussed in greater detail in a later section.

Viscosity. The influence of η_1 on the deformability of particles has already been discussed.

When preparing an emulsion the emulsifier is normally dissolved or dispersed in the liquid which will be the continuous phase. Sometimes, for example, when preparing an o/w emulsion with sorbitan monolaurate, the emulsifier disperses on agitation in the water phase, but it is soluble in the oil phase. When the emulsion is homogenised an appreciable part of the emulsifier migrates to the oil phase (Sherman, 1963a) so that η_1 increases and η_0 decreases. This change in the ratio η_1/η_0 affects fluid circulation within the particles, it reduces the deformation due to shear, and it also affects η_{rel} .

In concentrated emulsions any effect due to η_1 is more difficult to analyse because of superimposed particle interaction effects. Provided ϕ and particle size are kept constant, and only η_1 is altered, it should be possible to determine any change in η_{rel} due to η_1 . Toms (1941) examined a range of o/w emulsions prepared with eleven different organic liquids as internal phase, and with several monovalent soaps as the emulsifier. He found no correlation between emulsion viscosity and η_1 . Any influence exerted by the internal phase was attributed to its interaction with the emulsifier film around the particles. A similar conclusion was reached by Shotton & White (1960) who determined η_{rel} for a series of oil-in-acacia solution emulsions. They found that the highest η_{rel} was given by the emulsions prepared with the oil of lowest η_1 .

Different values of η_1 were obtained for w/o emulsions by using aqueous solutions of glycerol, propylene glycol, sorbitol, and triethylene glycol (Sherman, 1955b). Even when η_1 was increased fifty-fold η_∞/η_0 did not alter. This was probably due to the plastic properties of the emulsifier film around the particles. When carbon black was incorporated in the oil phase η_∞/η_0 did alter, the highest values being shown by the emulsion with the lowest η_1 , namely, the aqueous sorbitol solution-in-oil emulsion. The specific absorption of sorbitol solution by carbon black was greater

than the specific absorption of the other polyhydric alcohol solutions by carbon black, so that the chemical constitution of the internal phase can affect the configuration at the oil-water interface even when η_1 does not influence viscosity.

Particle size, and size distribution. The bulk of published literature makes little, or no, reference to the state of dispersion of the systems examined. Nothing more precise is given than generalised statements indicating that "fine" emulsions gave higher viscosities than "coarse" emulsions of the same formulation, or that the particle size did not exceed a certain value.

Until quite recently the only observations of any value were those of Leviton & Leighton (1936) and of Richardson (1950, 1953). Unfortunately, one or other of these observations, which appear contradictory, are quoted repeatedly without appreciating that they apply only under certain limiting conditions. Leviton & Leighton (1936) found that the viscosity of dilute o/w emulsions did not change when particle diameter was reduced from 3.0μ to 0.7μ . They believed that when ϕ did not exceed 0.5 any increase in the hydrodynamic volume of the particle due to adsorption of emulsifier might be counterbalanced by the increase in η_0 . Richardson (1950, 1953) restricted his attention to concentrated ($\phi = 0.75$) o/w emulsions which exhibited non-Newtonian flow. He found that η_∞ was proportional to the reciprocal of the mean particle diameter (D_m), and that $\eta_\infty D_m$ remained constant provided the spread of particle sizes around D_m was narrow.

This disregard of particle size analysis is partly due to the incompleteness of viscosity equations. With only few exceptions (Oldroyd, 1953, 1955; Rajagopal, 1960), and these apply only to very dilute emulsions, no equation recognises the influence of particle size on viscosity. This problem has been studied in much greater detail for suspensions of solid particles in liquid media than for emulsions, but even here most of the equations which have been proposed (for example, Roscoe, 1952; Orr & Blocker, 1955; Mari & Otatake, 1956) do not include a specific term for particle size. Instead, alternative forms of equations are suggested depending on whether the suspension has a homogeneous or heterogeneous particle size distribution.

The importance of recognising any effect due to particle size when interpreting viscosity data, especially when particle size does not exceed a few microns, is conveniently illustrated by reference to Fig. 4. The viscosity data for a series of w/o emulsions stabilised by sorbitan sesquioleate and sorbitan trioleate, are plotted as η_{rel} against ϕ for a number of mean particle sizes. Each emulsion showed a very narrow distribution of sizes about the mean value. The shape of each curve varies with particle size, η_{rel} increasing at any given value of ϕ as D_m decreases. Thus, if these data were inserted in eqns 24 or 26 the values derived for the various constants would vary with D_m .

