IX.   RHEOLOGY OF LYOPHOBIC SYSTEMS

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§ 1.   INTRODUCTION

The most important practical applications of the science of lyophobic colloids are doubtless to be found in the domain of mechanical and rheological properties. This becomes immediately obvious when one realizes that the soil, moulding clays, paints, varnishes, pastes are lyophobic systems. Unfortunately the theoretical knowledge in this field is still rather restricted, although a wealth of empirical data is available.

One point, however, has become abundantly clear, and that is the fundamental difference between stable and more or less flocculated systems. It is as a rule among the flocculated systems that interesting properties like plasticity are to be found, whereas the rheological peculiarities of stable systems are more often a nuisance than an advantage. Therefore it is the more regrettable that theories, as far as they go, are only quantitative in the field of stable systems, but remain wholly qualitative for flocculated systems. This means that one understands the mechanical interaction between a single particle and the surrounding liquid or between two particles at best, but not the interaction of a great number of particles.

The rheological properties are described by relations between stress and strain (elasticity) or between stress and rate of strain (flow). In the simplest cases these relations are a simple proportionality as in the viscosity of Newtonian liquids or the elasticity of Hookean solids (see chapter I, § 4c, p. 22, § 4d, p. 28). In the following sections we shall, however, mainly be interested in non-linear behaviour, the only exception being the Newtonian viscosity of dilute stable suspensions.

§ 2.   VISCOSITY OF STABLE SOLS

a.   The Einstein equation

The basis for considerations on the viscosity of suspensions has been given by Einstein[1] who calculated the viscosity of a dilute suspension of rigid spherical particles. Making the assumptions of incompressibility of the system, no slip between the particles and the liquid, no turbulence, absence of inertia effects, and assuming further that the flow of the liquid may be described by the macroscopic hydrodynamical equa-

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[1] A. Einstein, *Ann. Physik*, (4) 19 (1906) 289; 34 (1911) 591; *Kolloid-Z.*, 27 (1920) 137. See also R. Simha, *Kolloid-Z.*, 76 (1936) 16, who demonstrated the correctness of eq. (1) also for flow in a capillary, whereas Einstein had only derived this equation for a field of flow with constant rate of shear as approximated in a Couette viscosimeter.

tions, also in the immediate neighbourhood of the particles, he derived the following equation for dilute suspensions.

$$\eta_s = \eta_o \left(1 + 2.5\,\varphi\right) \tag{1}$$

where η_s is the viscosity of the suspension, η_o that of the medium of dispersion and φ the total volume fraction occupied by the spherical particles. It is remarkable that the viscosity η_s is wholly independent of the size or size distribution of the spheres.

Derivations of the EINSTEIN equation that are all rather complicated can be found in the papers by EINSTEIN and SIMHA cited above, further in papers by GUTH and MARK[1], by GUTH[2], by GUTH and SIMHA[3], by J. M. BURGERS[4]. We shall not reproduce these derivations here, but we wish to draw attention to a single point.

The velocity of a liquid in a field of flow with a constant rate of shear can be represented by

$$\begin{aligned} v_x &= \alpha\,y \\ v_y &= 0 \\ v_z &= 0 \end{aligned} \tag{2}$$

A particle brought into this field obtains a translatory and a rotatory motion in such a way that the total force and the total moment of forces on the particle are zero. If this were not so, the particle would be accelerated.

The motion represented in eq. (2) can be divided into a uniform rotation given in eq. (3) and a motion (a simple dilatation) given in eq. (4) and represented in Fig. 1 which does not exert either a force or a moment on a spherical particle in the origin.
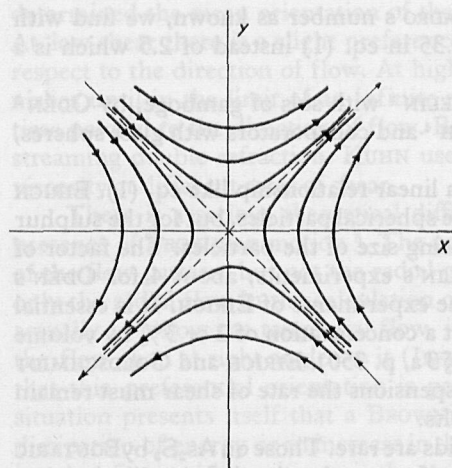

$$\begin{aligned} v'_x &= \tfrac{1}{2}\,\alpha\,y \\ v'_y &= -\tfrac{1}{2}\,\alpha\,x \\ v'_z &= 0 \end{aligned} \tag{3}$$

$$\begin{aligned} v''_x &= \tfrac{1}{2}\,\alpha\,y \\ v''_y &= \tfrac{1}{2}\,\alpha\,x \\ v''_z &= 0 \end{aligned} \tag{4}$$

