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A Mechanism for Non-Newtonian Flow in Suspensions of Rigid Spheres

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Introduction

Many colloidal suspensions and solutions of macromolecules exhibit a viscosity which decreases with increasing rate of shear. This non-Newtonian behavior has been attributed to mechanisms in which the shear stress, transmitted through the continuous medium, orients or distorts the suspended particles in opposition to the randomizing effects of Brownian motion. Variation of viscosity with shear rate is then a result of the lowered resistance to flow offered by the oriented or distorted arrangement. Kirkwood and Plock's¹ explanation of the viscosity of suspensions of rigid ellipsoids and F. Bueche's² theory for solutions involve this type of mechanism.

A more general theory of non-Newtonian flow, based on Eyring's theory of rate processes,³ has been developed by Ree and Eyring.⁴ In this theory the viscosity is the sum of contributions of an indefinite number of unspecified "flow units." Since it is not based on any particular model, the Ree-Eyring theory should be applicable to all systems. Unfortunately, the number of parameters required to describe the behavior of a given fluid is not fixed by the theory, nor is it possible to deduce the values of these parameters from other known properties of the system. Reference to a forerunner of the Ree-Eyring theory, in a paper by Tobolsky, Powell, and Eyring,⁵ discloses a point of similarity between this theory and the orientation-distortion theories mentioned earlier. Both involve a competition between shearing and thermal forces, and in this competition the size of the suspended particle plays a determining role.

* Firestone Tire and Rubber Fellow. This work forms part of the doctoral dissertation of T. J. Dougherty.

Suspensions of rigid spherical particles are known to exhibit non-Newtonian viscosity, but theories involving orientation or distortion are based on models which are not appropriate to isotropic rigid particles. The Ree-Eyring flow equation has been applied to such a system by Maron and Pierce.⁶ Using two flow units, one for the aqueous medium and the second for the spherical polymer particles, these authors were able to fit the viscometric data of Maron and Fok⁷ for a synthetic rubber latex. In their attempts to relate the fitted parameters to known properties of the system, however, Maron and Pierce achieved only limited success.

An important clue to the cause of non-Newtonian behavior in rigid sphere suspensions is the observation by Maron and his co-workers⁷⁻¹⁰ that the behavior of such systems is Newtonian up to relatively high concentrations; in none of their latex systems did they detect non-Newtonian behavior at concentrations below 20% by volume of suspended polymer. This fact suggests that crowding plays a vital role in the origin of non-Newtonian flow behavior in rigid sphere suspensions. The theory developed in this paper, therefore, takes explicit notice of the interactions between neighboring spherical particles. The resultant flow equation is compared with experimental viscometric data on synthetic latexes and solutions of high polymers.

Derivation of the Flow Equation

Consider a suspension of rigid spheres of radius a in a continuous medium of viscosity η_s . When a shear stress τ is applied, causing the suspension to flow with an overall rate of shear $\dot{\gamma}$, the individual spheres will tend to rotate with an angular velocity $\dot{\gamma}/2$, dragging with them the medium adhering to their surfaces. However, because of concentration fluctuations arising from Brownian movement, there will be at any instant pairs of spheres whose separation is small, i.e., of the order of one diameter. If these nearby spheres were to rotate independently, the shear rate in the medium between the spheres would be inordinately high, as may be seen in Figure 1A. To avoid the consequent high energy dissipation rate, the nearby spheres will tend to rotate as a dumbbell about their center of mass until the shearing motion has caused them to separate. Figure 1B illustrates the hypothetical dumbbell rotation, while Figure 1C is a more realistic picture, intermediate between the other two.

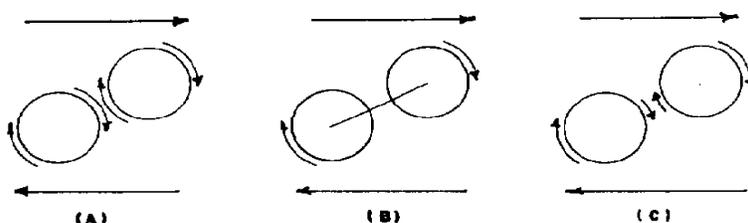


Fig. 1. (A) Schematic diagram of flow pattern if nearby spheres were to rotate independently. (B) Schematic flow pattern if they were to rotate as rigid dumbbell. (C) Diagram of actual flow pattern.