Pseudoplastic w/o emulsions showed a large curvilinear increase in η_∞ when the particle size fell below about 2μ (Sherman, 1960). For o/w emulsions the effect was less pronounced, and appeared only at values

THE FLOW PROPERTIES OF EMULSIONS

of ϕ exceeding 0.5. This difference in behaviour was attributed to differences in the rheological properties of the emulsifier films around the particles. At high rates of shear the particles in a suspension are equidistant from each other. Provided they behave as rigid spheres this distance (a_m) can be calculated from

$$a_m = D_m \left(\sqrt[3]{\frac{\phi_{\max}}{\phi}} - 1 \right) \quad \dots \quad (29)$$

where ϕ_{\max} is the maximum volume of disperse phase which can be incorporated in the emulsion. In many cases ϕ_{\max} is about 0.74, provided the particle size distribution is reasonably narrow. If η_{∞}/η_0 is plotted against a_m for emulsions of this type, an exponential relation is derived which covers viscosity data for all values of ϕ . When a_m falls below a critical value ($\sim 0.5\mu$), when D_m does not exceed 2-3 μ , η_{∞}/η_0 increases very rapidly (Sherman, 1960). Eqn 29 indicates that with small particles the critical value of a_m is reached at lower values of ϕ than with large particles.

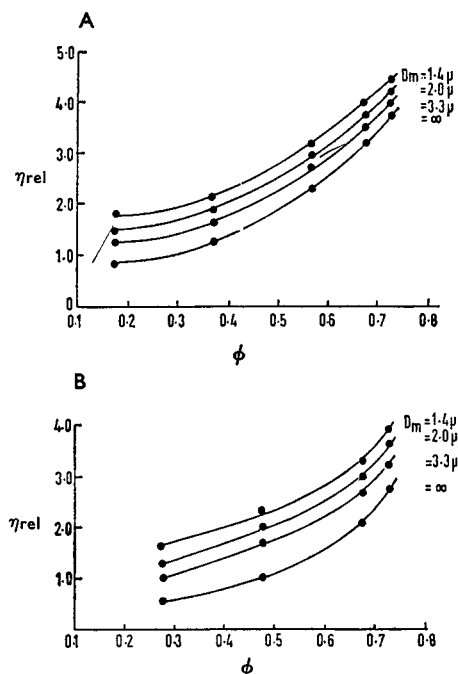


FIG. 4. Viscosity data for w/o emulsions stabilised with A, sorbitan sesquioleate and B, sorbitan trioleate.

Similar studies have been made on dilute o/w emulsions stabilised by monoglycerides and milk protein (Sherman, 1961). These studies also indicated that D_m depends on ϕ and homogenisation pressure.

Emulsions with a broad distribution of particle sizes will have a lower viscosity than comparable emulsions with a narrow distribution of

particle sizes. The depth of the secondary minimum in the potential energy curve, and the height of the potential energy barrier to flocculation in the primary minimum (Fig. 3), are both affected by D_m . This influence will be reflected in the flow behaviour at very low rates of shear.

CONTINUOUS PHASE

In spite of the lack of agreement regarding the relative effect of various factors on viscosity, all equations indicate a direct proportionality between η and η_0 . It should be appreciated that η_0 represents the viscosity of the entire continuous phase, and not the viscosity of the basic fluid in which other materials may be dissolved. Thus, it is the usual practice to dissolve, or disperse, the emulsifier, finely divided pigments, and hydro-colloids in this phase, and each of these contributes to η_0 .

Removal of emulsifier from the continuous phase, due to adsorption at the particle surface, will lower η_0 . For emulsifiers of simple chemical structure the concentration reduction is usually too small to be of any significance.

