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Rheological Properties of Corn Oil Emulsions with Methylcellulose

By B. B. SHETH, DUNCAN E. McVEAN, and ALBERT M. MATTOCKS

Flow properties of a series of emulsions containing methylcellulose 1,500 cps. in eight concentrations and corn oil in 10 concentrations were measured. Known equations for non-Newtonian flow were not satisfactory for these systems, and a new equation, called the "viscoelastic flow equation" was derived and fitted to the data. The equation is $\eta_a = Ae^{-\alpha S} + Be^{-\beta S} + \eta_\infty$, where η_a is apparent viscosity, S is shear rate, η_∞ is ultimate viscosity, and the other terms are constants. From this expression limiting viscosity, η_0 could be obtained as $A + B + \eta_\infty$. Values of η_0 were then fitted to fluidity plots to obtain intrinsic viscosities. These values agree with Taylor's equation only where the dispersion medium had high viscosity.

ALTHOUGH emulsions may be regarded as suspensions of spherical particles, their rheological properties are more complex than those of suspensions of solid particles. The equation of Einstein governing the viscosity of suspensions, may be expressed as

$$\eta_r = 1 + kC_v \qquad \text{(Eq. 1)}$$

where η_r is relative viscosity at low rates of shear, C_v is concentration by volume of suspended particles, and k is the Einstein constant or intrinsic viscosity, equal to 2.5 for spherical particles. This was modified for emulsions by Taylor (1), who took into account the flow induced in the suspended droplets. From hydrodynamic considerations Taylor derived the following

$$\eta_r = 1 + kC_v \left[\frac{\eta_1 + 0.4\eta_2}{\eta_1 + \eta_2} \right] \qquad \text{(Eq. 2)}$$

where η_1 is the limiting viscosity of the oil in the droplet, $\eta_{0\,(\text{oil})}$, and η_2 is that of the solvent, $\eta_{0(\text{solv.})}$. In a later work, Taylor (2) pointed out that deformation of fluid particles might occur during shear to form ellipsoids, and Oldroyd (3) showed that interfacial tension at the particle surface may retard flow within the particle. Other complexities which have been noted are the formation of adsorbed films with viscosities different from that of the medium or the droplet (3, 5).

In spite of these complicating factors, Nawab and Mason (6) found good agreement with Taylor's equation with one set of carefully prepared dilute emulsions, though most series did not agree, as has been the common result of other workers. In a most interesting fashion, Mason and Bartok (4) exhibited flow patterns and particle deformation of droplets in suspension with a rheometer which allowed the particles to be photographed in shear.

One of the difficulties encountered in the testing of the basic equations of Einstein and Taylor has

been the limitation that Eq. 1 is applicable only to infinitely dilute suspensions, and various modified equations have been used to extrapolate flow data of suspensions of finite concentrations and thus obtain values representing Einstein conditions. The Einstein equation, modified to allow for hydrodynamic interactions occurring at finite concentration may be expressed as

$$\eta_r = 1 + 2.5 \, C_v + k_1 C_v^2 + \ldots \quad \text{(Eq. 3)}$$

Some workers have applied this equation directly as a polynomial, others have utilized a curve of η_{sp}/C_v vs. C_v, where $\eta_{sp} = \eta_r - 1$, and extrapolated to $C_v = 0$ to obtain

$$\lim_{C_v \to 0} \eta_{sp}/C_v$$

as the Einstein constant. Other relationships, such as logarithmic functions, have been used with limited success. Recently, Ford (7) noted that if relative fluidity, ϕ_r, were used, plots of ϕ_r vs. C_v were usually linear up to rather high concentrations, as had been observed much earlier by Bingham (8), and that the fluidity relationship was a more suitable method for evaluating the Einstein constant. The equation was expressed as

$$\phi_r = 1 - 2.5 C_v + \ldots \quad \text{(Eq. 4)}$$

which is the reciprocal of the Einstein equation in the form

$$\eta_r = 1 + 2.5 C_v + 6.25 C_v^2 + \ldots \quad \text{(Eq. 5)}$$

The report by Ford has thus supplied a more reliable method for testing the basic flow equations with suspensions of finite concentration.

