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The Viscosity of Emulsions*)

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With 1 figure in 2 details and 1 table

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Introduction

The practical performance of emulsion products depends to a large extent on their flow properties. Thus the importance of correct formulation to obtain the desired viscosity for any particular working conditions.

The development of an equation that indicated the importance of factors influencing emulsion viscosity would facilitate greatly the formulation of these products.

An empirical expression of this type, could not account for the effects exerted by all possible factors without becoming very complex. However, some of these exert comparatively little effect so that they may be conveniently disregarded, without undue loss of accuracy, and attention focussed on those factors with major influence.

Several equations are to be found in published literature, but each suffers from the disadvantage that it holds only for the limited amount of practical data from which it was derived. None of the equations show wide application. Furthermore, no general agreement exists as to the principal factors that influence emulsion viscosity. The only point of similarity between these equations rests in the fact that they all indicate a linear relationship between emulsion viscosity (η) and the viscosity of the continuous medium (η_0).

Two principal trends of thought are apparent in the development of viscosity equations for emulsions.

The first assumes that small liquid droplets surrounded by an adsorbed layer of emulsifying agent, and dispersed in a fluid continuous medium, resemble suspensions of rigid particles (1). This view derives from the observations of *Bond* and *Newton* (2) who showed that droplets with radii less than a certain critical value behave like suspensions of rigid spheres

$$r = \sqrt{\frac{\sigma}{(\varrho_1 - \varrho)\, g}}\,; \qquad [1]$$

where r is the critical radius, σ is the interfacial tension, and $(\varrho_1 - \varrho)$ is the difference between the densities of the two liquids.

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On this basis, equations developed for solid suspensions of spherical particles in liquid media – that have been investigated in great detail – are equally applicable to emulsions. Consequently the viscosity of the liquid forming the dispersed internal phase (η_i) does not require consideration.

The second trend regards emulsions as suspensions of deformable liquid droplets. Factors of importance now include η_i, and the nature and physical properties of the adsorbed layer of emulsifying agent at the oil-water interface.

Discussion

In general, factors exerting an influence on emulsion viscosity may be summarised under the following headings, *provided the emulsions are always prepared in the same way, and no chemical interaction occurs between the emulsifying agent and the liquid phases.*

Volume concentration of disperse phase (φ). Effects arising from this in dilute and concentrated emulsions. Inter-particle interactions.

Viscosity of the external phase (η_0).

Viscosity of the internal phase (η_i).

Electroviscous effect.

The emulsifying agent; its chemical structure; the physical properties of the film adsorbed at the oil-water interface.

Size distribution of the dispersed globules. Homogenisation.

A summary of this form is not wholly satisfactory since some of the factors are inter-dependent, as will be shown later.

The net result of the effects due to some of the aforementioned factors is believed to be an increase in effective droplet size, due to the development of an additional layer around the globules. Whilst no published equation takes account of any effect due to globule diameter this undoubtedly affects φ and η.

Dilute Emulsions

a) Influence of φ, and Particle Interaction

Assuming that emulsion systems behave like suspensions of rigid spheres the simplest viscosity equation that can be applied is that due to *Einstein*

$$\eta = \eta_0 (1 + a\,\varphi)\,,$$

or

$$\frac{\eta_{sp}}{\varphi_{\varphi \to 0}} = [\eta] = a\,, \qquad [2]$$

where a is a constant, value 2.5, and $[\eta]$ is the intrinsic viscosity.

This equation applies only to extremely dilute systems, in which no interaction occurs between the particles, that are assumed to be perfect spheres, and the distance between them is very large compared with their diameter.

Most systems of practical importance have values of φ greater than those for which equation [2] holds. For these, values of a greater than 2.5 were found, and the general form of the equation had to be amended so as to include a power series of φ.

$$\eta = \eta_0 (1 + a\,\varphi + b\,\varphi^2 + c\,\varphi^3)\,, \qquad [3]$$

where b and c are constants. This allows for increased interaction between the particles with increasing φ.

Some typical values for these constants, derived from viscosity data for suspensions of solid particles and dilute emulsions, are given in table 1.