Recent studies on thin films (Derjaguin & Samygin, 1954, 1957, 1959; Elton & Picknett, 1957; Fuks, 1958) suggest that their viscosity is very much larger than the viscosity of the same liquids in bulk, for example, a film with a thickness of 1,000 Å has a viscosity which is twice the bulk value, whilst a film of 200 Å has a viscosity which is about five times the bulk value. For aqueous films these discrepancies are attributed to electrical charge effects. Similar phenomena have now been reported for films of a non-aqueous nature. In concentrated emulsions the particles are separated by very thin films of continuous phase when they are deflocculated. If the observations on the viscosity of thin films can be applied to emulsions, it could be that the high viscosity of concentrated emulsions is partly attributable to a hitherto unrecognised unduly large value of η_0 . Similarly, flocculated particles in emulsions are separated by very thin films of continuous phase. When shear is applied η decreases possibly due, in part, to a fall in η_0 as the distance between particles increases.

EMULSIFYING AGENT

Composition, and concentration. Wilson & Parkes (1936), Broughton & Squires (1938), and Sumner (1940), have all pointed out that the chemical nature of the emulsifier influences viscosity. A range of w/o emulsions with the same ϕ , but stabilised by different emulsifiers, showed quite different η_∞/η_0 values (Sherman, 1955a). The chemical structure of the emulsifier will affect the aggregation of particles when they flocculate, also the inter-particle attraction, and hence emulsion flow behaviour at low rates of shear.

Emulsifier concentration influences the value of ϕ at which an emulsion inverts, and also the optimum viscosity just before inversion (Sherman 1950a; Becher, 1958). Emulsion viscosity increases at any given ϕ with increasing emulsifier concentration. This has been attributed in some instances, for example, for protein, to increased adsorption of emulsifier at the particle surface, thus raising the value of ϕ . With many emulsifiers it

THE FLOW PROPERTIES OF EMULSIONS

is most unlikely that the adsorbed layer is ever more than one molecule thick, so that this explanation is not universally valid. Once a monomolecular layer has been formed around the particles the excess emulsifier molecules associate to form micelles in the continuous phase. Such units immobilise fluid within themselves so that the "free" volume of continuous phase decreases, and the effective volume ratio disperse phase : continuous phase increases (Sherman, 1963a). The larger the excess of emulsifier present the greater the volume of continuous phase immobilised. Calculation indicated that for w/o emulsions stabilised by sorbitan monooleate each excess molecule of sorbitan monooleate immobilised 28×10^{-23} ml of oil.

When o/w emulsions were prepared with sorbitan monolaurate dispersed in the water phase, multiphase particles appeared, their number, size, and structural complexity, increasing as the emulsifier concentration increased. With 6.0% emulsifier the emulsion inverted at a lower ϕ than for lesser emulsifier concentrations.

Emulsifier solubility; hydrogen ion concentration. Many of the polyoxyethylene sorbitan derivatives are oil soluble and only dispersible in water. The type of emulsion obtained initially with these emulsifiers depends on the phase to which they are added, the emulsifier concentration employed, and the method used to prepare the emulsion. At some value of ϕ the emulsion inverts, and this is accompanied by a pronounced change in viscosity.

Sorbitan monolaurate behaves in a similar way. The inversion of o/w emulsions stabilised by this emulsifier, which was referred to in the previous section, is attributable to distribution of the sorbitan monolaurate between the two phases, even though it was initially dispersed in the water phase. Its rate of migration to the oil phase depends on the concentration employed (Sherman, 1963a). Similarly, if the sorbitan monolaurate is apportioned between the two phases before mixing them inversion is dependent on the emulsifier concentration (Becher, 1958).

Solubility phenomena appear to be involved also in the inversion of w/o emulsions stabilised by non-ionic emulsifiers at alkaline pH. Concentrated w/o emulsions stabilised by sorbitan sesquioleate, mannitan monooleate, and mannide monooleate, for which the water phase was a series of buffer solutions of pH ranging from 3.0 to 10.0, showed no change in η_{∞} up to a pH of about 9. At a slightly higher pH the emulsions inverted to dilute o/w emulsions, and this was accompanied by a sharp drop in viscosity (Sherman, 1950b). The emulsifiers, which were insoluble in the buffer solutions at pH 7.0, became increasingly soluble as the pH approached 9.0. When BaCl_2 was added to the fluid o/w emulsions they inverted to more viscous w/o emulsions.

PHYSICAL PROPERTIES OF THE ADSORBED EMULSIFIER FILM

Reference has already been made to the influence of the rheological properties of the emulsifier film on the deformability of particles under shear, and on emulsion viscosity.