Pharmaceutical emulsions are usually non-Newtonian in nature, since they generally contain thickening agents such as natural gums and synthetic cellulose deratives which are, themselves, non-Newtonian. This fact makes it more difficult to apply the basic equations governing flow to such emulsions because the apparent viscosity measured will be variable, depending on the rate of shear of measurement. The difficulty may be overcome, however, if flow equations which will accurately predict the limiting viscosity, η_0, or viscosity at infinitely low shear rate, are available. Since the sedimentation of particles in emulsions is thought to occur at extremely low shear rates and since the flow characteristics at low shear rates show promise of furnishing a means for evaluating interfacial tension (6) and occurrence of aggregation (4), the objective of obtaining suitable flow equations is of importance.

An equation for describing non-Newtonian flow may be evaluated by three criteria: (a) its agreement with observed data, (b) its accuracy in furnishing correct values of η_0, and (c) its theoretical foundation.

Few theoretical equations have been derived for non-Newtonian flow, the exceptions being that of Ree and Eyring (9) involving an inverse hyperbolic sine which is difficult to evaluate, and that of Williamson (10) which was used empirically for some time before being derived theoretically (11).

The equation of Williamson has been shown to fit a wide variety of non-Newtonian flow curves (12–14), but it was also noted that the asymptote to the curve was unrealistic, and a new equation, called the "structure equation," was utilized which gave more accurate values of the asymptote at high shear rates (14, 15). Unfortunately, the structure equation could not be fitted to most flow curves without the assumption of a fixed yield value which often does not agree with the observed data. The concept of a yield value representing a nonyielding condition which suddenly disrupts at a fixed stress is also not in agreement with the recent findings of McVean (16), who measured the strain of gels to find them more aptly described by a viscoelastic equation

$$F = Ae^{-\alpha t} + Be^{-\beta t} \quad \text{(Eq. 6)}$$

where F is stress, A, α, B, β, are constants, and t is time at constant strain. A non-Newtonian flow equation utilizing this viscoelastic concept of yield value which has been devised and used in these laboratories is as follows

$$\eta_a = F/S = Ae^{-\alpha S} + Be^{-\beta S} + \eta_\infty \quad \text{(Eq. 7)}$$

where η_a is the apparent viscosity at a given shear, S, and η_∞ is the ultimate high shear viscosity. This equation has been found to fit a variety of experimental flow curves quite accurately without the assumption of a fixed yield value. Equations of this type have been used for viscoelastic bodies, being represented by models containing two Maxwell elements in parallel (17). It might be expected that more or fewer exponential terms may be required for a given system, since the number will depend on the breadth of distribution of relaxation times of the non-Newtonian components.

The work reported in this paper illustrates the application of Eq. 7, called the "viscoelastic flow equation," to a series of emulsions.

EXPERIMENTAL

Preparation of Emulsions.—A sol was prepared by adding methylcellulose 1,500 cps., with stirring, to about one-half the calculated amount of water, previously heated to 70°. A preservative consisting of 0.1% of a mixture of three parts methylparaben

and one part propylparaben was dissolved in the hot water before incorporation of the methylcellulose. The mixture was made up to volume with cold water and stirred with chilling until its temperature was 0–5°; it was then stored in a refrigerator for at least 2 days before being used. The concentration of methylcellulose was accurately determined by drying a weighed sample of the final sol.

A basic corn oil emulsion was prepared with 60% corn oil ($\eta = 0.4449$), 5% of a mixture of three parts of Span 80 and one part of Tween 80, and 35% water. The emulsion was homogenized in a Manton-Gaulin homogenizer (model 15M8BA) at 3000 lb./in.². Droplet size of the dispersed phase was found to be quite uniform, 90% of the particles being in the range of 0.5–3 μ, and the size varied little with variation in homogenization pressure or with dilution with varying amounts of methylcellulose sol or water. Emulsions containing varying concentrations of oil and methylcellulose were obtained by dilution of the basic emulsion with water and methylcellulose sol, so that only one lot of basic emulsion and sol were used throughout the study. The final emulsions were stirred gently to remove air and allowed to stand at room temperature for 3 days before measurement.

Measurement of Flow Properties.—The emulsions were placed in an automatic recording viscometer with rotating cup and fixed bob (18). Shear rates were varied from 129 to 2,500 sec.$^{-1}$, and from the recorded curves data points representing 19 equally spaced intervals of shear were recorded for computation.

Computation of Flow Constants.—From the shear-stress data, values of η_a were calculated and plotted *vs.* S on 12 $\times$ 18 inch graph paper. These were placed on an X-Y recorder and fitted to the viscoelastic flow equation by means of an analog computer. Values of the constants were read directly from the computer.

