6) von Smoluchowski, M., Physik 17, 557, 585 (1916).

- Winkler, H. G. F., Kolloid-Z. 105, 29 (1943).
 8) Dintenfass, L., Paint J. Australia March, 9, (1957).
- 9) Moore, F., Trans. British Ceramic Soc. 58, 470 (1959).
- 10) Dintenfass, L., J. Oil & Colour Chem. Assoc. 41, 125 (1958).
 - 11) Dintențass, L., Kolloid-Z. 163, 48 (1959).
 - 12) Dintenfass, L., J. Appl. Chem. 8, 349 (1958).
 - 13) Dintenfass, L., Kolloid-Z. 170, 1 (1960).
- 13a) Osborne, D. G. and S. Thornton, Brit. J. Appl., Phys. 10, 214 (1959).
- 14) *Mill*, C. C., J. Oil & Colour Chem. Assoc. 43, 77 (1960).
- 15) Kobakhidze, E. I. and M. E. Shishniashvilli, Kolloidn. Zhur. 19, 59 (1957).

- 16) McDowell, C. M. and F. L. Usher, Proc. Royal Soc. (London) A 131, 409 and 546 (1931).
 - 17) Dintenfass, L., Chem. & Ind. 1957, 560.
 - 18) Dintenfass, L., Kolloid-Z. 155, 121 (1957).
 - 19) Dintenfass, L., Kolloid-Z. 161, 60 and 70 (1958).
 - 20) Mosikhin, E. P. and G. V. Vinogradov, Kolloidn.
- Zhur. 19, 311 (1957).
 20a) Deryaguin, B. V. and M. M. Samygin, Akad.
 Nauk SSSR 1, 59 (1941).
- 21) Nissan, A. H., Proc. 2nd Intern. Congress Rheology (discussion of a paper by Saunders and Ward) Rheol. Acta 1, 284 (1954).
- 22) Roller, P. S. and C. K. Stoddard, J. Phys. Chem.
 48, 410 (1944).

Author's address:

Dr. L. Dintenfass, Department of Medicine, Sydney University, Sydney, N.S.W. (Australia)

From the Laboratory, Royal Mills of Laan Bros. Ltd., Wormerveer (The Netherlands)

Relative Viscosity of Suspensions of Rigid Spheres in Newtonian Liquids

By Ir. R. Rutgers

With 2 figures and 4 tables

(Received December 1, 1961)

Several investigations about the dependence of the relative viscosity on concentration have been described in the literature for rigid spheres of more or less monodispersoid character. A number of these results have been collected, choosing them for precision, great range of diameter, concentration or rate of shear, extreme fine particles size, or because they have been much cited in the literature or are otherwise illustrative. Table 1 gives a survey of the results with indication of the nature of the medium and the particles, of particle size, type of measurement, rate of shear (D) or shear stress (τ) . Furthermore the difference of specific gravity between particles and medium has been recorded, the viscosity of the medium and the concentration until which Newtonian behaviour had been observed, the medium being always Newtonian. Sometimes some results for varying sphere diameter, D or τ of the same investigator have been included. In the table the figures of η_r have been written with the point at the place of the valid volume concentration. In graph 1 the η_r -c-figures have been illustrated on a logarithmical scale for η_r and a linear one for c. The measurements of *Maron* (1), Eilers (2), Robinson (3) and Ting-Luebbers (4) have been connected each to separate curves. Those of Sweeney (5) for η_0 and η_{∞} have been indicated by a separate figure and the rest has been pictured without distinctions.

Through all the separate points and signs an average curve has been drawn, discarding the separate curves mentioned. For comparison the *Einstein*-formula has been represented too. A recent paper of *Fidleris* and *Whitmore* (6) mentions for c = 0.2 values of $\eta_r = 2.00 \pm 0.05$ for spheres up to 422μ .

If one wants to deduce from this material an "average sphere concentration curve" the first point to be looked at is whether the suspensions behave Newtonian. With one exception (Sweeney), all authors reported Newtonian flow until c = 0.25 and several even up to c = 0.45. Others found influence of D between 0.25 and 0.45, but this influence was not very great compared with the differences between the authors. This small structural viscosity at rather high concentrations is surprising. However, for these higher concentrations very low shear rates have not been used. Possibly a greater measure of structural viscosity might then be found. The drawing of one sphere-curve thus becomes, with regard to D-influence, somewhat uncertain between 0.25 and 0.45 and still more so above 0.45, where it must be quite incorrect not to differentiate for different rates of shear.