Fig. 1. Dilatory part of a uniform shearing motion parallel to the x-axis.

The uniform rotation (3) does not contribute to the dissipation as, according to this equation, the whole mass of liquid, including the particle, rotates as one bloc. The dissipation comes wholly on account of the dilatory part (eq. (4)) of the motion. In the neighbourhood of the particle this dilatory motion has to be modified in order to satisfy the condition that no slip occurs at the surface of the particle. It is

[1] E. GUTH and H. MARK, Ergeb. exakt. Naturw. 12 (1933) 115.
[2] E. GUTH, Kolloid-Z., 74 (1836) 147.
[3] E. GUTH and R. SIMHA, ibidem, 74 (1936) 266.
[4] J. M. BURGERS, Second Report on Viscosity and Plasticity, Amsterdam 1938, p. 113.

this modification which causes extra dissipation of energy and which may be interpreted as the direct cause of the increase of viscosity represented in eq. (1).

Fig. 1 and eq. (4) show that, apart from the direction of flow, also the directions making angles of 45° and 135° with the flow, are preferred directions. It is in these last two directions that the principal axes of streaming double refraction are situated (see chapter III § 3 b, p. 107, this chapter § 2 b, p. 345).

In the derivations of the EINSTEIN relation the question of the stability of the suspension is never explicitly mentioned. It is nevertheless an essential condition, because in a non-stable system the particles would soon form pairs and higher agglomerates, especially during viscous flow (see ch. VII, § 6, p. 289) which would increase the viscosity considerably.

The EINSTEIN equation has been repeatedly tested. The earliest, not very rigorous test may be considered to have been given by EINSTEIN himself, who determined AVOGADRO's number from the viscosity and the diffusion constant, D, of sugar solutions. From eq. (1) the hydrodynamic radius, a, of a sugar molecule was obtained and this was substituted into the diffusion equation (5).

$$D = \frac{RT}{N_{\text{Avog.}}} \cdot \frac{1}{6 \pi \eta a} \tag{5}$$

Reversing the procedure and taking AVOGADRO's number as known, we find with the best values at present available [1] a factor 3.35 in eq. (1) instead of 2.5 which is a reasonable agreement.

Other tests have been carried out by BANCELIN [2] with sols of gamboge, by ODÉN [3] with sulphur sols and most extensively by EIRICH [4] and collaborators with glass spheres, spores of fungi and yeast cells.

They all confirmed for dilute suspensions a linear relationship like eq. (1). EIRICH also confirmed the independence of the size of the spherical particles, but for the sulphur sols (ODÉN) the viscosity increased with decreasing size of the particles. The factor of proportionality turned out to be 2.9 in BANCELIN's experiments; about 4 for ODÉN's more dilute sulphur sols and very near 2.5 in the experiments of EIRICH. It is essential to consider only dilute suspensions; as already at a concentration of 2 or 3% by volume the deviation from linearity is appreciable. (See § 3 a, p. 350). EIRICH and GOLDSCHMIDT (l.c.) showed that with their relatively coarse suspensions the rate of shear must remain very low if inertia effects are not to spoil the results.

Investigations on typical hydrophobic colloids are rare. Those on As_2S_3 by BOUTARIC and VUILLAUME [5] confirm the EINSTEIN equation, if extrapolated to infinite dilution, but show a rapid increase of the viscosity for somewhat higher concentrations. FREUNDLICH and KROSS [6] found a factor somewhat larger than 2.5 in the case of TiO_2 suspensions.

[1] L. J. GOSTING and M. S. MORRIS, J. Am. Chem. Soc., 71 (1949) 2005.

[2] J. BANCELIN, Compt. rend., 152 (1911) 1582.