Experimental study of these properties has, so far, been possible only

with systems which have usually taken the form of films adsorbed at extended, flat, stationary oil-water interfaces (Criddle, 1960). It is questionable whether the results of such tests can be used to determine the rheological behaviour of emulsifier films in sheared emulsions. An attempt has been made to show theoretically how the properties of surface films are interlinked with the properties of a bulk colloidal system (Joly, 1954), but this approach has not been extended yet to the interpretation of experimental data.

ELECTROVISCIOUS EFFECT

When very dilute emulsions containing electrically charged particles are sheared, the configuration of the electrical double layer around each particle is distorted. The interaction between ions in the double layer and the electrical charge on the particle surfaces is affected, leading to an extra dissipation of energy, and an increased viscosity (Conway & Dobry-Duclaux, 1960).

Smoluchowski (1916) amended eqn 15 for rigid particles to allow for this effect.

$$\eta_{sp} = 2.5\phi \left[1 + \frac{1}{\eta_0 K r^2} \left(\frac{\epsilon \zeta}{2\pi} \right)^2 \right] \quad \dots \quad (30)$$

where ϵ is the dielectric constant of the continuous phase, ζ is the electrokinetic potential of the charged particles, K is the specific conductivity of the emulsion, and r is the radius of the particles. Smoluchowski assumed that the thickness of the double layer is small compared with r . Booth (1950) developed an equation of much greater complexity in which he introduced terms for double layer thickness, ion concentration, and valency of the ions. The significant point about this equation is that it predicts a lower contribution to η by the electroviscous effect than suggested by eqn 30. This agrees with experimental data. A simpler form of Booth's equation has been developed by Street (1958).

A measurable electroviscous effect is to be expected only when r is very small, e.g. 500 Å, so that the thickness of the electrical double layer is significant with respect to r .

At higher values of ϕ than those to which eqn 30 applies the particles may be packed close enough for the double layers to repel each other. The viscosity increase which ensues is due to a second electroviscous effect. It was first observed by Harmsen, Van Schooten, & Overbeek (1953). This effect is directly proportional to ϕ^2 . At constant ϕ it increases with decreasing ionic strength, because the thickness of the electrical double layer now increases, thus increasing the probability of double layer interaction.

Very little study has been made of electroviscous effects in emulsions. Van der Waarden (1954) determined the viscosity of a series of o/w emulsions stabilised by sodium naphthasulphonate for which the particle size was well below 1μ . At high emulsifier concentrations the viscosity data showed appreciable deviation from values calculated using eqn 15. The increase in viscosity was also much larger than suggested by eqn 30 or

THE FLOW PROPERTIES OF EMULSIONS

Booth's equation, so that it was inferred that the observed electroviscous effect could not be due to distortion of the diffuse parts of the electrical double layers. The strongly ionised emulsifier adsorbed at the particle surface was believed to produce a high electric field strength (10^5 – 10^6 V/cm), and a layer of water molecules was strongly bound by this. Calculation indicated that the thickness of the water layer was about 30 Å irrespective of particle size.

When preparing his emulsions van der Waarden introduced the emulsifier into the oil phase. Mukerjee (1957) suggested that the observed viscosities approximated to values calculated from Booth's equation provided one allowed for passage of emulsifier into the aqueous phase during the emulsification, which involved the preparation of a w/o emulsion followed by inversion. Another complicating factor could be that when an excess of emulsifier is present, the micelles formed in the continuous phase alter the ionic concentration.

Whilst each of these emulsions was monodisperse, the particle size for different emulsions varied from 276 to 2,050 Å, and no allowance was made for the effect of this variation on the observed values of η_{rel} . If van der Waarden's viscosity data are plotted as η_{rel} against $1/a_m$ several straight lines are obtained, their gradients (G) depending on the particle size for each particular series of emulsions. When G is plotted against particle size, and compared with similar data for monodisperse latex systems of similar particle sizes (Saunders, 1961), in which no electroviscous effect was observed, it is found that the two sets of data agree fairly closely (Fig 5). With two possible exceptions, the change in η_{rel} for van der Waarden's emulsions is about that anticipated from the variation in particle size (Sherman, 1963c). It is quite possible, therefore, that no electroviscous effect was to be found in these emulsions.