The observations show considerable scattering, even at low concentrations in the *Newtoni*an range. Reasons for deviating measurements may be many, e. g. low figures may be caused by capillary measure-

ı) (Column)		2a	$2\mathrm{b}$	3	4	ũ	9	-	8	9a	96	96	10a	10b	10e	10d
b) (Author)	Ward- Whitmore (7)	Higgin botham	(8)	Eveson (9, 10)	Eveson~(11)	Cheng (12)	Harvey (13)	Eirich (14)	Brough-ton(15)	W_i	lliams (16)		Robinso	n (17)	
c) (Nature)	methacryl- ate in Pb- nitrate, gly- cerol, water	methac ate in] nitrate, cerol, v	eryl- Pb- , gly- vater	methacryl- ate in Pb- nitrate, glycerol, water	methacryl- ate in Pb- nitrate, glycerol, water	poly- styrene in 0,1 n NaCl	iron in linseed- oil	glass in Hg-nitra- te, nitric acid	glass in chlorinat- ed hydro- carbons	glyc	glass in cerol, w	ater	glu- cose, water	glu- cose, water	s in glu- cose, water	su- crose, water
d) (particle size, μ)	152-177	76–89 53–76	$ 152 \\ -177$	40–54 15–30	345-435	0.264	1.5	160	$\frac{150-300}{75-150}$	appr. 4	appr. 8	appr. 12	3-4	4-10	10-30	10-30
e) (⊿ s.g.)	0.0	0.0	0.0	0.0	0.0	+ 0.05	+ 6.4	0.0	appr. 0	ap	$\frac{1}{1}$	2	_	appr.	$+ 1.0^{-1}$	
f) (measure- ment)	rising ball	capilla	ed	rotation	rotation	capillary	rotation	capillary	rotation		rotation			rotat	ion	
g) (D or τ)				$= \begin{array}{c} D \\ 0.05 - 1.1 \end{array}$	D = 1.35		1		1					D = 10	0-600	
0.0 cP.	.9	~	۵.	2.96	3.7	ca. l.	490.	19.4	low		59.		154-241.	134 - 234.	94. 1 16	71.
; →ひ	1.25	1.13	1.13	1.17	1.17	1.16		1.09	1.14				1.22	1.19	1.31	1.21
0.1	1.42	1.31	1.31	1.39	1.44	1.29		1.19 1.19	1.36	1.47	1.45	1.43			I.46	1.36
0.2	1.75	1.56	1.54	1.68	1.82			I.29	1.63	1.83		1.87	1.61	1.65	1.67	1.62
0.3	6 9 9K	1.96	1.88	2.11				1.43 1.55	1.93	2.30	2.49	2.50	2.01	2.07	1.94	1.75
0.4	2.9	2.6					3.35						2.27 3.25	2.36	2.72	2.80
1		3.5								3.94	4.72	4.83		7.5	5.9	6.3
0.5							8.6				12.9	22.7				
0.6										-17	۲. ۲.	364		24.5		
0.7															7.9	18.5
Newtonian until c =	0.3	;		> 0.2			< 0.3	> 0.2	> 0.2		0.5			ca		

203

 $\mathbf{14}$

$Table \ Ia$ Relative Viscosity of Suspensions of spheres

a)	lla	11b	12	13	14	15a	15b	16a	16b
b)	Vand (1	8)	Manley- Mason (19)	Dobry (20)	Maron (21)	Sweeney-Ge	ckler (5)	Maron (1)	
c)	glass in glycerol	ZnJ₂,	glass in ZnJ ₂ , glycerol	gummigut in water	latex in soap- solution	glass in Znl glycerol, wa	Br ₂ , ater	latex in soa solution	p-
d)	appr. 13	0	1–10	1.5	0.2	44-	-53	0.	14
e)	0.	0	0.0	-0.06	0.07	+0	0.11	(0.08
f)	rotation capillary correc without stirring	and 7, ted with stirring	capillary, corrected	capillary	rotation	rotati	ion	capil	lary
g)	-			·	$\tau = 0-90$	D = 0 - 147 D = 0 - 17	D = 0 - 192 D = 0 - 17	$\tau = 50$	$\tau = 800$
0,0	80.		low	1.0 1.12	low	${\eta_0} \over 270$	η_{∞}	lo	w
Ċ			1.15					1.16	1.16
0,1	1.34	1.34	1.44	1.28				1.36	1.36
0,2			$\begin{array}{c} 1.59 \\ 1.86 \end{array}$					1.82	1.82
0,3	2.02	2.02				2.08	1.88	2.48	2.48
	3.64	3.64				5.5	4.0	3.25	3.10
0,4									
0.5	10.5	11.8			10.3 22.5	9.3 19	7.3 12.0	9.7	7.6
	33.3	20.0			80	47	27.2	17.0	11.4
0,6	00.0	20.0			570.	47. 62.	54.	99.1	33.2
0,7					$\begin{array}{c} 259.00\\ 163.000\end{array}$			1110.	101.
New- tonian until c	0.4	17		—	0.4	< ().2	0.25	-0.3