[3] S. ODÉN, Der Kolloide Schwefel, Nova Acta Regiae Soc. Sci. Upsaliensis, (4) 3 (1913).

[4] F. EIRICH, M. BUNZL, and H. MARGARETHA, Kolloid-Z., 74 (1936) 276; F. EIRICH and O. GOLDSCHMID, Kolloid-Z., 81 (1937) 7.

[5] A. BOUTARIC and M. VUILLAUME, J. chim. phys., 21 (1924) 247.

[6] H. FREUNDLICH and W. KROSS, Kolloid-Z., 52 (1930) 37.

b. Non-spherical particles

Several authors have extended the calculations of EINSTEIN to non-spherical particles. The models that have been used are oblate or prolate ellipsoids of revolution, long cylinders or a stiff row of spheres [1]. The calculations are more difficult than in the case of spherical particles, not only in the mathematical sense, but also on account of two new physical aspects of the problem. It will be evident that the contribution to the viscosity of a long or flat particle depends upon its orientation. This orientation is constantly modified by the "toppling over" of the particles in the field of shear and by the rotational BROWNian motion of the particles. The viscosity is therefore dependent upon the rate of shear. At low rates of shear, the BROWNian motion prevails and the orientation of the particles is completely at random. At high shear, however, or for large particles, the BROWNian motion is negligible and the orientation completely determined by hydrodynamics.

JEFFERY [2] made the first calculations on ellipsoidal particles neglecting BROWNian motion. He solved the hydrodynamic problem, determined how the orientation of an ellipsoid changes with time and from that calculated the surplus dissipation of energy. The viscosity calculated in this way is, however, not constant and depends rather sensitively upon the initial orientations. JEFFERY therefore did not give an equation for the viscosity of a suspension of ellipsoids.

The problem has been taken up by several authors. BOEDER [3] and KUHN [4] both determined the mean orientation of the particles in the presence of BROWNian motion. At low shear there is a slight preference for orientation of rod-like particles at 45° with respect to the direction of flow. At higher rates of shear the angle of orientation diminishes until in the limit of an infinite rate of shear the particles are practically all the time parallel to the direction of flow. BOEDER tested this by means of determinations of streaming double refraction. KUHN used the partition function found to calculate the viscosity at different rates of shear.

There is a serious theoretical difficulty in the calculation of the viscosity in the presence of BROWNian motion [5]. The particle can in principle follow the tangential part of the flow pattern, but not the radial part. One might therefore be inclined to include only the radial flow in the calculation of the viscosity increase. But if the particle were actually to follow the tangential flow, it would be much longer in positions parallel to the flow than at right angles to it (JEFFERY), and it is just due to the BROWNian motion that this preferential orientation is partly or wholly destroyed. Then the paradoxical situation presents itself that a BROWNian motion, which in itself should not cause any dissipation of energy or an increase in the viscosity, nevertheless, by bringing the particle into less favourable positions, is the cause of an increase in the viscosity. This was clearly discerned by KUHN and KUHN [6] and by KRAMERS [7], but not in most of the earlier work.

[1] For the viscosity of flexible chains, see volume II, chapter IV, § 6, p. 106; chapter V, § 6, p. 140; chapter VI, § 3, p. 166.

[2] G. B. JEFFERY', Proc. Roy. Soc. London, A 102 (1923) 163.

[3] P. BOEDER, Z. Physik, 75 (1932) 258.

[4] W. KUHN, Z. physik. Chem., A 161 (1932) 1; Kolloid-Z., 62 (1933) 269.

[5] A discussion of the problem is given by H. C. BRINKMAN, J. J. HERMANS, L. J. OOSTERHOFF, J. TH. G. OVERBEEK, D. POLDER, A. J. STAVERMAN, and E. H. WIEBENGA, Proceedings of the international Congress on Rheology, Holland 1948, Amsterdam 1949, p. II — 77.

[6] W. KUHN and H. KUHN, Helv. Chim. Acta, 38 (1945) 97.

[7] H. A. KRAMERS, Physica, 11 (1944) 1; J. Chem. Phys., 14 (1946) 415.