Results.—Since the original stress-shear data are quite extensive and would require excess space, they are not reproduced in this paper. They are available, however, in the original thesis (18). The constants of the viscoelastic flow equation are presented in Table I. The constants of the equation were used to compute limiting viscosities, η_0, by the following relationship

$$\eta_0 = \lim_{S \to 0} \eta_a = A + B + \eta_\infty$$

These, in turn, were used to calculate values of ϕ_r, which were plotted *vs.* C_v to obtain slopes comparable

to Einstein's constant. Constants of the viscoelastic flow equation and values of ϕ_r are presented in Table I, and slopes, or intrinsic viscosities, are given in Table II, along with values calculated from Taylor's equation. A typical curve fitted on the computer is shown in Fig. 1, a typical fluidity plot is given in Fig. 2, and the relationship between values of k and η_2 are presented in Fig. 3.

DISCUSSION

It was found that the viscoelastic flow equation fitted all the flow curves of this series of emulsions quite well. The fitting of five constants, however,
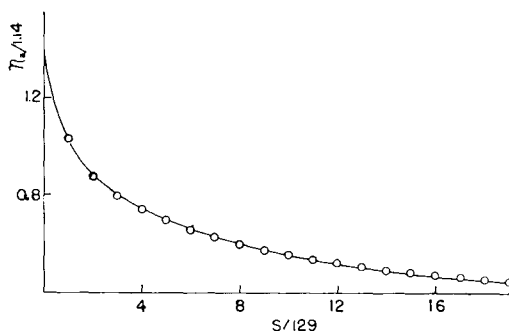

Fig. 1.—Typical flow curve for emulsion. Oil, 16.2%, methylcellulose 1.170%. Circles represent experimental points; line is computer-drawn.
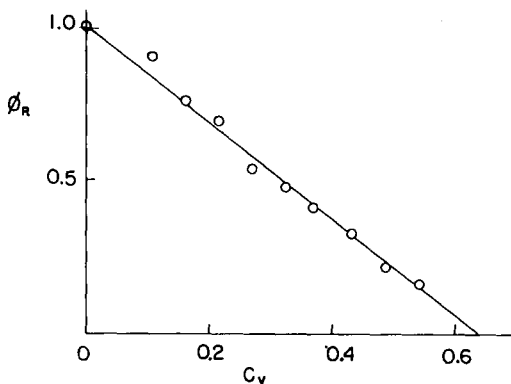

Fig. 2.—Typical fluidity plot, for 0.651% methylcellulose as continuous medium.

TABLE I.—CONSTANTS OF THE VISCOELASTIC FLOW EQUATION AND RELATIVE FLUIDITIES

Methyl-cellulose, % w/v	Corn Oil, % v/v	A Poises	B Poises	η_∞ Poises	$\alpha \times 10^3$ sec.	$\beta \times 10^2$ sec.	ϕ_r
0.326	0.0	0.0094	0.0440	0.0440	0.798	0.593	1.0000
	10.8	0.0212	0.0418	0.0728	1.426	0.655	0.7172
	16.2	0.0183	0.0533	0.0655	1.112	0.880	0.7104
	21.6	0.0185	0.0755	0.0749	0.977	1.019	0.5767
	27.0	0.0309	0.0819	0.0898	1.159	0.922	0.4808
	32.4	0.0278	0.0910	0.0949	1.225	0.915	0.4558
	37.9	0.0593	0.1191	0.1399	1.225	1.070	0.3060
	43.3	0.0772	0.1789	0.1416	1.151	1.070	0.2449
	48.7	0.1463	0.2497	0.1923	1.178	1.070	0.1656
	54.2	0.2684	0.3768	0.2474	1.426	0.911	0.1091

TABLE I (*continued*)