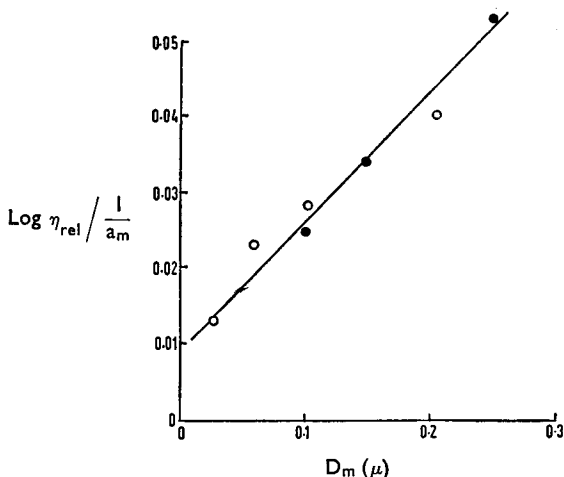


FIG. 5. Correction of van der Waal's data for particle size variation before assessing the influence of electroviscous effect.

○ Van den Waarden's data. ● Saunder's data.

P. SHERMAN

Albers (1957) measured η_{sp}/ϕ for w/o emulsions containing different emulsifiers, and showing different ζ potentials. Similar values of η_{sp}/ϕ were obtained for emulsions with widely different ζ potentials. He concluded that the electroviscous effect is very small in w/o emulsions, contributing no more than 1% to the viscosity of dilute emulsions.

STABILISERS

Hydrocolloids dissolved in an aqueous continuous medium may increase η_o , thereby retarding flocculation, but may show no surface activity.

Finely divided pigments migrate to the oil-water interface and form a protective layer around the particles. Hydrous oxides, for example, the hydrated form of vanadium pentoxide, ferric oxide, or alumina, are also surface-active. Apart from any increase in the initial emulsion viscosity which may result from their use, further increases in viscosity may occur over a period of time due to progressive hydration of the oxide. Eventually a gel-like layer may form around each particle. Concentrated w/o emulsions, in which alumina was dissolved in the aqueous phase, showed this phenomenon when aged at room temperature (Sherman, 1955c). When propylene glycol was incorporated in the aqueous phase, in concentrations ranging up to 20% these changes were retarded to an extent dependent on the propylene glycol concentration. At higher concentration the formation of gel layer was completely inhibited. Other poly-alcohols behaved in the same way.

VISCOSITY CHANGES IN EMULSIONS WHEN AGED

When emulsions are aged the particle size increases appreciably before the disperse phase separates in bulk. Provided the only change involved is a gradual increase in D_m , there being no appreciable change in the limits of particle size distribution, the decrease in viscosity as D_m increases should be predictable from the viscosity- D_m curves for fresh emulsions of the same formulation, calculated as described in the section on particle size. The rate of increase in D_m can be determined readily from the kinetics of globule coalescence (Lawrence & Mills, 1954; Van den Tempel, 1957), so that changes in η_{rel} on ageing for any given time can be predicted without resorting to dubious accelerated ageing techniques. Accelerated ageing by high speed centrifugation, or storage at elevated temperatures, may lead to changes in D_m which are quite different from those occurring under normal ageing conditions.

This approach has been used to predict changes in η_∞ in pseudoplastic w/o and o/w emulsions on ageing (Sherman, 1963b). The $\eta_\infty - D_m$ curves for both freshly prepared and aged emulsions were identical, thus confirming that growth in particle size, due to particle flocculation and coalescence, is the principal change during ageing. By studying the change in particle size for a few days, or in the concentration of particles per unit volume of emulsion, the rate of growth in particle size was calculated by using either of the two following equations.

THE FLOW PROPERTIES OF EMULSIONS

$$\ln D_t = \ln D_o + Ct/3 \quad \dots \quad (31)$$

or

$$D_t^3 = D_o^3 + \frac{8kT\phi t}{\pi\eta_o} \cdot \exp(-E/RT) \quad \dots \quad (32)$$

where D_o and D_t are the mean particle diameters at zero time and after any ageing time t respectively, C is the rate of particle coalescence, k is the Boltzmann constant, T is the absolute temperature, and E is the energy barrier to particle coalescence. Values of η_{rel} calculated for any ageing time t agreed most satisfactorily with values determined experimentally over long ageing periods at room temperature.