Although therefore the work of Eisenschitz [1], W. Kuhn [2], Guth and Gold [3], Peterlin [4] J. M. Burgers [5] and Huggins [6] contains many important features, their final equations for the viscosity cannot be trusted.

It is not quite clear how Simha's [7] work should be judged. He calculates the dissipation for particles which are on the average at rest (which is incorrect, they rotate with an average speed given by eq. (3)) but arrives at equations closely resembling those obtained by Kuhn and Kuhn.

In the paper of Kuhn and Kuhn the viscosity factor $(\eta_s-\eta_o)/\eta_o$ for a dilute suspension of very long prolate ellipsoids is given by eq. (6)

$$\frac{\eta_s-\eta_o}{\eta_o} = 1.6 + \frac{p^2}{5}\left(\frac{1}{3\ln 2\,p - 1.5} + \frac{1}{\ln 2\,p - 0.5}\right) \tag{6}$$

where p is the axial ratio.

For larger rates of shear where the Brownian motion does not completely disorient the particles they are on the average more in the direction of the flow and then contribute less to the viscosity. Figs. 2 and 3 show for prolate and oblate ellipsoids how the viscosity factor depends upon the rate of shear.
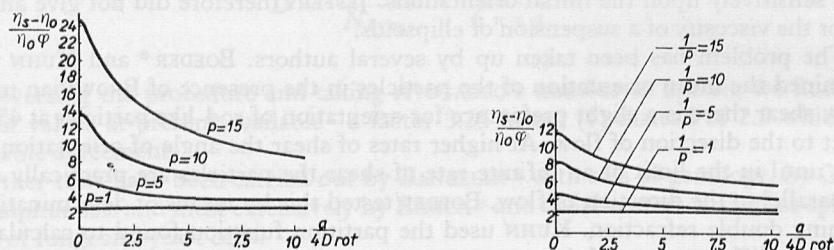
Figs. 2 and 3.　Viscosity factor for prolate and oblate ellipsoids of revolution with axial ratio p. φ is the volume fraction of ellipsoids, α the rate of shear (see eq. 2, p. 343). D_{rot}, the constant of rotational diffussion of the ellipsoids, is for very long ellipsoids approximately equal to $D_{rot} = \dfrac{kT \ln 2\,p.}{\eta_o V p^2}$ and for very flat prolate ellipsoids to $D_{rot} = \dfrac{\pi\,kT\,p}{8\,\eta_o\,V}$ where V is the volume of the ellipsoid. For more exact equations see the literature cited.

Recently Riseman and Kirkwood [8] extended a treatment previously developed for coiled macromolecules to the calculation of the viscosity of solutions of rod-like particles in strong Brownian motion. Although their method of calculation is beyond reproach, it is difficult to compare the results either with other theories or with experiments. They use as a model a series of "pearls" fixed at equal distances on a stiff "rod"

[1] R. Eisenschitz, Z. physik. Chem., A 158 (1932) 78; A 163 (1933) 133.
[2] W. Kuhn, l.c. p. 345.
[3] E. Guth, Kolloid-Z., 74 (1936) 147; E. Guth and O. Gold, Monatsh., 71 (1937) 67.
[4] A. Péterlin, Z. Physik, 111 (1938) 232; Kolloid-Z., 86 (1939) 230.
[5] J. M. Burgers, Second Report on Viscosity and Plasticity, Amsterdam 1938, p. 113.
[6] M. L. Huggins, J. Phys. Chem., 42 (1938) 911; 43 (1939) 439.
[7] R. Simha, J. Phys. Chem., 44 (1940) 25; Proceedings of the International Congress on Rheology, Holland 1948, Amsterdam 1949, p. II — 68.
[8] J. Riseman and J. G. Kirkwood, J. Chem. Phys. 18, (1950) 512.

which itself causes no friction. Their final equations for the viscosity are expressed through an infinite sum, not further evaluated. One can see, however, a similarity in the equation of RISEMAN and KIRKWOOD and that of KUHN and KUHN with respect to the dependence of the viscosity on the length of the rods.