The behavior described above can be treated quantitatively in the following approximate manner. If the separation between two spheres permits them to rotate independently of each other, the spheres will be called singlets and denoted by P_1 ; if the pair of spheres tends to rotate as a dumbbell, the pair will be called a doublet and denoted by P_2 . In the absence of shearing forces, the distribution of singlets and doublets can be represented formally as a chemical equilibrium:



Here k_f and k_b represent the specific rate constants for the formation and dissociation of doublets, respectively. Imposition of a shearing force introduces a second mechanism for the decomposition of doublets, since they will be separated during the dumbbell rotation.



Here k_s is the specific rate constant for the shear-induced dissociation. Letting n_1 and n_2 be the number of singlet and doublet particles respectively per unit volume, an overall rate equation can be written for the net rate of doublet formation:

$$dn_2/dt = k_f n_1^2 - (k_b + k_s)n_2 \quad (3)$$

The condition for a steady state is $dn_2/dt = 0$, and hence

$$\frac{n_2}{n_1^2} = \frac{k_f}{k_b + k_s} = \frac{k_f}{k_b} \left(1 + \frac{k_s}{k_b}\right)^{-1} \quad (4)$$

Since k_s will be zero in the absence of shear forces, the zero-shear concentrations of singlets and doublets, denoted by \bar{n}_1 and \bar{n}_2 respectively, will obey the relationship

$$\bar{n}_2/\bar{n}_1^2 = k_f/k_b \quad (5)$$

At this point it is necessary to postulate a relationship between the viscosity of the suspension, $\eta = \tau/\dot{\gamma}$, and the concentrations of singlets and doublets. We assume that

$$\eta/\eta_s = f_1 n_1 + f_2 n_2 = f_1 n + (f_2 + 2f_1)n_2 \quad (6)$$

Here n is the total concentration of spheres,

$$n = n_1 + 2n_2 \quad (7)$$

The factors f_1 and f_2 are assumed to be functions of n , but independent of $\dot{\gamma}$. At zero shear rate n_2 will equal \bar{n}_2 , and hence the viscosity η_0 in this limit will be

$$\eta_0/\eta_s = f_1 n + (f_2 - 2f_1)\bar{n}_2 \quad (8)$$

At infinite shear rate, all doublets will be dissociated, and hence n_2 will be zero. The viscosity η_∞ at infinite shear rate will then be given by

$$\eta_\infty/\eta_s = f_1 n \quad (9)$$

Equations (6), (8), and (9) may be combined to give

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{n_2}{\bar{n}_2} \quad (10)$$

and from eqs. (4) and (5),

$$\frac{n_2}{\bar{n}_2} = \frac{n_1^2}{\bar{n}_1^2} \left(1 + \frac{k_s}{k_b}\right)^{-1} \quad (11)$$

We now assume that only a small fraction of the spheres will be paired as doublets, and hence that n_1 and \bar{n}_1 are not greatly different from n . With this assumption, eqs. (10) and (11) combine to give

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left(1 + \frac{k_s}{k_b}\right)^{-1} \quad (12)$$

To evaluate their ratio, we make use of the fact that k_s and k_b are first-order rate constants for the decomposition of a doublet by the different mechanisms and hence each is reciprocally related to the corresponding mean lifetime. Letting t_b be the mean lifetime of a doublet undergoing thermal dissociation and t_s the mean lifetime of a doublet dissociating solely by shearing forces, we obtain

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left(1 + \frac{t_b}{t_s}\right)^{-1} \quad (13)$$

The lifetime of a doublet dissociating under shear is the time required for the dumbbell to rotate to a position such that the two spheres are in different lamina so that they can separate. Taking the angular velocity of the dumbbell as $\dot{\gamma}/2$ and estimating the angle of rotation as $\pi/2$, we obtain

$$t_s = \left| \frac{\alpha_1 \pi / 2}{\dot{\gamma} / 2} \right| = \alpha_1 \pi / |\dot{\gamma}| \quad (14)$$