Table 1

a	*b*	*c*	*Reference*
	Suspensions of solid particles		
2.5	2.5		*Saito* (4)
2.5	4.7		*de Bruijn* (5)
2.5	4.94	8.78	*Eilers* (6)
2.5	8.0		*Eirich, Bunzl* u. *Margaretha* (7)
2.5	12.6		*Simha* (8)
2.5	14.1		*Guth* a. *Simha* (9)
2.5	($\varphi > 5.0\%$)		*Roscoe* (10)
	Dilute emulsions		
4–5		(W/O emulsions)	*Albers* (11)
2.3–2.8	0–9.7	(W/O emulsions)	*Sherman* (12)
1.5–2.3	1.6–8.5	(O/W emulsions)	*Nawab* and *Mason* (13)
2.6–5.0		(O/W emulsions)	*van der Waarden* (14)

b) Influence of η_i on η

Assuming the disperse phase droplets to be deformable *Taylor* (15) modified *Einstein*'s equation, on the basis of hydrodynamic theory, to show the influence of η_i on η. He assumed that the droplets were so small that they remained spherical, that there was no slippage on the surface of the droplets, and that any film surrounding the droplets did not hinder the transmission of tangential stress from one fluid medium to the other.

$$\eta = \eta_0 \left[1 + 2.5\,\varphi \left(\frac{\eta_i + {}^2/_5\,\eta_0}{\eta_i + \eta_0}\right)\right]. \qquad [4]$$

$\left(\frac{\eta_i + {}^2/_5\,\eta_0}{\eta_i + \eta_0}\right)$ accounts for the internal currents in a liquid drop falling through a liquid medium.

Leviton and *Leighton* (16) extended *Taylor*'s equation in their studies of oil-in-water emulsions of milk fat with φ values up to 40%.

$$\ln \frac{\eta}{\eta_0} = 2.5 \left(\frac{\eta_i + {}^2/_5\,\eta_0}{\eta_i + \eta_0}\right)(\varphi + \varphi^{5/3} + \varphi^{11/3}). \quad [5]$$

The power series of φ conformed with *von Smoluchowski*'s suggestion (17) that to extend the range of application of *Einstein*'s equation $\varphi^{5/3}$ should be included as a close approximation to the next term. $\varphi^{11/3}$ has no theoretical significance. It was introduced merely to obtain closer agreement between measured and calculated values of η.

Nawab and *Mason* (13) examined the applicability of *Taylor*'s equation to dilute emulsions with φ values no greater than 17%. Very dilute systems were chosen so as to minimise complicating factors that arise in more concentrated systems, e. g. interparticle interaction, aggregation effects, droplet distortion, etc. They found that *Taylor*'s equation held for certain systems but not for others. The viscosity data indicated that agreement was obtained only where the interfacial film of emulsifying agent did not inhibit internal circulation within the droplets, i. e., when the interfacial film was fluid. When a rigid film surrounded the droplets they behaved as rigid spheres. Thus, the physical nature of the adsorbed layer of emulsifying agent was of primary importance.

Oldroyd's theoretical studies (18) agree with these observations. He examined the effect of an interfacially adsorbed layer on the elastic and viscous properties of emulsions. When the layer was 'ideally elastic' the flow of the emulsion resembled that of a suspension of solid spheres. When the layer was 'purely viscous' the flow resembled that of a suspension of liquid droplets in a fluid continuous medium.

The general forms of equations [4] and [5] indicate that η_i cannot exert a great effect on η. Other workers (19) consider the nature of the internal phase to be more important than its viscosity.

c) Electroviscous Effect

Von Smoluchowski (20) extended *Einstein*'s equation to allow for this effect in suspensions of solid particles.

$$\frac{\eta}{\eta_0} - 1 = 2.5\,\varphi\left[1 + \frac{1}{\eta_0\,K\,r^2}\left(\frac{D\,\zeta}{2\,\pi}\right)^2\right], \quad [6]$$

where r is the radius of the particles, K is the specific conductivity of the suspension, D is the dielectric constant, and ζ is the electrokinetic potential of the charged particles. *Booth* (20) has also demonstrated the dependence of η_{sp} on the nature of the diffuse double layer.

Street (21) developed an equation of the general form of equation [3] for solid suspensions in electrolyte solutions.

$$\frac{\eta}{\eta_0} - 1 = 2.5\,\varphi\left[1 + \frac{\varphi}{2\,r^2\,\eta_0\,K}\left(\frac{D\zeta}{2\,\pi}\right)^2 (1 + k\,r^2)\right] \quad [7]$$

where k is the reciprocal of the *Debye* characteristic length.

Both *van der Waarden* (14) and *Albers* (11) attribute deviations from *Einstein*'s equation in dilute emulsions to an electroviscous effect. The former worker considered this due to the presence of an electric charge on the surface of the droplets that leads to an increase in droplet radius of 30–35 Å. This increase appeared independent of droplet size.

On the other hand *Harmsen*, *van Schooten*, and *Overbeek* (22) consider that the electroviscous effect in silver iodide sols results from the interaction between the electrical double layers of the particles. They disregarded any effect at very low φ values.

Mukerjee (23) claimed that *van der Waarden*'s data could be explained without assuming volume increase of the globules.

Examination of *van der Waarden*'s relative viscosity (η_{rel}) data (14) indicates that no appreciable change of η resulted from any electroviscous effect until an extremely high concentration of emulsifying agent was used. In general, the increase in η was quite small.