 $Table \ 1b$ Relative Viscosity of Suspensions of Spheres

ment, by slip, by polydispersity and high figures by insufficient dispersion, by adsorption, by turbulency, by occurrence of sedimentation. It would be difficult to weigh the results of the various authors in all these respects. Ford (24) discussed some of them. We have drawn an average curve, which must be rather arbitrary. This curve then could be valid (above c = 0.25) for moderate rates of shear, say some hundreds sec⁻¹. For lower concentrations this curve coincides very well with the accurate rotation measurements at very low values of D of Eveson (9, 10) for stable suspensions of varying particle size and distribution. If the tendencies to find too high or too low viscosities neutralize each other as good for higher concentrations, the curve might merit reasonable confidence until 0.45 and less above that. There are not much observations for high concentrations.

The medium viscosity was always rather low, often only some c.P, never more than 3 P. Very high medium viscosities might cause deviations. The density of the spheres was sometimes rather much higher than for the medium and some of these results (*Williams*) were on the higher side. The rigidity of the spheres may be taken as sufficient, for bitumen and latices too,

a)	17	18a	18b	18c	18d	19	20a	20 b	21
b)	Eilers (2)	-	Robins	son (3)		Ting- Luebbers (4)	Oden (22	;)	Harmsen (23)
c)	bitumen in soap- solution	sucrose, water	glas sucrose, water	s in min. oil	min. oil	glass in castor oil, Br.ethane	sulphur solution	in NaCl-	AgJ in HJ- solution
d)	appr. 2.7		. 5–	45		230	0.1	0.01	0.03
e)	0.0	+1.0	+1.0	+1.3	+1.3	0.0	+0.9	+0.9	+4.6
f)	capillary		rota	ation	1	rotation	capil	lary	capillary
g)		D = 296	D = 1860	D = 296	D = 1860			-	D = 500
0,0	low	155–188		74		29.6	1.	0	0.894 1.08
č						1.10	1.25	1.35	1.19
0,1	1.25	1.26	1.16	1.12	1.10	1.27	1.55	1.75	
0.2						1.41	2.0	2.42	
́л я	1.84	1.47	1.48	1.26	1.28	$\begin{array}{c} 1.71 \\ 1.95 \end{array}$	$2.75 \\ 3.2 \\ 2.7$	$3.7 \\ 4.5$	
0,3	2.55	1.83	1.87	1.45	1.49	2.60	0.1		
						3.56			
0,4	4.0	2.60	2.64	1.92	1.88	4.8			
0,5						$\begin{array}{c} 7.3 \\ 10.0 \end{array}$			
	7.6	5.03	4.78	2.81	2.73	19.3			
0,6		7.28	6.8	3.66	3.94				
	18.0	(18)	(14)	5.32	4.85				
0.7	34.			8.49	6.65				
0,1	90.			14.0	10.0				
Ne	108. ?	0.4	-0.5	0.	35	_		2	

 Table 1b (Continuation)

 Relative Viscosity of Suspensions of Spheres

regarding the small particle sizes. The sphericity and smoothness of the particles will not always have been ideal. Most measurements have been done at 20–30 °C.

The sphere diameter varied very considerably, mostly between 4 and 400 μ . Greater spheres have not been investigated. Some of the results with even lower particle size, down to some tenths of microns, show agreement with the average sphere-curve, viz. Cheng's observations (12) for very beautiful and monodisperse polystyrene spheres of 0.26 μ , measured with a capillary method up to c = 0.08 and part of Mason's investigations (21), measuring with a rotation meter synthetic latex particles of 0.2 μ , even onto c = 0.50. Saunders' (25) recent results with polystyrene latices, using capillaries without applying wall-corrections, agree with the average curve for 0.1 μ and are somewhat lower for 0.9 μ sphere diameter. Bancelin (26) already stated to have found, with a capillary meter no difference in viscosity for watery suspensions of gummigut particles of 0.6 μ compared with 8 μ , although he gave no figures. It would seem that with good dispersion, no structure-formation, no adsorption or solvation, no slip, no electrical disturbance, the relation between η_r and c may be very widely independent of sphere size. For still finer particles, below $0.1-0.5 \ \mu$, considerably higher relative viscosities have been found always, although in some cases the difference is not extremely great, at lower concentrations. Oden's (22) measurements on sulphur-particles (of uncertain shape) of 0.1 and 0,01 μ have been figured in graph 1, putting the density at 1.95. Harmsen et al. (23, 27) found for a hydrophobic AgJ-sol with electrolytes added, an *Einsteinian k*-value of 3.55 instead of 2.50.