Experimental tests of the rheological behaviour of suspensions of elongated particles have been given by EIRICH, BUNZL and MARGARETHA [1], who used suspensions of cut silk or cut glass threads. As their particles are very long (0.1–1 mm) their results should be compared to theoretical values for negligible BROWNian motion. The viscosities measured by them are larger than the theoretical ones [2], especially for the more elongated particles, and in contradistinction to the theoretical prediction, these particles are not oriented nearly completely in the direction of flow but partly even more at right angles to it. It looks as if either wall effects, or too high a concentration are the cause of this behaviour.

A test of eq. (6), that has to be carried out with particles in overwhelming BROWNian motion, can only be given with much smaller particles. SIMHA [3] compares axial ratio's of corpuscular proteins as derived from viscosity measurements (eq.(6)) [4] with the axial ratio as determined from the combination of sedimentation and diffusion experiments or from electron microscopic measurements. On the whole the accordance is excellent. See Table 1.

TABLE 1.

AXIAL RATIO'S OF CORPUSCULAR PROTEINS DETERMINED BY VISCOSITY MEASUREMENTS ACCORDING TO EQ. (6) [4] AND BY OTHER MEANS

	Viscosity		sedimentation + diffusion	electron microscope and X-ray diffraction
	SIMHA	KUHN and KUHN		
Egg albumin	5.0	4.3	3.8	
Serum·albumin . . .	5.6	5.0	5.0	
Hemoglobin	4.6	3.7	3.7	
Amandin	6.0	5.5	5.4	
Octopus hemocyanin . .	7.3	6.8	7.2	
Gliadin	10.5	10	10.9	
Homarus hemocyanin .	5.5	4.9	5.2	
Helix pomatia hemocyanin	5.5	4.9	4.8	
Serum globulin . . .	7.3	6.8	7.6	
Thyroglobulin	7.9	7.4	7.8	
Lactoglobulin	5.1	4.4	5.2	
Pepsin	4.5	3.6	2.5	
Helix hemocyanin (pH 6.8)	12.0	11.5	16.6	
Tobacco mosaic virus. .	20.3	20	18.6	23.0
Tobacco mosaic virus. . (partially aggregated)	31.5	31		28.7

[1] F. EIRICH, M. BUNZL, and H. MARGARETHA, *Kolloid-Z.*, 75 (1936) 20.
[2] See for instance A. PÉTERLIN, *l.c.* p. 346.
[3] *l.c.* 1949.
[4] Actually SIMHA used an equation with 14 15 instead of 1.6 as in KUHN and KUHN's equation, but this does not greatly influence the results (on the whole, it rather improves them).

Good experiments on true hydrophobic suspensions of elongated or flattened colloidal particles are rare. One might cite here the work of FREUNDLICH and SCHALEK [1] and of FREUNDLICH, NEUKIRCHNER and ZOCHER [2] on V_2O_5-sols and on sols of certain dyestuffs, where the decrease of the viscosity with increasing rate or shear has been most convincingly observed; especially for the aged sols which are known to contain the more elongated particles, the effect is very large. However, it is not certain that part of this non-NEWTONian behaviour is not due to too large a concentration and a kind of gel formation (See also § 5a, p. 356, § 5b. 2, p. 359).

c. Influence of the charge of the particles

It is found that the viscosity of a suspension is increased if the particles are charged and especially so if the medium is poor in electrolyte. This increase in viscosity is called *electroviscous* or *quasiviscous* effect. It is evidently connected with the existence of a double layer. An explanation can be based upon the fact that in a laminar field of flow, the outer parts of the double layer are drawn away from the particle. The original situation in the double layer tends to restore itself by conduction, and the dissipation of energy in this conduction may be seen as the cause of the increased viscosity.

Fig. 4. ''Viscosity'' of 0.36% V_2O_5 sols as a function of the rate of shear. The numbers on the curves indicate the age of the sol in days.

For hydrophilic colloids recently a different explanation of the electroviscous effect has been suggested, based upon a swelling of the particles under the influence of the electrical repulsion between the charges [3].

Evidently the excess dissipation of energy is proportional to the square of the conduction current $(\backsim \zeta^2)$ and inversely proportional to the conductivity λ. For a suspension of spherical non-swelling particles with radius a, VON SMOLUCHOWSKI [4] gave the following equation.

$$\frac{\eta_s - \eta_o}{\eta_o \varphi} = 2.5 + \frac{2.5}{\lambda \, \eta_o \, a^2} \left(\frac{\varepsilon \zeta}{2\pi} \right)^2 \tag{7}$$

The correction term may be very important. For a radius of 10^{-6} cm and a conductivity $\lambda = 10^{-4} \, \Omega^{-1}$ cm^{-1} it can easily amount to 10 times the main term.