Alber's findings (11) confirm this. The η_{sp}/φ values, where η_{sp} is the specific increase in viscosity, were very similar for all the emulsifying agents examined, in spite of the fact that very wide variations in ζ potential occurred. He concluded that the electroviscous effect exerted little influence on the viscosity of water-in-oil emulsions.

Concentrated Emulsions

a) Influence of φ

Equations exist, as for dilute emulsions, that have been developed purely for emulsion systems, and others that have been adapted by analogy from studies with concentrated suspensions of solid particles. The latter type will be considered first.

Eilers (6) investigated 'emulsions' of asphalt in water. He found *Bredée* and *de Booij*'s equation for polymer solutions (24).

$$\frac{\eta}{\eta_0} = \eta_{\text{rel}} = [1 + 2.5\,\varphi/6\,(1 - \varphi)]^6 \qquad [8]$$

valid for values of φ up to 65%. He proposed an amended form in which η becomes infinite when φ reaches 74%.

$$\eta_{\text{rel}} = [1 + 2.5\,\varphi/2(1 - a\,\varphi)]^2\,. \qquad [9]$$

Good agreement with the experimental data was obtained for values of the constant a between 1.28 and 1.35.

Mooney (25) proposed a power series of the form

$$\ln\frac{\eta}{\eta_0} = \frac{2.5\,\varphi}{1 - z\varphi}\,, \qquad [10]$$

where z is a constant – the 'self crowding' factor.

Maron and his coworkers (26) developed an equation of similar form for soap stabilised latex emulsions.

$$\log\frac{\eta}{\eta_0} = \frac{x\,y\,\varphi}{1 - x\varphi}\,, \qquad [11]$$

where x and y are constants. This equation, which held for values of φ up to 60%, allows for the crowding effect of the dispersed globules on each other with increasing φ. *Maron* and his coworkers claimed that this equation gave better agreement with their experimental data than *Mooney*'s equation, particularly for concentrated systems exhibiting non-Newtonian flow.

The flow characteristics of concentrated emulsions, with φ values exceeding 50% approximately, differ from those of dilute emulsions. Whereas the latter generally behave as Newtonian fluids the former do not. They exhibit decreasing η with increasing rate of shear, and η attains a steady value at high rates of shear only. Often such emulsions develop a yield value, i. e. a certain shearing stress has to be applied before flow commences.

To define η at high rates of shear for such systems *Hatschek* (27) proposed the relationship.

$$\eta = \frac{\eta_0}{1 - \sqrt[3]{\varphi}} \qquad [12]$$

Sibree (28) found that this equation gave η values lower than those found experimentally for a series of paraffin-in-water emulsions. He attributed the discrepancy to the existence of a hydrated layer of emulsifying agent around the droplets which produced an increase in their size. *Hatschek*'s equation was modified to read

$$\eta = \frac{\eta_0}{1 - \sqrt[3]{h\,\varphi}}\,, \qquad [13]$$

where h is the 'volume factor', or thickness of the layer surrounding the globules

$$h = \frac{\varphi\,(\text{calculated})}{\varphi\,(\text{observed})}\,. \qquad [14]$$

φ was calculated from *Hatschek*'s equation.

For the systems examined by *Sibree* h usually had a value around 1.3. But since all these systems were prepared with the same continuous phase he admitted the possibility that its value might depend on the emulsifier, the concentration employed, and other factors. This belief was confirmed later by other workers who attempted to apply *Sibree*'s equation to their own data.

Sibree's amended form of *Hatschek*'s equation proved to have limited application. It was found that h sometimes decreased with increasing φ, and sometimes the calculated values of h were below unity.

Richardson (1) developed an equation from theoretical considerations relating φ exponentially to η . η at any particular rate of shear is given by

$$\eta = \eta_0 e^{A\,\varphi} \quad \text{or} \quad \ln\frac{\eta}{\eta_0} = A\,\varphi\,, \qquad [15]$$

where A is a constant.

Broughton and *Squires* (1) later modified this so as to obtain better agreement with their viscosity data for oil-in-water emulsions stabilised by sodium oleate, triethanolamine, and saponin.

$$\ln\frac{\eta}{\eta_0} = A\,\varphi + B\,, \qquad [16]$$

where B is a constant. This equation fitted the experimental findings of *Simpson* (29).

Equations [13] and [16] have been applied to viscosity data for water-in-oil emulsions stabilised by sorbitan sesqui-oleate (12). Neither equation showed a satisfactory fit. The values of the constants h, A, and B varied with φ and the concentration of emulsifying agent employed. For values of φ greater than 50% the values of the constants A and B showed appreciable change.