Viscosity changes at very low rates of shear (η_n) are more difficult to predict, because the η_n-D_m relationship is complicated by the superimposition of particle aggregation. At these low rates of shear an aged emulsion will exhibit a much larger degree of particle flocculation than when it is first prepared. Furthermore, the contribution of these phenomena to η_n increases with ageing time so that the η_n-D_m curve for a fresh emulsion cannot be used to obtain information about changes in η_n on ageing without precise knowledge of the rate of flocculation and its effect on η_n .

Conclusions

It is evident from the preceding discussion that there is a great diversity of opinion regarding factors which influence emulsion viscosity, and their relative importance. In spite of this disagreement some factors are undoubtedly more important than others. For example, the electroviscous effect, and η_i when the adsorbed emulsifier film around the particles is not rigid, cannot themselves influence emulsion viscosity to any great extent. On the other hand, ϕ , D_m , particle size distribution, the chemical constitution and concentration of the emulsifier, and η_o , can be used to effect large changes in emulsion viscosity. Many of the latter series of factors involve the internal phase in some way. If η_o is to be adjusted by the use of suitable additives, then it is necessary to make an additional study of the rheological properties of the appropriate continuous phases following incorporation of these additives, since they may exhibit non-Newtonian flow.

The chemical constitution and concentration of the emulsifier, and particle size distribution, usually exert a marked influence only on the viscosity of concentrated emulsions. In very dilute emulsions, viscosity is best adjusted by altering η_o .

The major difficulty in relating viscosity-rate of shear data for non-Newtonian emulsions to their practical performance is the lack of information regarding the shear stress-rate of shear conditions prevailing in practice. An attempt has been made recently (Henderson, Meer & Kostenbänder, 1961) to calculate this information for some simple pharmaceutical operations, for example, spreading of an ointment on the skin, milling operations, flow of liquid through a hypodermic needle, or pouring materials out of a bottle. In milling operations, and extrusion

from a hypodermic needle, v is very high, whilst in ointment-spreading and pouring a liquid from a bottle v is comparatively low. More detailed calculations of this kind are essential if emulsion rheological data are to be used to full advantage.