(The absolute value is necessary since t_s must be positive, and a factor α_1 is included because of the approximation involved in the value of the angle.) The mean lifetime under thermal decomposition is taken as the time required for the two particles to diffuse apart a distance X ,

$$t_b = \overline{X^2} / 2D \quad (15)$$

The diffusion constant D is given by the Stokes-Einstein relation

$$D = kT / 6\pi a \eta \quad (16)$$

We are assuming here that the diffusion constant of the particle is governed by $\eta = \tau / \dot{\gamma}$, the viscosity of the medium at the prevailing rate of shear. Combining eqs. (15) and (16) we obtain

$$t_b = 3\pi \eta a \overline{X^2} / kT \quad (17)$$

From dimensional considerations it is evident that the magnitude of X , the distance the two particles of a doublet must diffuse apart before they can be considered to be singlets, is proportional to the particle radius a , and hence

$$\overline{X^2} = \alpha_2 a^2 \quad (18)$$

Thus eq. (17) becomes

$$t_b = 3\pi\eta\alpha_2 a^3/kT \quad (19)$$

(Einstein's analysis¹¹ of the distribution under shear of the velocity of the medium about a spherical particle leads us to believe that α_2 should be close to unity.)

The ratio of mean lifetimes is then

$$t_b/t_s = 3\alpha_2 a^3 \eta |\dot{\gamma}| / \alpha_1 kT = 3\alpha^3 |\tau| / \alpha kT = |\tau| / \tau_c \quad (20)$$

where $\alpha = \alpha_1/\alpha_2$ and

$$\tau_c = \alpha kT / 3\alpha^3 \quad (21)$$

Equation (13) then becomes

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left(1 + \frac{|\tau|}{\tau_c}\right)^{-1} \quad (22)$$

This relation between η and τ is our flow equation. Except for the significance attached to τ_c and the use of the absolute magnitude of the shear stress, our flow equation is identical to that proposed on empirical grounds by Williamson¹² and by Peek and MacLean.¹³

Test of the Equation of Flow

The proposed mechanism was tested by fitting the resultant flow eq. (22) to previously published experimental data obtained in this laboratory for two synthetic latex suspensions and a polymer solution. The data of Maron and Fok described the behavior of a butadiene-styrene latex whose average particle diameter was 1390 A. as measured by conductimetric soap titration. Maron and Levy-Pascal's data for a Neoprene latex of 1100 A. diameter were also used for this test, although the presence of an alginate-type creaming agent conferred somewhat anomalous flow behavior on this latex. The polymer solution data of Maron, Nakajima, and Krieger¹⁴ describe the viscosity of a solution of polystyrene of molecular weight 250,000 in *o*-dichlorobenzene. For each of the three sets of measurements, the experimental temperature was 30°C.

The following procedure was used in fitting the flow equation to the experimental data. By inspection of the data, a trial value of τ_c is selected to correspond to a viscosity midway between estimated high

and low-shear limiting values. A graph of the viscosity η vs. $\tau_c/(\tau + \tau_c)$ is prepared; if the selected value of τ_c is correct, the experimental points should lie on a straight line. If the points indicate a curvature, a new value of τ_c is selected and the process repeated until a linear graph is obtained. The intercept of this graph is η_∞ and the slope is $\eta_0 - \eta_\infty$. In this manner, the fitted values of τ_c , η_0 , and η_∞ were obtained for each of the three systems at the various concentrations.

For each of the two latex systems studied, essentially the same value of τ_c was found at all concentrations. In other words, τ_c was found to