Fig. 1. • _____ 1 Average sphere curve; • _____ 2 Einstein formula; × ______ 3 Oden, 10 $\mu\mu$; × ______ 4Oden 100 $\mu\mu$; × ---- 5 Maron, $\tau = 50$; × ---- 6 Maron, $\tau = 800$; × --- 7 Robinson, sucrose, D = 1860; × ---- 8 Robinson, oil, D = 1860; $\diamond \longrightarrow 9$ Ting-Luebbers; $\Box \longrightarrow 10$ Eilers; $\odot 11$ Sweeney, 49 μ , η_0 , D = 0-147; $\otimes 12$ Sweeney, 49 μ , η_{∞} , D = 0-192

The particles were nearly spherical, but rather polydisperse, 0,01 till 0.08 μ , average 0.035 μ . Double layers may have been present. *Donnet* (28, 29) investigated carbon black particles in water up to c = 0.01 with capillary and rotation meter, using shear rates between 0.25 and 2000 sec⁻¹, which had no influence. The particles were approximately spherical, but polydisperse, from 0.009–0.064 μ , average 0.03 μ . The *K*-value found was 7.8.

It is dubious whether spheres below $0.1 \,\mu$ may be said to have smooth surfaces.

Brownian movement then may have a viscosity increasing effect. The surface may no longer be uniform in a chemical-physical sense. Adsorption of double layers and other electric and electroviscous effects must occur. There may be theoretical reasons for higher relative viscosities of very small particles see e. g. Broersma (30), Happel (31). Below 0.1–0.5 μ , which limit will vary with the nature of the particles, the medium and the type of interaction forces, even completely dispersed spheres will show higher suspension viscosity.

Several authors investigated for one type of particles the influence of sphere-size. Their results are conflicting, in the range above 4 μ diameter. For greater sphere size there has been found higher viscosity up to c = 0.25and lower above 0.25 (Robinson). Williams reported lower values unto c = 0.10 and higher viscosities for higher concentrations. Higginbotham gave somewhat lower η_r figures for greater sphere size, with concentrations up to 0.2. Sweeney found somewhat lower viscosity for glass spheres in water, but no difference in organic liquids. *Eveson* observed no effect of sphere size between 15 and 300 μ (c up to 0.225), and somewhat higher viscosity for spheres of 400 μ diameter. In the particle range below 1 or 0.5 μ greater sphere size always causes lower viscosity, e. g. for the latices-measurements of Maron (32) and Saunders (25).

In the greater size-range the experimental results thus are not conclusive. The influence of sphere diameter is small in any case. Theoretically de Bruyn (33) stated that greater particles should have higher suspension-viscosity, but Rajagopal (34) gave a formula indicating decreasing viscosity. Inertia forces may play a role. A practical point is that the particle Reynolds number increases with the size, and movement of large particles will very soon cause turbulent flow of the medium around them (35).

The particle size distribution used in the investigations was often rather wide. For polydisperse systems lower relative viscosities are found generally. The size ratio and type of distribution are of importance. *Eveson* (10), working with a rotation meter and concentrations up to 0.225, found no difference for continuous sphere-distributions for size ratios from 1.6 to 24.0 and average diameters of 80-116 μ . Bimodal distribution curves with widely differing particle sizes however caused considerably lower visco-sities e. g. *Sweeney* (5), *Eveson* (11). An effect of polydispersity may be more marked at high concentrations, as has been found by *Maron* (32) for mixtures of two latices with a sphere size of some tenths of a micron, differing by a factor 2. Viscosity minima were found here above c = 0.45.

Theory generally predicts a lower relative viscosity for polydisperse systems, even at low concentrations, e.g. *Roscoe* (36), *Rajagopal* (34).

When the influence of sphere size is negligible and of polydispersity restricted for narrower limits of size ratios and a continuous distribution, the experimental "deviations" from the average sphere curve should have some other explanation. It might be expected that there will be a tendency to find too high viscosity on account of aggregation of the small spheres used. Most observations indeed crowd in the higher viscosity region. The average curve however has been drawn just here. There are several series of measurement giving lower viscosities, which have been discarded. Firstly these results show wide divergences from each other. Secondly the lower of them give, at lower concentration, figures even below the *Einstein*-curve. Thirdly these lower curves are lower too at smaller concentrations, e. g. 0.1-0.2, where the average curve would seem to be rather well founded, as most experiments have been done in this range. The "deviating" curves show appr. the same type of curving as the average line. Then the deviating curves probably are low too at higher concentrations. It is possible however that the average curve has been drawn too high at higher concentrations, but this cannot be deduced with the experimental results available.