Other theories have been advanced to explain the effect of high values of φ on η. Some of these are based on the view that the internal phase droplets are deformable, whilst others compare their behaviour to that of solid spheres.

Richardson (30), and *Lawrence* and *Rothwell* (31) assume that for values of φ greater that 50% the globules must be deformed if the flow is linear. *Lawrence* and *Rothwell* further suggest that the factors involved depend on the applied rate of shear. At low rates of shear the droplets require time to recover their shape after deformation. For intermediate rates of shear two factors contribute to energy dissipation, viz., the work done in distorting the globules – the non-Newtonian contribution, and the work done against the continuous phase, which is approximately Newtonian. At very high rates of shear η becomes independent of rate of shear because the droplets do not have sufficient time to recover between successive distortions.

Goodeve (32) also suggested that two factors are involved in the viscosity behaviour of concentrated emulsions. He explained *Sibree*'s observations (28) in terms of Newtonian and thixotropic factors. The latter he attributed to interference between the droplets and the formation of links. When these links are stretched and broken momentum is transferred from a moving layer to the adjacent layer. *Goodeve* also pointed out that for φ values greater than 50% droplets cannot roll over each other without being distorted.

Vand (33) points out that aggregates form in suspensions of spherical particles. For high values of φ quite a number of particles may be in contact at any one time. This results in the aggregate behaving as a single sphere with a much greater volume than the sum of the independent volumes of the spheres, due to immobilisation of continuous medium between the spheres. At very high values of φ these aggregates may link up across the entire space occupied by the suspension.

Robinson (34) also believes that solvent is immobilised between suspensions of solid particles at high values of φ, so that the 'free volume' of continuous medium in which the particles can pass each other is less than the difference between the volume of the suspension and φ.

$$\text{'free volume'} \propto 1 - S\,\varphi\,, \qquad [17]$$

where S is the volume occupied by the sediment when the solid particles themselves occupy unit volume, and

$$\eta_{sp} = \frac{G\,\varphi}{1 - S\,\varphi}\,. \qquad [18]$$

G is a constant (frictional coefficient) dependent on the shape, surface roughness, etc., of the particles.

Yet another view (35) regards the mutual hydrodynamic interactions between the suspended particles as the factor of primary importance at high values of φ. Unfortunately very little is known about the nature of these forces, or indeed the structure of such suspensions.

b) Influence of η_0

All viscosity equations, irrespective of whether they apply to dilute or concentrated emulsions, indicate a linear relationship between η and η_0.

η_0 represents the viscosity of the whole continuous medium and not the viscosity of the fluid phase alone that forms its basis. Thus, if the emulsifying agent is dissolved in the continuous phase, as is the normal practice, its viscosity contributes to η_0. Any further stabilising agent, e. g. finely divided solids, hydrocolloids, etc., colloidally dispersed therein, also influences η_0.

Adsorption of emulsifying agent at the oil-water interface tends to lower η_0. However, the concentration adsorbed is usually so small with respect to the total amount of emulsifying agent employed that any lowering of η_0 may be disregarded (13).

Interpretation of the term η_0 in concentrated emulsions may require revision in the light of recent work on the viscosity of very thin films of liquid.

Derjaguin and *Samygin* (36) showed that the viscosity of very thin films is quite different from their viscosity in bulk. A film of 1000 Å thickness possesses a viscosity of twice the normal value, whilst a film of 200 Å thickness shows a viscosity of five times the normal value in bulk. More recent work (37) confirms these observations, and indicates that the thickness of the film, and consequently its viscosity, are influenced by the presence of electrolytes. The latter affect the repulsion between the charged droplets.

Flocculated oil droplets in concentrated emulsions are separated by films of water with a minimum thickness of 100 Å.

At shear rates large enough to cause deflocculation the globules in concentrated emulsions will be separated from each other by very thin films of continuous medium. The larger the value of φ the thinner these layers will be, and presumably, the greater the deviation from the bulk viscosity of the continuous phase. It appears possible, therefore, that η_0 does not represent the true viscosity of the continuous medium in concentrated emulsions.

The increase in viscosity of an emulsion on homogenisation has been attributed to increased adsorption of emulsifier at the now extended interface. Another contributory factor could be the increase in viscosity of the continuous phase due to its presence now as a much thinner film between the globules.

c) *Influences of* η_i

The same considerations should apply as for dilute emulsions.

Investigations with concentrated water-in-oil emulsions of identical φ values (38) indicated that η_i had no influence on η when the adsorbed interfacial layer of emulsifying agent formed a rigid envelope. It was suggested that the mechanical rigidity of the interfacial barrier prevented the transmission of any effects due to shear.

It was further found that when finely divided carbon black was incorporated in the emulsions, the chemical nature of the internal phase influenced η. This resulted from the effect on the orientation of the carbon black particles at the oil-water interface.

d) *Globule Size*

None of the equations quoted above indicate an effect on η due to the size, or size distribution, of the dispersed globules.