TABLE I
Values of Parameters of Flow Equations

Volume fraction, v	τ_c , dynes/cm. ²	η_∞/η_s	η_0/η_s
Data of Maron and Fok			
0.2990	46	3.070	3.532
0.3970	"	5.421	7.499
0.4398	"	7.330	12.689
0.4876	"	10.907	24.193
0.5390	"	18.39	88.80
0.5603	"	26.92	167.08
0.5866	"	44.67	448.1
0.6017	"	48.0	1048.0
Data of Maron and Levy-Pascal			
0.2393	20	2.711	3.151
0.2821	"	3.561	4.599
0.3263	"	4.871	7.168
0.3713	"	7.040	13.690
0.4147	"	11.37	31.39
0.4429	"	15.65	66.95
0.4617	"	30.60	165.72
0.5115	"	86.08	1199.4
Data of Maron, Nakajima, and Krieger			
0.02986	1000	6.205	8.619
0.04516	1500	9.56	17.54
0.06627	2000	22.03	35.38
0.09625	2000	23.85	85.40
0.12102	4000	57.64	173.53
0.14549	5000	52.30	398.3
0.15948	10000	25.3	921.3
0.17556	10000	151.7	1673.7

be independent of concentration for these systems. For the polymer solutions, however, the fitted τ_c values increased regularly with increasing concentration. Table I lists the values obtained for the parameters τ_c, η_0 , and η_∞ for each system and concentration. Due to experimental scatter in the polymer solution data, the accuracy with which the parameters could be determined was considerably lower than for the latexes.

To test the accuracy of the flow equation, the viscosities were calculated at the experimental shear stresses, using the tabulated values of the parameters. Comparison of observed and calculated values is shown in Tables II-IV. For the latex suspensions, agreement between calculated and observed viscosities was within 1% for all except the three highest concentrations; even for these concen-

TABLE II
Comparison of Calculated and Observed Relative Viscosities. Data of Maron and Fok

τ , dynes/ cm. ²	$v = 0.2990$			$v = 0.4876$			$v = 0.5866$		
	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	% error	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	% error	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	% error
50	3.293	3.291	0.06	17.18	17.28	0.58	404.10	238.16	41.1
100	3.218	3.216	0.06	15.17	15.10	0.46	208.78	171.77	17.7
200	3.157	3.156	0.03	13.44	13.39	0.37	122.21	120.11	1.72
300	3.132	3.131	0.03	12.70	12.68	0.16	96.58	98.28	1.76
500	3.110	3.109	0.03	12.03	12.03	0.00	79.28	78.68	0.76
800	—	—	—	11.66	11.63	0.26	68.01	66.62	2.04
	$v = 0.3970$			$v = 0.5390$			$v = 0.6017$		
50	6.424	6.417	0.11	52.20	52.12	0.15	1089.3	527.1	51.6
100	6.081	6.076	0.08	40.02	40.58	1.40	464.0	363.1	21.8
200	5.802	5.810	0.03	31.55	31.56	0.03	241.8	235.0	2.8
300	5.689	5.697	0.14	27.96	27.75	0.75	176.9	180.9	2.3
500	5.607	5.596	0.20	24.51	24.33	0.73	131.2	132.3	0.84
800	—	—	—	21.98	22.22	1.09	105.3	102.4	2.7
	$v = 0.4398$			$v = 0.5603$					
50	9.879	9.897	0.28	107.07	94.07	12.14			
100	8.993	9.019	0.29	71.18	71.08	0.14			
200	8.363	8.332	0.37	52.20	53.13	1.78			
300	8.082	8.042	0.49	45.39	45.55	0.35			
500	7.790	7.782	0.10	39.15	38.74	1.05			
800	7.597	7.621	0.32	34.80	34.54	0.75			

trated suspensions the agreement is within experimental error except for the low shear stress range. The low-shear, high-concentration points are in the region where triplet and higher multiplet interactions are important, so that the discrepancies in this range are not unexpected. (In fact, these data can be fitted quite well by using smaller values of τ_c , corresponding to an increase in the average dimensions of the interacting particles.) For the polymer solutions, the deviations between observed and calculated values range up to 5%. In view of the larger experimental error in these data, this is considered to be a reasonably good fit.