VON SMOLUCHOWSKI published his equation without indicating the derivation. It was not until 1936 that KRASNY-ERGEN [5] gave a derivation resulting in an equation of the same form as eq. (7), but with a correction term that was $3/2$ times as large as that of eq. (7).
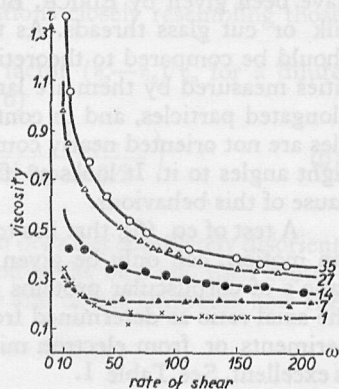
[1] H. FREUNDLICH and E. SCHALEK, *Z. physik. Chem.*, 108 (1924) 153.

[2] H. FREUNDLICH, H. NEUKIRCHNER, and H. ZOCHER, *Kolloid-Z.*, 38 (1926) 43, 48.

[3] Vol. II, chapter VII, § 1 b, p. 185, § 6, p. 211; W. KUHN, O. KUENZLE, and A. KATCHALSKY, *Bull. soc. chim. Belges*, 57 (1948) 421; *Helv. Chim. Acta*, 31 (1948) 1994; R. M. FUOSS and U. P. STRAUSS, *J. Polymer Sci.*, 3 (1948) 246; J. J. HERMANS and J. TH. G. OVERBEEK, *Bull. soc. chim. Belges*, 57 (1948) 154; *Rec. trav. chim.*, 67 (1948) 761.

[4] M. VON SMOLUCHOWSKI, *Kolloid-Z.*, 18 (1916) 194.

[5] W. KRASNY-ERGEN, *Kolloid-Z.*, 74 (1936) 172.

More recently, however, BOOTH [1] reconsidered the whole question and concluded [2] that both KRASNY-ERGEN's and VON SMOLUCHOWSKI's results were far too large and that the electroviscous effect, although existing, was much smaller than that predicted in eq. (7). In particular he finds that the electroviscous effect vanishes irrespective of the value of the ζ-potential for large particles and for thin double layers.

His equation reads

$$\frac{\eta_s - \eta_0}{\eta_0 \, \varphi} = 2.5 + 2.5 \, q^* \left(\frac{e\zeta}{kT}\right)^2 (1 + \varkappa \, a)^2 \, Z \, (\varkappa \, a) \tag{8}$$

where $q^* = \dfrac{\varepsilon kT \Sigma \, n_i \, z_i^2 \, \rho_i}{\eta_0 \, e^2 \, \Sigma \, n_i \, z_i^2}$, ρ is the frictional constant of an ion, and Z is a rather complicated function of $\varkappa a$ represented in Fig.5.

An equation resembling eq. (8) has been published by FINKELSHTEIN and CHURSIN [3]. Their equation, apart from an evident mistake in the Chemical Abstracts and a difference of about a factor two in the numerical constant, is equivalent to the BOOTH equation for large values of $\varkappa a$.

Experimental investigations on the electroviscous effect have been mainly carried out on hydrophillic colloids.

In investigations by KRUYT and BUNGENBERG DE JONG [4] it was conclusively shown that with increasing concentration of electrolyte the viscosity drops to a limiting value, independent of the type of electrolyte which is in accordance with equations (7) and (8) but which may preferably be explained by a shrinking of the particles (see footnote 3 of page 348).

Fig. 5.   Functions $Z \, (\varkappa \, a)$ (curve 2) and $(1 + \varkappa \, a)^2 \, Z \, (\varkappa \, a)$ (curve 1) plotted against $^{10}\log \varkappa \, a$. To be used in eq. (8).

More relevant tests have been carried out by BULL [5] on egg albumin and by BRIGGS [6] on β-lactoglobulin.