Little work has been carried out on this problem with emulsions. Much recent work on suspensions of solid particles suggests that globule size does exert an influence, and that the form of the viscosity equation depends on whether the globules are of equal size or whether they have different sizes.

The relative viscosity of suspensions depends, not on the absolute size of the spheres at a given concentration but, on their size distribution (39). *Roscoe* (40) showed theoretically that the relative viscosity of suspensions with a very wide distribution of particle sizes was defined by

$$\eta_{\mathrm{rel}} = (1 - \varphi)^{-2.5} \qquad [19]$$

for all values of φ. When the spheres were all of equal size *Einstein*'s equation held only for values of φ below 5%. For all other values of φ

$$\eta_{\mathrm{rel}} = (1 - 3.5\,\varphi)^{-2.5}\,. \qquad [20]$$

Orr and *Blocker* (41) defined η in terms of η_0, φ, the packed sediment volume of the solid particles, and the geometric standard deviation of sphere diameters.

$$\log\left(1 - \frac{\eta_0}{\eta}\right) = \log h + g \log \varphi\,, \qquad [21]$$

where h is a constant inversely proportional to the limiting volume fraction, and g is inversely proportional to the geometric standard deviation of sphere diameters.

Mari and *Otatake* (42) proposed the following equation for suspensions of spheres with unequal diameters.

$$\frac{\eta}{\eta_0} = 1 + \left[\frac{dS_r}{2}\left(\frac{1}{\varphi_v} - \frac{1}{\varphi_{vc}}\right)\right], \qquad [22]$$

where d is the average effective diameter of the particles, φ_v and φ_{vc} are the volumes of solid fraction and volume of solid fraction in limiting concentration respectively, and S_r is the volume base specific surface.

For suspensions of spheres of equal size this equation becomes

$$\frac{\eta}{\eta_0} = 1 + \frac{3}{\left[\frac{1}{\varphi_v} - \frac{1}{0.52}\right]}\,. \qquad [23]$$

Eveson (43) claims that the relative viscosity of stable suspensions of spheres exhibiting Newtonian flow is independent of the mean particle diameter provided their size exceeds 15 μ. For smaller particles it increases with increasing mean particle diameter. He suggests further that the form of the size distribution curve should have greater influence on η than the ratio of the sphere diameters.

e) *The Emulsifying Agent*

Several workers stress the importance of the chemical nature of the emulsifying agent with respect to η (44). *Becher* (45) showed that emulsion inversion – a point at which major changes in η usually occur – is also influenced.

The effect due to concentration of emulsifying agent (C) has not been studied in any detail. The little date available derives from studies with emulsions of constant φ values, (46) and the possibility of variation in the effect due to C at different φ values has not been considered.

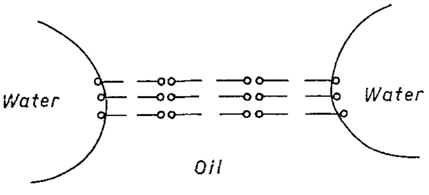
Experiments with water-in-oil emulsions over a wide range of φ (12) showed that the influence of C on η becomes more pronounced at higher values of φ i. e., the effect of C on η depends on the value of φ at which the determination is made. In emulsion systems exhibiting non-Newtonian flow the extrapolated *Bingham* yield value is similarly affected.

Re-examination of the aforementioned references (46) in the light of these latter observations suggests that the effect of C on η can be represented most satisfactorily by

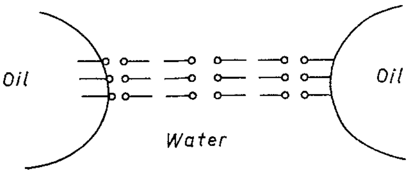
$$\ln \frac{\eta}{\eta_0} = A\,C\,\varphi + B\,, \qquad [24]$$

where A and B are constants (47).

This equation closely resembles equation [16], the modified form of equation [15]. It suggests that the constant A in equation [16] may be a function of C.



a) Water-in-oil emulsions



b) Oil-in-water emulsions

Fig. 1. Dispersed globules in emulsions linked together by oriented multilayers of emulsifying agent

Equation [24] has been found to fit the data of several other workers quite satisfactorily. Thus the data of *Broughton* and *Squires* (1), *Axon* (46), *Lawrence and Rothwell* (31), *van der Waarden* (14), and of *Sibree* (28) all fit this equation. It has the advantage over equations [13] and [16] that it holds over a much wider range of φ values viz., from very dilute to concentrated emulsions, and that single values of the constants A and B apply over the whole range of φ and C.