Since the average radii of the particles is known for the butadiene-styrene latex, it is possible to compute the factor α in eq. (21), namely

$$\alpha = 3a^3\tau_c/kT \quad (23)$$

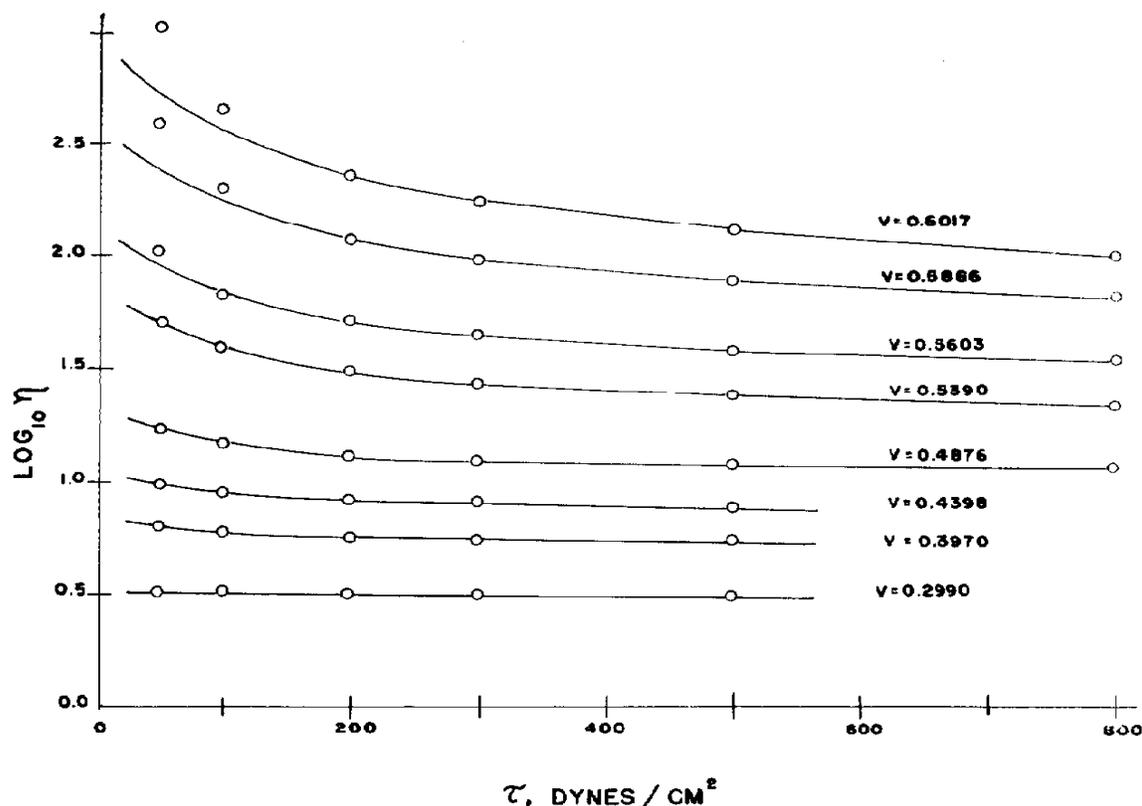


Fig. 2. Graphical comparison of observed (points) and calculated (solid line) viscosities using the experimental data of Maron and Fok.

TABLE III
Comparison of Calculated and Observed Relative Viscosities. Data of Maron
and Levy-Pascal

τ dynes/ cm. ²	$v = 0.2393$			$v = 0.3713$			$v = 0.4617$		
	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	% error	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	% error	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	% error
30	2.888	2.887	0.03	9.712	9.700	0.12	88.85	84.65	4.7
50	2.834	2.837	0.10	8.910	8.940	0.33	69.61	69.20	0.58
100	2.779	2.784	0.18	8.088	8.149	0.75	52.31	53.12	1.54
150	2.759	2.763	0.14	7.799	7.822	0.29	45.89	46.49	1.30
200	2.751	2.751	0.00	7.640	7.644	0.05	42.40	42.88	1.13
300	2.745	2.739	0.22	7.459	7.456	0.04	38.91	39.05	0.35
500	2.744	2.728	0.58	7.311	7.296	0.20	35.79	35.80	0.03
800	—	—	—	—	—	—	33.88	33.90	0.06
	$v = 0.2821$			$v = 0.4147$			$v = 0.5115$		
30	3.984	3.976	0.20	19.34	19.38	0.21	—	—	—
50	3.851	3.858	0.18	17.09	17.09	0.00	481.8	404.2	15.9
100	3.714	3.734	0.53	14.80	14.71	0.61	278.4	271.7	2.41
150	3.667	3.683	0.43	13.81	13.72	0.65	214.1	217.0	1.35
200	3.651	3.655	0.11	13.29	13.19	0.75	186.2	187.3	0.59
300	3.633	3.626	0.19	12.72	12.62	0.78	156.2	155.7	0.32
500	3.621	3.601	0.55	12.22	12.14	0.66	131.0	129.0	1.52
800	—	—	—	11.85	11.86	0.08	113.1	113.2	0.09
	$v = 0.3263$			$v = 0.4429$					
30	5.793	5.790	0.05	36.47	36.17	0.82			
50	5.539	5.527	0.21	30.29	30.31	0.07			
100	5.247	5.254	0.13	23.70	24.20	2.10			
150	5.139	5.141	0.04	21.37	21.68	1.44			
200	5.083	5.080	0.06	20.12	20.31	0.94			
300	5.023	5.015	0.16	18.97	18.86	0.58			
500	4.951	4.959	0.16	17.95	17.63	1.78			
800	—	—	—	17.08	16.90	1.05			