Methyl-cellulose, % w/v	Corn Oil, % v/v	A Poises	B Poises	η_∞ Poises	$\alpha \times 10^3$ sec.	$\beta \times 10^2$ sec.	ϕr
0.434	0.0	0.0168	0.0600	0.0710	0.837	0.601	1.0000
	10.8	0.0251	0.0688	0.0872	0.709	0.702	0.8161
	16.2	0.0359	0.0593	0.0948	0.806	1.194	0.7779
	21.6	0.0318	0.0497	0.1131	0.961	0.674	0.7595
	27.0	0.0583	0.0963	0.1146	0.953	0.880	0.5490
	32.4	0.0742	0.0745	0.1468	0.953	1.039	0.5002
	37.9	0.1002	0.1248	0.1723	0.953	0.845	0.3720
	43.3	0.1262	0.1318	0.1968	0.829	0.465	0.3250
	48.7	0.1724	0.3095	0.2376	0.860	0.640	0.2054
	54.2	0.3795	0.4933	0.2994	1.229	0.829	0.1261
0.543	0.0	0.0405	0.0510	0.1015	1.050	0.671	1.0000
	10.8	0.0459	0.0436	0.1163	0.791	0.957	0.9378
	16.2	0.0488	0.0491	0.1307	0.891	0.911	0.8443
	21.6	0.0702	0.0834	0.1458	0.783	0.911	0.6446
	27.0	0.0718	0.0898	0.1610	0.597	0.481	0.5983
	32.4	0.0944	0.0997	0.1829	0.705	0.512	0.5119
	37.9	0.1380	0.1895	0.2144	0.950	0.814	0.3562
	43.3	0.1966	0.2439	0.2345	0.853	0.814	0.2859
	48.7	0.2954	0.3337	0.2890	1.046	0.744	0.2102
	54.2	0.3787	0.7670	0.3418	0.950	0.667	0.1297
0.651	0.0	0.0872	0.0669	0.1285	0.558	1.209	1.0000
	10.8	0.0974	0.0559	0.1606	0.616	0.450	0.9003
	16.2	0.1238	0.0541	0.1865	0.833	0.864	0.7548
	21.6	0.1476	0.0673	0.1944	0.833	0.841	0.6904
	27.0	0.1670	0.1443	0.2190	0.903	0.880	0.5329
	32.4	0.2028	0.1596	0.2309	0.717	0.791	0.4763
	37.9	0.2281	0.1971	0.2666	0.740	0.547	0.4085
	43.3	0.3079	0.2619	0.3014	0.764	0.574	0.3244
	48.7	0.3981	0.5849	0.3396	0.702	0.562	0.2137
	54.2	0.5887	0.7943	0.3868	0.833	0.655	0.1597
0.780	0.0	0.1286	0.0664	0.1735	0.767	0.659	1.0000
	10.8	0.1448	0.0917	0.1886	0.473	0.244	0.8669
	16.2	0.1703	0.0258	0.2359	0.853	0.481	0.8530
	21.6	0.1899	0.1093	0.2302	0.853	0.721	0.6961
	27.0	0.2323	0.1052	0.2653	0.795	0.430	0.6113
	32.4	0.2796	0.1864	0.2940	0.798	0.574	0.4849
	37.9	0.4643	0.3497	0.3825	0.981	0.705	0.3080
	43.3	0.4496	0.5510	0.3804	0.981	0.578	0.2668
	48.7	0.5516	0.7150	0.4485	0.981	0.721	0.2149
	54.2	0.6360	1.2299	0.4625	0.771	0.942	0.1583
1.002	0.0	0.2387	0.1789	0.2711	0.593	0.198	1.0000
	10.8	0.3690	0.3093	0.3203	0.886	1.260	0.6897
	16.2	0.3668	0.3832	0.3403	0.886	0.578	0.6317
	21.6	0.3905	0.3394	0.3832	0.822	0.453	0.6187
	27.0	0.4854	0.2609	0.4270	0.961	0.453	0.5870
	32.4	0.5597	0.5044	0.3805	0.671	0.628	0.4767
	37.9	0.5475	0.5091	0.4750	0.798	0.388	0.4497
	43.3	0.6922	0.7071	0.5063	0.860	0.465	0.3614
	48.7	0.8183	1.0831	0.5746	0.919	0.484	0.2782
	54.2	0.9837	1.5268	0.6427	0.922	0.461	0.2184
1.170	0.0	0.5352	0.3303	0.3325	0.674	0.578	1.0000
	10.8	0.6577	0.3471	0.4248	0.961	0.899	0.8380
	16.2	0.6783	0.5412	0.4659	1.074	1.101	0.7108
	21.6	0.6787	0.5557	0.4965	0.934	0.694	0.6921
	27.0	0.7837	0.5262	0.5019	0.895	0.655	0.6612
	32.4	0.8929	0.7083	0.5576	0.969	0.752	0.5549
	37.9	0.9305	1.0850	0.5726	0.860	0.643	0.4629
	43.3	1.0732	1.3143	0.6327	0.891	0.578	0.3967
	48.7	1.2111	1.6743	0.6502	0.891	0.597	0.3388
	54.2	1.4789	2.4507	0.7586	1.027	0.640	0.2555
1.337	0.0	0.9380	0.3622	0.5324	1.085	0.647	1.0000
	10.8	0.8580	0.7305	0.5178	0.756	0.469	0.8701
	16.2	0.8610	0.7329	0.5422	0.760	0.469	0.8579
	27.0	1.2201	0.8764	0.6702	0.973	0.554	0.6624
	32.4	1.4200	1.1021	0.7121	1.089	0.729	0.5666
	37.9	1.4793	1.5896	0.7630	1.050	0.694	0.4782
	43.3	1.5302	1.8524	0.7630	0.946	0.578	0.4421
	48.7	1.6955	2.6111	0.7960	0.953	0.601	0.3592
	54.2	1.5514	3.1197	0.8478	0.903	0.461	0.3304