References

- Albers, W. (1957). Doctoral Thesis, Utrecht University.
- Albers, W. & Overbeek, J. Th. G. (1960). *J. Colloid Sci.*, **15**, 489–502.
- Becher, P. (1958). *J. Soc. cos. Chem.*, **9**, 141–148.
- Bingham, E. (1922). *Fluidity and Plasticity*, New York: McGraw-Hill.
- Booth, F. (1950). *Proc. Roy. Soc.*, **A203**, 533–551.
- Brinkman, H. C. (1952). *J. Chem. Phys.*, **20**, 571.
- Broughton, J. & Squires, L. (1938). *J. phys. Chem.*, **42**, 253–263.
- Bruijn, H. de (1942). *Rev. trav. chim. Pays-Bas*, **61**, 863–874.
- Bruijn, H. de (1948). *Proc. 1st Intern. Congr. Rheology*, **II**, 95–100.
- Casson, N. (1959). *Rheology of Disperse Systems*, Editor, Mills, C. C., Oxford: Pergamon Press.
- Conway, B. E. & Dobry-Duclaux, A. (1960). *Rheology, Theory and Applications*, Editor, Eirich, F. R., Vol. 3, New York: Academic Press.
- Criddle, D. W. (1960). *Ibid.*
- Denny, D. A. & Brodkey, R. S. (1962). *J. appl. Phys.*, **33**, 2269–2274.
- Derjaguin, B. V. & Samygin, M. H. (1954). *Disc. Faraday Soc.*, **18**, 24–41.
- Derjaguin, B. V. & Titijevskaya, A. S. (1957). *Proc. 2nd Intern. Congr. Surface Activity*, **1**, 211–219.
- Eilers, H. (1941). *Kolloid-Z.*, **97**, 313–321.
- Eilers, H. (1948). *Ibid.*, **102**, 154–169.
- Einstein, A. (1906). *Ann. Phys. Lpz.*, **19**, 289.
- Einstein, A. (1911). *Ibid.*, **24**, 591–592.
- Eirich, F. R., Bunzl, M. & Margaretha, H. (1936). *Kolloid-Z.*, **74**, 275–285; **75**, 20–37.
- Elton, G. A. & Picknett, R. G. (1957). *Proc. 2nd Intern. Congr. Surface Activity*, **1**, 288–294.
- Faxen, H. (1922). *Arkiv. Mat. Astronom. Fyz.*, **17**, 1.
- Flowers, A. E. (1914). *Proc. Amer. Soc. Test. Mater.*, **14**, 565–616.
- Fuks, G. I. (1958). *Colloid J., U.S.S.R.*, **20**, 705–715.
- Gillespie, T. (1960). *J. Colloid Sci.*, **15**, 219–231.
- Gillespie, T. (1963). *Ibid.*, **18**, 32–40.
- Glasstone, S., Laidler, K. J. & Eyring, H. (1941). *The Theory of Rate Processes*, New York: McGraw-Hill.
- Goodeve, C. F. (1939). *Trans. Faraday Soc.*, **35**, 342–358.
- Guth, E. & Simha, R. (1936). *Kolloid-Z.*, **74**, 266–275.
- Harmsen, G. J., van Schooten, J. & Overbeek, J. Th. G. (1953). *J. Colloid Sci.*, **8**, 64–71, 72–79.
- Hatschek, E. (1911). *Kolloid-Z.*, **8**, 34–39.
- Henderson, N. L., Meer, P. M. & Kostenbänder, H. B. (1961). *J. pharm. Sci.*, **50**, 788–791.
- Herschel, W. H. & Bulkley, R. (1926). *Kolloid-Z.*, **39**, 291–300.
- Higginbotham, G. H., Oliver, D. R. & Ward, S. G. (1958). *Brit. J. Appl. Phys.*, **9**, 372–377.
- Joly, M. (1954). *Proc. 2nd Intern. Congr. Rheology*, 365–370. London: Butterworth.
- Joly, M. (1956). *J. Colloid Sci.*, **11**, 519–531.
- Karasov, V. V. & Derjaguin, B. V. (1959). *Zhur. Fiz. Khim.*, **33**, 100–106.
- Kim, W. K., Hirai, N., Ree, T. & Eyring, H. (1960). *J. appl. Phys.*, **31**, 358–361.
- Krieger, I. M. & Dougherty, T. J. (1959). *Trans. Soc. Rheology*, **3**, 137–152.
- Kynch, G. J. (1956). *Proc. Roy. Soc.*, **A237**, 90–116.
- Ladenburg, R. (1907). *Ann. Physik.*, **23**, 447.
- Lawrence, A. S. C. & Mills, O. S. (1954). *Disc. Faraday Soc.*, **18**, 98–104.
- Leviton, A. & Leighton, A. (1936). *J. Phys. Chem.*, **40**, 71–80.
- Manley, R. St. J. & Mason, S. G. (1954). *Can. J. Chem.*, **32**, 763–767.
- Mari, Y. & Otatake, N. (1956). *Chem. Eng. Japan*, **20**, 488.
- Maron, S. H. & Madow, B. P. (1953). *J. Colloid Sci.*, **8**, 130–136.
- Maron, S. H., Madow, B. P. & Krieger, I. M. (1951). *Ibid.*, **6**, 584–591.