Using 695 A. for a and 46 dynes/cm.² for τ_c , we obtain an α -value of 1.10; as anticipated, this value is close to unity. Using $\alpha = 1.10$ in conjunction with the τ_c value of 20 dynes/cm.² from Table I, we calculate for the Neoprene latex a particle radius of 920 A. as compared with Maron and Levy-Pascal's measured value of 550 A. The probable source of this discrepancy is the effect of the alginate thickener mentioned earlier.

TABLE IV
Comparison of Calculated and Observed Relative Viscosities. Data of Maron and Nakajima

τ , dynes/ cm. ²				τ , dynes/ cm. ²			
	$\eta_{\text{meas.}}$	$\eta_{\text{calc.}}$	% error		$\eta_{\text{meas.}}$	$\eta_{\text{calc.}}$	% error
$\nu = 0.04516$				$\nu = 0.14549$			
99	17.03	17.03	0.00	1291	308.7	322.9	4.60
207	16.55	16.55	0.00	3345	259.0	251.5	2.90
321	16.17	16.11	0.37	4817	223.7	218.6	2.28
435	15.80	15.73	0.44	9841	148.2	155.6	5.00
549	15.32	15.39	0.46	22685	102.5	98.5	3.90
$\nu = 0.09625$				$\nu = 0.17651$			
117	85.71	81.95	4.39	6500	1125	1074	4.67
308	78.81	77.15	2.11	16478	745	726	2.57
2076	54.82	54.01	1.48	22200	641	624	2.68
4120	44.59	43.92	1.50	30150	522	531	1.65
8315	38.93	39.18	0.64	50050	394	405	2.67

TABLE V
Concentration Dependence of Limiting Viscosities

Data of	λ	Low-shear limit		High-shear limit	
		η_0/η_s	p	η_∞/η_s	p
Maron and Fok	1.119	2.76	0.670	2.58	0.782
Maron and Levy-Pascal	1.093	3.44	0.541	2.79	0.591

The increase of τ_c with concentration exhibited by the polymer solutions implies that the polymer molecule, regarded as a spherical particle, progressively shrinks as concentration increases, changing in volume over a 10-fold range. Maron, Nakajima, and Krieger arrived at a similar conclusion from the concentration dependence of η_∞ , which they obtained by fitting the experimental data to the Ree-Eyring flow equation. The dimension a computed from the extrapolated zero-concentration value of τ_c is of the order of magnitude of the average end-to-end chain length of a freely-jointed polymer chain of 2300 styrene monomer units, corresponding to the given molecular weight.