C is expressed as w/w percentage concentration, and the values of A and B depend on the emulsifying agent employed. There is no indication that the values of these two constants can be standardised for all emulsifying agents by expressing C in terms of molecular concentration.

To account for the effect of C on η it is suggested that adsorption of the emulsifying agent at the water-oil interface results in the development of polymolecular layers at values of C greater than the C.M.C. At high values of C and φ the disperse phase globules may be linked together by oriented multilayers of emulsifying agent (48) as shown in fig. 1.

a) Water-in-oil Emulsions

Pairs of emulsifier molecules oriented so that the hydrophobic 'tails' face outwards to oil phase.

b) Oil-in-water Emulsions

Pairs of emulsifier molecules oriented so that the hydrophobic 'heads' face outwards to water phase.

This could lead to plasticity and high *Bingham* yield values in concentrated emulsions. Deflocculation of the droplets at appropriate shear rates, so as to make η independent of shear rate, would have to be preceded by rupture of these linkages.

Conclusions

In spite of the diversity of opinion apparent from the data discussed in the preceding sections, some factors undoubtedly exert much greater influence on η than others.

The electroviscous effect, and η_i when the interfacially adsorbed layer of emulsifying agent is not rigid, cannot in themselves produce large changes in η.

The most important factors appear to be φ, η_0, the chemical constitution of the emulsifying agent employed, C and particle size distribution. By their control large changes in η can be effected.

Of these factors the last two exert a marked influence on η at φ values of approximately 50% upwards. The η of very dilute emulsions can be increased pronouncedly by suitably adjusting η_0.

Summary

The viscosity of emulsion products is often of practical importance.

Formulation so as to achieve a desired viscosity is not an easy task since numerous factors must be considered. Several equations have been proposed as mathematical representations of the effects exerted by these factors, but they all suffer the disadvantage of limited application. The only point on which all equations agree is in the existence of a direct relationship between η (emulsion viscosity) and η_0 (viscosity of the continuous phase).

Published viscosity equations are reviewed. The relative importance of factors influencing viscosity is discussed with reference to dilute and concentrated emulsions containing the same ingredients.

For concentrated emulsions the correct interpretation of η_0 and φ (volume concentration of disperse phase) may be difficult. The structure of the stabiliser film at the oil-water interface requires consideration.

None of the viscosity equations allow for the influence of C (concentration of emulsifying agent) on η. At values of C greater than the C.M.C. there is a marked effect, probably due to the development of a polymolecular adsorbed layer at the interface. φ controls the magnitude of this effect; it increases rapidly with increase of the former.

An exponential relationship is proposed, $\ln \eta/\eta_0 = A\,C\,\varphi + B$ where A and B are constants to account for these observations. This equation, which applies over the whole practical range of φ, also fits the viscosity data published by several workers.

Zusammenfassung

Die Viskosität von Emulsionsprodukten ist oft von praktischer Bedeutung. Die Herstellung einer Emulsion mit einem gewünschten Viskositätswert ist keine leichte Aufgabe, da zahlreiche Faktoren berücksichtigt werden müssen. Verschiedene Gleichungen sind aufgestellt worden, welche die durch diese Faktoren ausgeübten Wirkungen mathematisch beschreiben sollen, aber sie haben alle den Nachteil einer nur begrenzten Anwendbarkeit. Der einzige Punkt, für den alle Gleichungen übereinstimmen, ist die Existenz eines direkten Zusammenhangs zwischen der Emulsionsviskosität η und derjenigen der kontinuierlichen Phase η_0.

Die veröffentlichten Viskositätsgleichungen werden zusammengestellt. Die relative Bedeutung der die Viskosität beeinflussenden Faktoren wird für verdünnte und konzentrierte Emulsionen, die dieselben Bestandteile enthalten, diskutiert.

Für konzentrierte Emulsionen kann die korrekte Interpretation von η_0 und der Volumenkonzentration der dispersen Phase φ schwierig werden. Die Struktur des stabilisierenden Films an der Öl-Wasser-Grenzfläche muß berücksichtigt werden.

Keine der Viskositätsgleichungen berücksicht den Einfluß der Konzentration des Emulgators C auf η. Bei Werten von C oberhalb einer kritischen Molekelkonzentration (C.M.C.) beobachtet man einen ausgeprägten Effekt, der wahrscheinlich von der Ausbildung polymolekularer Adsorptionsschichten an den Grenzflächen herrührt. φ bestimmt die Größe dieses Effektes; es wächst mit dem Größerwerden der vorigen Größe schnell an.

Es wird eine Exponentialbeziehung

$$\ln \eta/\eta_0 = A\,C\,\varphi + B$$

aufgestellt, in welcher A und B Konstanten zur Anpassung der beobachteten Werte darstellen. Diese Gleichung, welche für den ganzen praktischen Bereich von φ anwendbar ist, gibt die von verschiedenen Forschern veröffentlichten Viskositätsdaten gut wieder.