Of Marons' series one, measured with a rotation meter, agreed with our curve, and others done with capillaries did not. *Eilers* capillary measurements are lower still, and he used rather polydisperse bitumen material. It is remarkable that he was able to make a concentration of 0.71 (and found only 108 for η_r), a packing which is unattainable with random dense piling of monodisperse spheres. Robinson has found higher viscosities too; there may have been slip, especially in oil. For rotation measurements the influence of vortices in the anulus must be considered and may play a role for low relative viscosity measurements, as those of *Ting* and *Luebbers*, performed with a *Brookfield* apparatus.

The average sphere curve gives the following figures for relative viscosity (table 2):

Table 2Concentration and Relative Viscosity

<i>c</i>	η_r
0.00	1.00
0.05	1.16
0.10	1.38
0.15	1.67
0.20	2.11
0.25	2.76
0.30	3.8
0.35	5.7
0.40	10
0.45	20
0.50	58
(0.55	250)

It is illustrative to calculate the distance δ , expressed in relation to the sphere diameter, between the surfaces of equisized spheres at varying concentrations. For a rhombohedral distribution this has been done with the formula $(1 + \delta)^3 = 0.74/c$. Some figures are given in table 3.

Table 3 Concentration and sphere distance

С	δ
0.01	3.20
0.02	2.33
0.07	1.20
0.10	0.95
0.15	0.70
0.20	0.54
0.25	0.44
0.35	0.28
0.45	0.18
0.50	0.14
0.55	0.10
0.74	0.00

When other types of array with lower maximal packing density are assumed, these distances become somewhat smaller. For random dense packing of equal spheres a volume density of 0.64 has been reported, e. g. by *Scott* (37) and for sheared suspensions a somewhat higher figure e. g. 0.67 has been found by the author.

The average sphere curve shows a continuously increasing deflection from the concentration axis, viscosity increasing steeper than logarithmical. The Einstein curve has the opposite, slightly convex course. Strictly speaking the average curve could only coincide with the *Einstein*ian at a low concentration, if it had a flexion point. Otherwise the *Einstein* equation could be valid only at infinite low concentration. Practically both curves touch below c = 0.02or 0.01. The average sphere distance than would be several times the sphere diameter.

It would be possible that the average log η_r -c curve becomes linear at low concentration. It is difficult to conclude that from the measurements which should be very accurate in this range. For the precision measurements of *Cheng* and of *Eveson*, the semilogarithmical relation is well-nigh linear up to c = 0.07. The sphere distance at this concentration is somewhat more than one sphere diamater. There is room for one sphere between 2-spheres at this average distance.

The general power formula for the relative viscosity with c^2 , c^3 etc. terms will be shown in another article to be valid up to c = 0.15, or a distance of 0.7 d.



 $\begin{array}{c} \text{If g. 2. } \bullet \underbrace{ \begin{array}{c} \text{If } c \text{ and } \eta_r, \ & \ \ ---2 \ c \text{ and } \log \eta_r, \\ \bullet \underbrace{ \begin{array}{c} \text{If } c \text{ and } \log \log \eta_r; \\ \bullet \underbrace{ \begin{array}{c} \text{O} \end{array}} \\ \text{----3 } c \text{ and } \log \log \eta_r; \\ \text{O} \underbrace{ \begin{array}{c} \text{O} \end{array}} \\ \text{----5 } c \text{ and } \sqrt{\eta_r}; \\ \text{o} \underbrace{ \begin{array}{c} \text{O} \end{array}} \\ \text{and } 1/\eta_r \end{array}} \\ \end{array} \\ \begin{array}{c} \text{f} c \text{ and } \log \eta_r; \\ \text{o} \underbrace{ \begin{array}{c} \text{O} \end{array}} \\ \text{o} \end{array} \\ \begin{array}{c} \text{f} c \text{ and } \log \eta_r; \\ \text{o} \underbrace{ \begin{array}{c} \text{o} \end{array}} \\ \text{f} c \text{ and } \eta_r; \\ \end{array} \\ \end{array}$

Above c = 0.2-0.25 the viscosity rises definitely steeper. Non-Newtonian behaviour, at first rather small, starts at this concentration or somewhat higher. The sphere distance then has become $\frac{1}{2} d$ or $\delta = r$ (sphere radius).