TABLE VI
Limiting Viscosities in the Newtonian Range

Volume fraction, v	$(\eta/\eta_s)_{obs.}$	η_{∞}/η_s	η_0/η_s
Data of Maron and Fok			
0.0000	1.000	1.000	1.000
0.0306	1.089	1.093	1.139
0.0515	1.164	1.166	1.181
0.1010	1.361	1.369	1.408
0.1795	1.845	1.821	1.933
0.2481	2.491	2.420	2.688
Data of Maron and Levy-Pascal			
0.0000	1.000	1.000	1.000
0.0091	1.009	1.012	1.035
0.0391	1.106	1.136	1.166
0.0769	1.283	1.288	1.370
0.1160	1.513	1.489	1.642
0.1560	1.775	1.755	2.023
0.1975	2.257	2.118	2.585

Concentration Dependence of Parameters

The parameters of the flow equation which were obtained for the three systems by the fitting procedure described above vary in a regular manner with volume fraction. Because the behavior of τ_c for the polymer solution indicates a variation in the size of the unit of flow, it can not be properly considered as a suspension of rigid spheres. The constancy of τ_c for the two latexes, however, has led us to attempt to apply functional relationships for the concentration dependence of the viscosity of rigid sphere suspensions to the variation of η_0 and η_{∞} with volume fraction v .

Those functional relationships which have been proposed and successfully applied over a wide concentration range have two features in common. (1) At very low concentrations, they all reduce to the linear form

$$\eta/\eta_s = 1 + [\eta]v \quad (24)$$

where $[\eta]$ is the "intrinsic viscosity;" and (2) at some characteristic volume fraction p the viscosity becomes infinite. The quantity p is called the packing fraction, since the approach to infinite viscosity is usually ascribed to the attainment of a close-packed structure. Two well-known equations of this form are those of Eilers¹⁵

$$\eta/\eta_s = \left[\frac{1 + \frac{1}{2}[\eta]v}{1 - v/p} \right]^2 \quad (25)$$

and of Mooney¹⁶

$$\ln(\eta/\eta_s) = [\eta]v/(1 - v/p) \quad (26)$$

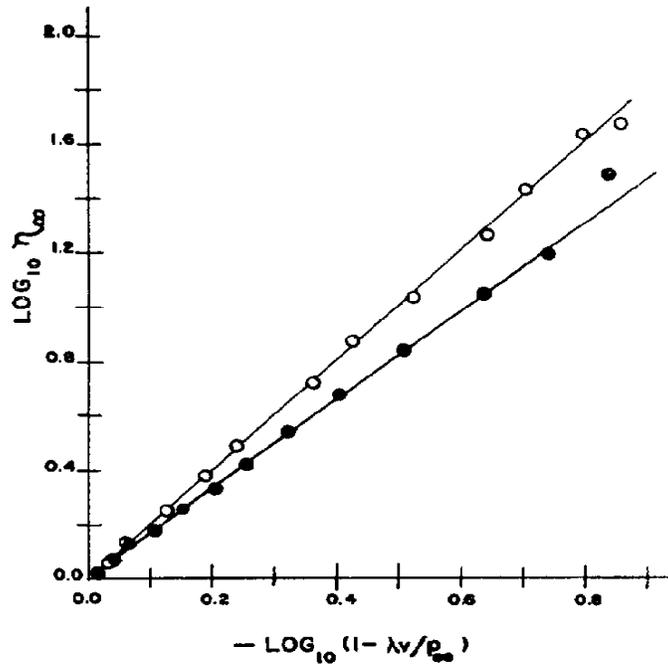


Fig. 3. Graphical test of eq. (29) for high-shear limiting viscosity data. Straight lines are calculated results. Filled circles represent data of Maron and Levy-Pascal; unfilled circles the data of Maron and Fok.

These equations can be fitted to our values of η_0 and η_∞ over most of the concentration range, but an excellent fit over the entire range was obtained using an equation derived by a modification of Mooney's functional analysis:

$$\eta/\eta_s = (1 - v/p)^{-b[\eta]} \quad (27)$$

The derivation of this relationship will be published elsewhere. Because of the adsorbed soap monolayer on the latex particles, the volume fraction of spherical particles is λv rather than v , where λ has been shown to be