Note Added in Proof

Since this paper was submitted for publication, further work has confirmed the observations of *Leviton* and *Leighton* (16) and *Richardson* (30) on the influence of globule size on η. The precise effect by globule size on η, *at such rates of shear that flow is Newtonian*, depends on the physical nature of the adsorbed emulsifier layer around the globules; also, on φ for certain systems. [*P. Sherman*, Proc. 3rd Intern. Congr. Surface Activity, Cologne, II, 596 (1960); Food Technol. **15**, 394 (1961).]

If the adsorbed emulsifier layer is rigid, and probably of polymolecular thickness, η increases curvilinearly with decreasing mean globule size (d_m) over a very wide range of φ, provided the globule size distribution is fairly narrow. Such systems include water-in-liquid paraffin emulsions stabilised by sorbitan sesquioleate, and dilute vegetable fat-in-water emulsions stabilised by a monoglyceride-lipoprotein complex. When d_m falls below $2\,\mu$, η increases greatly with further decrease in d_m. For values of d_m exceeding $5\,\mu$, d_m exerts little influence on η. The globules in these emulsions should resist deformation when subjected to shearing forces.

Liquid paraffin-in-water emulsions stabilised by sorbitan monolaurate exhibit a different pattern of behaviour. The adsorbed emulsifier layer in these emulsions shows no rigidity, and d_m does not affect η until μ exceeds 0.5. Then η increases linearly with decreasing d_m over the d_m range examined ($d_m > 5\,\mu$). The more concentrated the emulsion the greater the rise in η on decreasing d_m. The globules in these emulsions probably undergo deformation when sheared to an extent dependent on the rate of shear and d_m.

For those emulsions in which the globules behave as solid particles the η — d_m data for different values of φ can be summarised on a single curve, if one assumes that in *Newton*ian flow hydrodynamic effects exerted over the mean distance separating the globules (a_m) are primarily responsible for η.

$$a_m = d_m\left(\sqrt[3]{\frac{74}{\varphi}} - 1\right).$$

This equation has been applied to those emulsion systems mentioned previously to which it is applicable, and more recently to several other emulsions systems. Statistical analysis of the data over the complete range of φ values studied (approx. 0.2–0.7) indicates, in each case, an exponential-relationship of very high statistical significance.

$$\ln \eta_{\text{rel}} = C - X\,a_m\,,$$

where C and X are constants.

$C = \ln \eta_{\text{rel}}$ when $a_m = 0$, i. e. $\ln \eta_{\text{rel}}$ when the globules are in the most closely (dodecahedral) packed form.

Calculation of a_m for emulsions in which the globules deform under shear is more difficult. Deviations from the spherical form will undoubtedly exert much greater effect on η when the globules are separated by distances of 0.05 to $0.2\,\mu$ than when they are 0.4–$0.5\,\mu$ apart.

References

1) *Richardson, E. G.*, Kolloid-Z. **65**, 32 (1933); *Broughton* and *L. Squires*, J. Phys. Chem. **42**, 253 (1938).

2) *Bond, W. N.* and *D. A. Newton*, Phil. Mag. **5**, 794 (1928).

3) *Einstein, A.*, Ann. Phys. **18**, 289 (1906); **24**, 59 (1911).

4) *Saito, H.*, J. Phys. Soc. Japan **5**, 4 (1950).

5) *de Bruijn, H.*, Rev. Trav. Chim. **61**, 863 (1942); Proc. 1st. Int. Congress Rheology, II, 95 (1948).

6) *Eilers, H.*, Kolloid-Z. **97**, 313 (1941); **102**, 154 (1943).

7) *Eirich, F.*, *M. Bunzl* and *H. Margaretha*, Kolloid-Z. **74**, 276 (1936); **75**, 20 (1936).

8) *Simha, R.*, J. Appl. Phys. **23**, 1020 (1952).

9) *Guth, E.* and *R. Simha*, Kolloid-Z. **74**, 266 (1936).

10) *Roscoe, R.*, Brit. J. Appl. Phys. **3**, 367 (1952).

11) *Albers, W. A.*, Doctorate Thesis (Utrecht 1957).

12) *Sherman, P.*, J. Soc. Chem. Ind. Lond. Suppl. Issue No. 2, S 70 (1950).

13) *Nawab, M. A.* and *S. G. Mason*, Trans. Faraday Soc. **54**, 1712 (1958).

14) *van der Waarden, M.*, J. Colloid Sci. **9**, 215 (1954).

15) *Taylor, G. I.*, Proc. Roy. Soc. **A 138**, 41 (1932).

16) *Leviton, A.* and *A. Leighton*, J. Phys. Chem. **40**, 71 (1936).