THE FLOW PROPERTIES OF EMULSIONS

- McKennell, R. (1956). *Analyt. Chem.*, **28**, 1710-1714.
- Mooney, M. (1951). *J. Colloid Sci.*, **6**, 162-170.
- Mukerjee, P. (1957). *Ibid.*, **12**, 267-270.
- Nawab, M. A. & Mason, S. G. (1958). *Trans. Faraday Soc.*, **54**, 1712-1723.
- Oldroyd, J. G. (1953). *Proc. Roy. Soc.*, **A218**, 122-132.
- Oldroyd, J. G. (1955). *Ibid.*, **A232**, 567-577.
- Orr, J. C. & Blocker, H. G. (1955). *J. Colloid Sci.*, **10**, 24-28.
- Ostwald, W. (1925). *Kolloid-Z.*, **36**, 99-117, 157-167, 248-249.
- Rajagopal, E. S. (1960). *Zeit. Physik. Chem.*, **23**, 342-347.
- Ree, T. & Eyring, H. (1955). *J. appl. Phys.*, **26**, 793-800.
- Richardson, E. G. (1933). *Kolloid-Z.*, **65**, 32-37.
- Richardson, E. G. (1950). *J. Colloid Sci.*, **5**, 404-413.
- Richardson, E. G. (1953). *Ibid.*, **8**, 367-373.
- Robinson, J. (1949). *J. Phys. Colloid Chem.*, **53**, 1042-1056.
- Robinson, J. (1957). *Trans. Soc. Rheology*, **1**, 15-24.
- Roscoe, R. (1952). *Brit. J. Appl. Phys.*, **3**, 267-271.
- Saito, H. (1950). *J. Phys. Soc. Japan*, **5**, 4.
- Saunders, F. L. (1961). *J. Colloid Sci.*, **16**, 13-22.
- Scott, J. R. (1931). *Trans. Inst. Rubber Ind.*, **7**, 2.
- Scott-Blair, G. W. and Oosthuizen, J. C. (1960). *Brit. J. Appl. Phys.*, **11**, 332-334.
- Sherman, P. (1950a). *J. Soc. Chem. Ind.*, **69**, Supplementary Issue No. 2, S70-S74.
- Sherman, P. (1950b). *J. Soc. Chem. Ind.*, **69**, Supplementary Issue No. 2, S74-S75.
- Sherman, P. (1955a). *J. Colloid Sci.*, **10**, 63-70.
- Sherman, P. (1955b). *Kolloid-Z.*, **141**, 6-11.
- Sherman, P. (1955c). *Mfg. Chem.*, **26**, 306-310.
- Sherman, P. (1960). *Proc. 3rd Intern. Congr. Surface Activity*, **B**, 596-609.
- Sherman, P. (1961). *Food Technol.*, **15**, 394-399.
- Sherman, P. (1963a). *Rheology of Emulsions*, Editor, Sherman, P. Oxford: Pergamon Press.
- Sherman, P. (1963b). Paper to be published in *J. Phys. Chem.*
- Sherman, P. (1963c). Paper to be published in *Proc. 41st Intern. Cong. Rheol.*, Providence U.S.A.: Brown University.
- Shotton, E. & White, R. F. (1960). *J. Pharm. and Pharmacol.*, **12**, 108T-112T.
- Sibree, J. O. (1930). *Trans. Faraday Soc.*, **26**, 26-36.
- Sibree, J. O. (1931). *Ibid.*, **27**, 161-176.
- Simha, R. (1952). *J. appl. Phys.*, **23**, 1020-1024.
- Simpson, J. (1949). *J. Oil Chem. Assoc.*, **32**, 60-71.
- Smoluchowski, M. von (1916). *Kolloid-Z.*, **18**, 190-195.
- Street, N. (1958). *J. Colloid Sci.*, **13**, 288-290.
- Sumner, C. G. (1940). *Trans. Faraday Soc.*, **36**, 272-278.
- Sweeny, K. H. & Geckler, R. D. (1954). *J. appl. Phys.*, **25**, 1135-1144.
- Taylor, G. I. (1932). *Proc. Roy. Soc.*, **A138**, 41-48.
- Taylor, G. I. (1934). *Ibid.*, **A146**, 501-523.
- Tempel, M. van den (1957). *Proc. 2nd Intern. Congr. Surface Activity*, **1**, 439-446.
- Tempel, M. van den (1963). *Rheology of Emulsions*, Editor, Sherman, P. Oxford: Pergamon Press.
- Toms, B. A. (1941). *J. chem. Soc.*, 542-547.
- Vand, V. (1948). *J. Phys. and Coll. Chem.*, **52**, 277-321.
- Verwey, E. J. W. & Overbeek, J. Th. G. (1948). *Theory of the Stability of Lyophobic Colloids*. Amsterdam: Elsevier.
- Vries, A. J. de (1963). *Rheology of Emulsions*, Editor, Sherman, P. Oxford: Pergamon Press.
- Waarden, M. van den (1954). *J. Colloid Sci.*, **9**, 215-222.
- Waele, A. de (1925). *Kolloid-Z.*, **36**, 332-333.
- Williamson, R. V. (1929). *Industr. engng Chem.*, **21**, 1108-1111.
- Wilson, C. L. & Parkes, J. (1936). *Quart. J. Pharm. and Pharmacol.*, **9**, 188-197.