At c = 0.4 to 0.5 viscosity increases sharper still and non-Newtonian behaviour becomes important. The cubic piling of spheres, with a density of 0.52 is approached. The sphere distance is about 0.2 x sphere diameter, and particle interaction must be very important. Above 0.45 there is an insufficient number of measurements available for rigid spheresuspensions. The $c - \log \eta_r$ relation may be again approximately linear in a certain concentration range. For non-spherical particles the relative viscosity has been found by *Rigden* (38) not to increase to infinity at very high concentrations, but to reach a maximum. This has yet to be proved for spheres.

There may thus be distinguished several "critical" concentrations. Eveson (11) stated that particle interaction becomes important above ${}^{3}/_{4} d$ distance of the spheres (c = 0.15). Ford (24) concluded to critical concentrations of 0.25 and 0.45. In cubical arrangement the least distance was then 0.22 x and 0.05 x diameter. At c = 0.25 rotation of the spheres might begin to be hindered and at c = 0.45 interlocking will start.

For the measurements with rotating cylinders, mostly the outer cylinder was rotated. The dimensions used of maximal sphere size and of the annulus are tabulated in table 4.

Table 4

Author	sphere diameter	width of annulus	ratio
	$m \mu$, maximai	m mm, muimai	mmmai
Vand	160	11.75	1:73
Eirich	320	3.8	1:12
Robinson	45	0.5	1:11
Eveson	182	2.0	1:11
G. Broughton	ı 32 0	2.54	1:8
Sweeneŭ	262	2.0	1:8
Eveson	350	1.9	1:6

A often used ratio would be about 10. Applying the correction of *Guth-Simha* (39) for the wall effect with dilute suspensions in a *Couette* apparatus:

$$\eta_r = 1 + 2.5 \left(1 + \frac{5 r}{16 a} \right) \cdot c$$
 [1]

(a = annulus width), would give as a result that the viscosity figures are found a factor 1.016 too high. Average curve might be placed a little too high.

Formulas for the η_r -c-relation

The average sphere curve can be subjected to all sorts of transformations by making use of η_r , $\log \eta_r$, $\log \log \eta_r$, $\sqrt{\eta_r}$, $\frac{1}{\eta_r}$, the same for $\eta_{sp} = \eta_r - 1$ and furthermore of c, c^2 , $\log c, \sqrt{c}$ etc. in varying combinations. Fig. 2 gives some examples. It is not possible to obtain complete linearization, which would give a simple formula. \sqrt{c} against $\sqrt{\eta_r}$ or $\sqrt{\eta_r - 1}$ or $\sqrt{\eta_r} - 1$ neither gave much improvement. Working with c and $1/\eta_r$ or $1 - 1/\eta_r$, one finds a straight line at lower concentration, up to c = 0.20, but curving at higher c-values. This method of presenting the viscosity figures has been proposed by Oliver and Ward (40).

Several lines of fig. 2 suggest some hyperbolic relation. It would be simplest to take rectangular axes for these hyperboles. Introduction of a maximal concentration c_m , where the relative viscosity becomes infinite is necessary and gives equations with a (1 - s.c) term, s being > 1.

Starting from η_r and c it is possible thus to derive a formula, which has been proposed by W. R. Hess (41), Bingham, and recently by Oliver and Ward (40).

$$\eta_r = \frac{1}{1 - \mathrm{s.c.}} \,. \tag{2}$$

Taking the curve for $\sqrt{\eta_r}$ and c one may obtain an equation:

$$\eta_r = \frac{1}{(1-\mathrm{s.\,c.})^2}$$
. [3]

This is the *Roscoe* type of formula.

On refining the last approach as regards the asymptotical value of $\gamma \eta_r$, it is possible to derive an equation of the following type:

$$\eta_r = \left(1 + \frac{\mathrm{k.c.}}{1 - \mathrm{s.c.}}\right)^2. \qquad [4]$$

This equation has been used by *Eilers* (2).

It would seem possible to get still better agreement between experiment and formula by further changing the formulas, which can be done in various ways. However this procedure is rather arbitrary. In another article we will first survey the many formulas that have been proposed for the relation between η_r and c, a number of which have theoretical foundations.