$$\lambda = 1 + 6\Delta/D_s \quad (28)$$

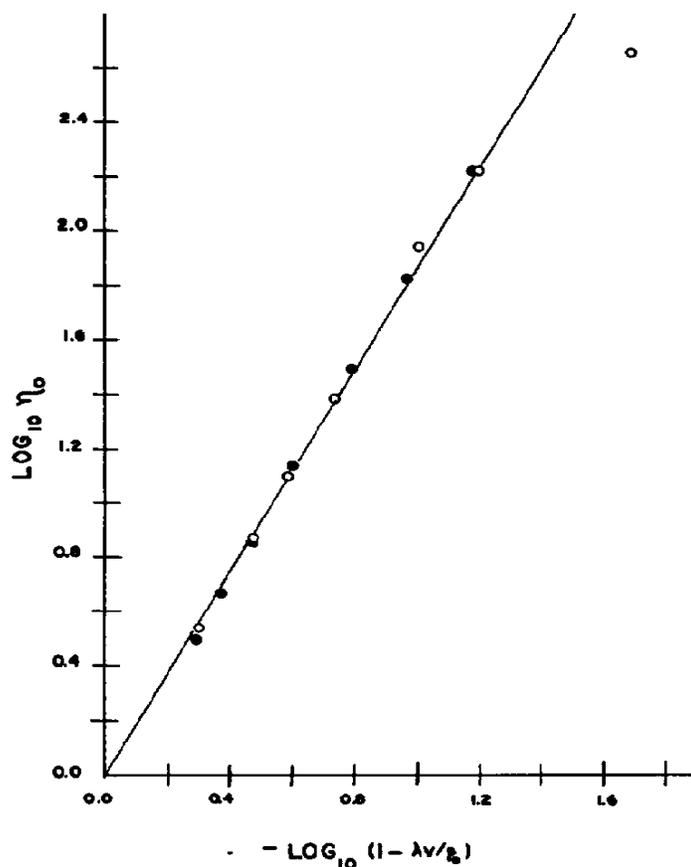


Fig. 4. Graphical test of eq. (29) for low-shear limiting viscosities. Filled circles represent the data of Maron and Levy-Pascal; unfilled circles the data of Maron and Fok.

Here Δ is the thickness of the soap monolayer and D_s the average diameter of the polymer sphere. Equation (27) was modified by substituting λv for v , and written in logarithmic form:

$$\ln (\eta/\eta_s) = -p[\eta] \ln (1 - \lambda v/p) \quad (29)$$

Table V lists the values of λ given by Maron et al., and also the values of $[\eta]$ and p obtained by fitting both high and low-shear limiting viscosities for the two latexes. The goodness of fit can be judged from Figures 3 and 4, which is a graph of eq. (29) together with data from Tables I and II. The values for $[\eta]$ are quite close to Einstein's theoretical prediction of $5/2$ except for the low-shear value for the

Neoprene latex, where the presence of the thickening agent is presumably affecting the intrinsic viscosity.

One further point which requires elaboration is the fact that observed flow behavior of the latexes was Newtonian at volume fractions below ca. 0.20, whereas a small but not negligible difference between η_0 and η_∞ is indicated from the fitted equations. This discrepancy as shown in Table VI is a real one; the Newtonian viscosities observed in this concentration range fall between the calculated η_0 and η_∞ , and can be represented well by η_∞ . A possible explanation is that in this range the counter-ion concentration is not yet large enough to screen the coulombic repulsion between particles, which arises from the adsorbed soap anions, and hence doublet formation is prevented.

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Synopsis

A mechanism is postulated to account for non-Newtonian flow in suspensions of rigid spheres. On the basis of this mechanism, the flow equation $(\eta - \eta_\infty)/(\eta_0 - \eta_\infty) = (1 + |\tau/\tau_c|)^{-1}$ is derived, where η is the viscosity at the shear stress

τ , η_0 and η_∞ are the limiting values of η at zero and infinite shear, respectively, and τ_c is a parameter determined by temperature and particle size. This equation correlates well with published data on latex and polymer systems. For latex suspensions, the parameter τ_c does not depend on concentration and for these systems the dependence of the relative viscosity at a fixed shear stress, η_r , on volume fraction of suspended phase, v , is accurately described by the equation $\ln \eta_r = -p[\eta] \ln (1 - v/p)$, where $[\eta]$ is the intrinsic viscosity and p is the volume fraction at close-packing. In general, the parameters $[\eta]$ and p depend on the shear stress.