TABLE II.—RELATIONSHIP OF INTRINSIC VISCOSITY OF EMULSION, k, TO VISCOSITY OF CONTINUOUS PHASE, η_2

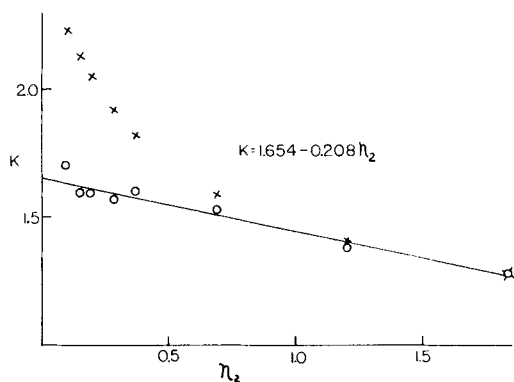| η_2, Poises	Found, k	k Calcd. from Taylor's Equation
0.0974	1.699	2.231
0.1478	1.585	2.126
0.1930	1.587	2.046
0.2826	1.572	1.917
0.3685	1.595	1.821
0.6887	1.527	1.589
1.1980	1.384	1.406
1.8326	1.283	1.280

Fig. 3.—Relationship between k and η_2. Circles represent experimental points, X's are values calculated from Taylor's equation. The least squares equation for the line is given.

allows errors in one to be corrected for by errors in another, so that a given constant might not vary in a regular fashion with increases in concentration of emulsion. Nevertheless, the complete equation describes the flow curve quite accurately and the combined constants, such as η_0, do vary in an orderly manner. One might question whether a single value of α and β would suffice for a complete series involving a given suspending agent, since most of the non-Newtonian character might be ascribed to this component. This was attempted, using an approximate average value for α and β, but the errors were increased considerably by this procedure, while approximately the same values of intrinsic viscosity were obtained. It is obvious that accuracy of evaluation of the constants can be improved by extending the range of shear of the measurements.

Values of ϕ_r were invariably linear with respect to C_v, which supports the concept of Ford that fluid-

ities are the terms of choice in evaluating intrinsic viscosity. These findings also favor the use of the viscoelastic flow equation for obtaining low shear viscosities.

From Fig. 3 it is seen that a linear relationship appears to exist between intrinsic viscosity and viscosity of the suspending medium. This is not in agreement with Taylor's equation which predicts nonlinearity throughout the range of η_2. The discrepancy could not be attributed to the formation of a hydrated sheath to give the particle a hydrodynamic volume above the apparent volume, since in such case the constants would be greater than 2.5. Neither could this be attributed to an apparently consistent decrease in viscosity of one of the components, since such a prediction would still call for the nonlinear portion described by Taylor's equation. Doublet formation or aggregation would yield high values for k. Thus, by elimination, the failure to agree with Taylor's equation at low values of η_2 is perhaps best explained by slippage of an adsorbed layer at the surface of the particles, as suggested by Oldroyd (3). It does seem reasonable that the degree of slippage might decrease with increase in η_2, since the layer involved would most likely be of a modified stratum of the medium itself.

These results indicate that the viscoelastic flow equation is of value in describing non-Newtonian flow data. It has the advantage of fitting the observed flow curves quite well without requiring a rigid yield value. It seems likely to have wide applicability by modification of the number of exponential terms, and extrapolated values of limiting viscosity appear to be useful in investigating basic relationships.

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