Summary

From viscosity measurements on suspensions of spheres from the literature, the relation between relative viscosity and volume concentration was derived up to 0.5. This relation should be valid at room temperature for rigid smooth spheres, well dispersed without more than loose and random contacts, well wetted, without slip, in a *Newton*ian low viscous medium of about the same specific gravity, which spheres do not swell nor are electrical charged, whose diameter may vary between e. g. 0,3 and 400 μ and whose particle size distribution may be moderately polydisperse. The relation of η_r and c is valid for all rates of shear up to c = 0.25 and for sizeable shear rates above that concentration. For higher concent-

rations the viscosity figures are more uncertain, especially at very low shear rates. The viscosity behaviour above c = 0.5 is still largely unknown. There is still much need for more accurate experimental work on sphere suspensions of varying concentrations at varying rates of shear. There seem to be several critical concentrations, where the flow behaviour shows changes, e. g. at c = 0.02 - 0.07 - 0.15 - 0.20 à 0.25 - 0.02 - 0.07 - 0.15 - 0.20 $0.45 - c_{\max}$.

The relation between η_r and c can be pictured in several ways. Starting from the assumption of a hyperbolic relation between some η_r and some c term, several equations may be derived for the relation between η_r and c.

Zusammenfassung

Aus den in der Literatur veröffentlichten Viskositätsmessungen an Kugelsuspensionen wird eine Beziehung zwischen der relativen Viskosität und der Volumenkonzentration (bis herauf zu 50%) abgeleitet. Diese Beziehung sollte gelten bei Raumtemperatur für starre, glatte Kugeln, die gut dispergiert sind und höchstens schwache, zufällig angeordnete Bindungen besitzen, gut benetzt werden und keine Gleitung zeigen, sowie für ein niederviskoses Newtonsches Suspensionsmittel, das weder Quellung noch elektrische Aufladung der Kugeln hervorruft. Der Kugeldurchmesser kann etwa zwischen 0,3 und 400 μ variieren, und es kann eine mäßig polydisperse Verteilung vorliegen.

Diese Beziehung zwischen η_r und c ist bis zu einer Konzentration von 25% für alle Schergeschwindigkeiten gültig, oberhalb derselben jedoch nur für größere Geschwindigkeiten. Für höhere Konzentrationen werden die Viskositätsdaten unsicherer, insbesondere bei sehr niedrigen Schergeschwindigkeiten. Das Viskositätsverhalten oberhalb von c = 50% ist noch weitgehend unbekannt. Man benötigt hier noch genauere Messungen an Kugelsuspensionen als Funktion der Konzentration und der Schergeschwindigkeit. Es scheinen verschiedene kritische Konzentrationen zu existieren, bei denen das Fließverhalten sich ändert, und zwar bei etwa 2, 7, 15, 20–25, 45% und c_{max} .

Die Beziehungen zwischen η_r und c sind auf verschiedene Weisen darstellbar. Ausgehend von der Annahme einer hyperbolischen Beziehung zwischen einer Funktion von c und einer Funktion von η_r können verschiedene Gleichungen abgeleitet werden.

References

1) Maron, S. H. and Sh. Ming Fok, J. Colloid Sci. 10, 482 (1955).

- 2) Eilers, H., Kolloid-Z. 97, 313 (1941).
- Robinson, J. V., Trans. Soc. Rheol. 1, 15 (1957).
 Ting, A. P. and R. M. Luebbers, Amer. Inst.
- Chem. Eng. J. 3, 111 (1957). 5) Sweeney, K. H. and R. D. Geckler, J. Appl. Phys.
- 25, 1135 (1954).
 6) Fidleris, V. and R. L. Whitmore, Rheol. Acta 1, 573 (1961).
- 7) Ward, S. G. and R. L. Whitmore, Brit. J. Appl. Phys. 1, 286 (1950).
- 8) Higginbotham, G. H., D. R. Oliver and S. G. Ward, Brit. J. Appl. Phys. 9, 372 (1958).
- 9) Eveson, G. F., J. Oil Col. Chem. Ass. 40, 456 (1957)
- 10) Eveson, G. F., J. Oil Col. Chem. Assoc. 41, 150 (1958).
- 11) Eveson, G. F., in C, C. Mill, Rheology of Disperse Systems, 61-83 (London 1959).
 12) Cheng, P. Y. and H. K. Schachman, J. Polym.
 Sci. 16, 19 (1955).
- - 13) Harvey, E. N., J. Colloid Sci. 8, 453 (1953).