17) *von Smoluchowski, M.*, Kolloid-Z. **18**, 190 (1916).

18) *Oldroyd, J. G.*, Proc. Roy. Soc. **A 232**, 567 (1955).

19) *Broughton, J.* and *L. Squires*, J. Phys. Chem. **42**, 253 (1938); *Toms, D. A.*, J. Chem. Soc. **1941**, 542.

20) *von Smoluchowski, M.*, Kolloid-Z. **18**, 194 (1916). *Booth, F.*, Proc. Roy. Soc. (London) **A 203**, 533 (1950).

21) *Street, N.*, J. Colloid Sci. **13**, 288 (1958).

22) *Harmsen, G. J., J. van Schooten* and *J. Th. G. Overbeek*, J. Colloid Sci. **8**, 64, 72 (1953).

23) *Mukerjee, P.*, J. Colloid Sci. **12**, 267 (1957).

24) *Bredée, H. L.* and *J. de Booij*, Kolloid-Z. **79**, 31 (1937).

25) *Mooney, M.*, J. Colloid Sci. **6**, 162 (1951).

26) *Maron, S. H.* and *B. P. Madow*, J. Colloid Sci. **6**, 590 (1951); **8**, 130 (1953). *Maron, S. H., B. P. Madow* and *I. M. Krieger*, ibid. **6**, 584 (1951).

27) *Hatschek, E.*, Kolloid-Z. **8**, 34 (1911).

28) *Sibree, J. O.*, Trans. Faraday Soc. **26**, 26 (1930); **27**, 161 (1931).

29) *Simpson, J.*, J. Oil Col. Chem. Assoc. **32**, 68 (1949).

30) *Richardson, E. G.*, J. Colloid Sci. **8**, 367 (1953).

31) *Lawrence, A. S. C.* and *E. Rothwell*, Proc. 2nd. Intern. Congr. Surface Activity London **1**, 499 (1957).

32) *Goodeve, C. F.*, Trans. Faraday Soc. **35**, 342 (1939).

33) *Vand, V.*, J. Phys. and Colloid Chem. **52**, 277 (1948).

34) *Robinson, J. V.*, J. Phys. and Colloid Chem. **53**, 1042 (1949).

35) *Frisch, H. L.* and *R. Simha*, Rheology; Theory and Applications (Academic Press, New York) **1**, 525 (1956).

36) *Derjaguin, B. V.* and *M. H. Samygin*, Akad. Nauk. S. S. S. R. Rastvorov., **1** 59 (1941).

37) *Derjaguin, B. V.* and *A. S. Titjevskaja*, Discussions Faraday Soc. **18**, 27 (1954). Proc. 2nd. Intern. Congr. Surface Activity London **1**, 536 (1957). *Elton, G. A.* and *R. G. Picknett*, Proc. 2nd Intern. Congr. Surface Activity London **1**, 287 (1957). *M. van den Tempel*, ibid. **1**, 40 (1957).

38) *Sherman, P.*, Kolloid-Z. **141**, 6 (1955).

39) *Ward, S. G.* and *R. L. Whitmore*, Brit. J. Appl. Phys. **1**, 286 (1950).

40) *Roscoe, R.*, ibid. **3**, 267 (1952).

41) *Orr, J. C.* and *H. G. Blocker*, J. Colloid Sci. **10**, 24 (1955).

42) *Yoshiro Mari* and *Naoshi Otatake*, Chem. Eng., (Japan) **20**, 488 (1956).

43) *Eveson, G. F.*, J. Oil Colour Chem. Assoc. **40**, 456 (1957); **41**, 150 (1958).

44) e. g. *Wilson, C. L.* and *J. Parkes*, Quart. J. Pharm., Pharmocol. **9**, 188 (1936) – *Broughton, J.* and *L. Squires*, J. Phys. Chem. **42**, 253 (1938) – *Sumner, C. G.*, Trans. Faraday Soc. **36**, 272 (1940) – *Sherman, P.*, J. Colloid Sci. **10**, 63 (1955).

45) *Becher, P.*, J. Soc. Cosmetic Chemists **9**, 141 (1958).

46) *Wilson, C. L.* and *J. Parkes*, Quart. J. Pharm. Pharmocol. **9**, 188 (1936) – *Toms, B. A.*, J. C. S. 542 (1941) – *Axon, A.*, J. Pharm. Pharmacol. **8**, 762 (1956) – *Lawrence, A. S. C.* and *E. Rothwell*, Proc. 2nd Intern. Congr. Surface Activity London **1**, 499 (1957).

47) *Sherman, P.*, Kolloid-Z. **165**, 156 (1959).

48) *Cockbain, E. G.*, Trans. Faraday Soc. **48**, 185 (1952).