- 14) Eirich, F. et al. Kolloid-Z. 74, 276 (1936).
- 15) Broughton, G. and C. S. Windebank, Ind. Eng. Chem. 30, 407 (1938)
- 16) Williams, P. S., J. Appl. Chem. 3, 120 (1953). 17) Robinson, J. V., J. Phys. Colloid Chem. 55, 455 (1951)
- 18) Vand, W., J. Phys. Colloid Chem. 52, 277, 300, 314 (1952).
- 19) Manley, R. St. and S. G. Mason, Can. J. Chem. 32, 763 (1954).
- 20) Dobry, A., J. Chim. Phys. 52, 809 (1955).
 21) Maron, S. H., B. P. Madow and I. M. Krieger, J. Colloid Sci. 6, 584 (1951).
- 22) Oden, Sven, Z. physik. Chem. 80, 709 (1912).
- 23) Harmsen, G. J., J. v. Schooten and J. T. G. Over-beek, J. Colloid Sci. 8, 64 (1953).
 - Ford, T. F., J. Phys. Chem. 64, 1168 (1960).
 Saunders, F. L., J. Colloid Sci. 16, 13 (1961).

 - Bancelin, M., Kolloid-Z. 9, 154 (1911).
 Harmsen, G. J., J. v. Schooten and J. T. G. Over-
- beek, J. Colloid Sci. 8, 72 (1953).
 28) Donnet, J. B., J. Chim. Phys. 48, 536 (1951).

- 29) Donnet, J. B., J. Chim. Phys. 50, 380 (1953).

- Broersma, G., J. Chem. Phys. 28, 1158 (1958).
 Happel, J., J. Appl. Phys. 28, 1288 (1957).
 Maron, S. H. and B. P. Madow, J. Colloid Sci. 8, 300 (1953).
- 33) Bruyn, H. de, Disc. Faraday Soc. 11, 86 (1951). 34) Rajagopal, E. S., Z. physik. Chem. N. F. 23,
- 342 (1960). 35) Whitmore, R. L., J. Instit. Fuel. 31, 422 (1958).
 - 36) Roscoe, R., Brit. J. Appl. Phys. 3, 267 (1952).
 - 37) Scott, G. D., Nature 188, 908 (1960).
- 38) Rigden, P. J., Road Res. Techn. Paper Nr. 28 (1954).
- 39) Guth, E. and R. Simha, Kolloid-Z. 74, 266 (1936)
- 40) Oliver, D. R. and S. G. Ward, Nature 171, 396 (1953).
 - 41) Hess, W. R., Kolloid-Z. 27, 1 (1920).

Author's address:

Dr. Ir. R. Rutgers, Laboratory, Royal Mills of Laan Bros. Ltd., Wormerveer (Netherlands)

From the Department of Chemistry, St. John's College, Agra (India)

Studies on the Viscosity of Solid Stabilized Emulsions

By S. N. Srivastava

With 4 figures and 3 tables

(Received December 28, 1961)

Introduction

Published work on the viscosity of solid stabilized emulsions is not abundant. Wilson and Park (1) found that the relative viscosity increases with the concentration of the emulsifying agent and with the uniformity of globule size in concentrated emulsions. Smith (2) carried out work on the interfacial viscosity of emulsions promoted by solid powders. Sherman (3) studied the viscosity of emulsions stabilised with surface active emulsifiers and proved that the viscosity is influenced both by concentration of the inner phase and the emulsifier. He also examined the effect of average globule diameter on the viscosity of O/W and W/Oemulsions stabilised by non-ionic emulsifying agents. Axon (4) also showed the effect of the concentration of the emulsifying agent, sodium lauryl sulphate on emulsions of liquid paraffin in H₂O containing cetyl alcohol.

Recently Lawrence and Rothwell (5) have shown that the viscosity of a concentrated O/W emulsion is governed by the intermolecular attraction of the interfacial film. stabilized Richardson (6)studiedsoap emulsions and found that the viscosity was inversely proportional to average globule diameter at high rate of shear. Specific

viscosity of suspensions has also been related to the mean globule size for heterodispersed and monodispersed systems (7). The results of Ward and Whitemore (8) showed that the relative viscosity of a concentrated emulsion is proportional to its size distribution at a particular concentration. Thus the most important aspect of the viscosity of stabilized emulsions is that it has some bearing on the adsorbed film at the interface and that it is influenced both by the droplet distribution and the average particle size (9).

In the present work the variation of viscosity with the concentration of the oil, concentration of the emulsifier, the nature of the oil and the homogenization has been studied using some typical solid emulsifying agents (10) with kerosene/H₂O and olive oil/ water systems. Since from the point of view of emulsion stability the distribution of globule sizes is not so important as the variation of the total interface with time (10), to study the effect of dispersion characteristics on the viscosity, the latter property has been related with the interfacial areas of the various emulsions experimented, both the properties being determined at regular intervals of time. Correlation between viscosity and stability of an emulsion has also been attempted.