In both cases the electroviscous effect is about 100 times smaller than that calculated from eq. (7) and of the order of magnitude following from BOOTH's equation (8). In Table 2 we show the data obtained by BULL compared with the two different theoretical estimates. The interpretation of the measured viscosities is based upon the assumption that the increase in viscosity above the value at the iso-electric point is the electroviscous contribution. In the I.E.P. the viscosity is about 2 times the value ex-

[1] F. BOOTH, *Nature*, 161 (1948) 83; *Proc. Roy. Soc. London*, A 203 (1950) 533.

[2] The difference in the results of BOOTH and KRASNY-ERGEN is due to the neglection by the latter author of diffusion as a restoring factor in the double layer and to at least one mathematical error.

[3] B. N. FINKELSHTEIN and M. P. CHURSIN, *Akad. Nauk S.S.S.R., Otdel. Tekh. Nauk, Inst. Mashinovedeniya, Soveschchanie Vyazkosti Zhidkost. i Kolloid Rastvorov*, 2 (1944) 43; *Chem. Abstracts*, 41 (1947) 1529.

[4] H. R. KRUYT and H. G. BUNGENBERG DE JONG, *Z.physik. Chem.*, 100 (1922) 250; *Kolloidchem. Beihefte*, 28 (1928) 1; H. G. BUNGENBERG DE JONG, *Rec. trav. chim.*, 43 (1924) 189; H. R. KRUYT and H. J. C. TENDELOO, *Kolloidchem. Beihefte*, 29 (1929) 413. See also Volume II, chapter VII, § 5, p. 203.

[5] H. B. BULL, *Trans. Faraday Soc.*, 36 (1940) 80.

[6] D. R. BRIGGS, *Rec. trav. chim.*, 65 (1946) 591; D. R. BRIGGS and M. HANIG, *J. Phys. Chem.*, 48 (1944) 1.

pected from the EINSTEIN equation, probably owing to solvation and a certain deviation from the spherical form.

<div align="center">TABLE 2.</div>

ELECTROVISCOUS EFFECT OF EGG ALBUMIN SOLUTIONS FROM EXPERIMENTS BY BULL [1] AND CALCULATED ACCORDING TO EQ. (7) (SMOLUCHOWSKI) OR EQ. (8) (BOOTH).

pH	$\varkappa a$	$\dfrac{\eta_s - \eta_o}{\eta_o \varphi} - 5.2$		
		observed	calculated	
			SMOLUCHOWSKI	BOOTH
Without NaCl added				
5.25	0.0186	0.6	40	0.01
5.85	0.00941	1.8	169	0.01
6.62	0.00135	2.9	362	0.02
7.72	0.00594	3.9	621	0.02
9.65	0.0504	4.6	865	0.2
10.20	0.1661	4.3	750	0.8
10.85	0.3570	3.2	430	1.4
11.16	0.5101	2.5	282	1.5
With 0.01 N NaCl				
5.71	0.7892	0.4	9.6	0.1
7.38	0.7892	0.6	24.7	0.3
8.82	0.7892	0.5	69	0.75
10.60	0.8333	0.3	60.5	0.7

At high salt content the agreement is relatively good with the theory of BOOTH. The bad accordance for the first entries of Table 2 may well be due to an estimation of $\varkappa a$, which is too low.

§ 3   RHEOLOGY OF CONCENTRATED STABLE SYSTEMS

a. Extensions of the Einstein equation to higher concentrations

In EINSTEIN'S treatment of the viscosity of suspensions the interaction between particles is not taken into account. It is therefore not surprising that eq. (1) holds only for small concentrations and that for larger concentrations corrections must be applied.

Apart from more or less incidental empirical relations [2] equations with a theoretical

See H. B. BULL, p. 349.

[2] See H. MARK, *The general chemistry of high polymeric substances*, New York, Amsterdam 1940, p. 285. H. MARK and A. V. TOBOLSKY, *Physical chemistry of high polymeric systems*, New York 1950, p. 301; W. PHILIPPOFF, *Viskosität der Kolloide*, Dresden, Leipzig 1942, p. 169.

background have been published by GUTH, GOLD and SIMHA [1], SIMHA [2], DE BRUYN [3], SAITÔ [4] and by VAND [5].

Unfortunately, all these authors arrive at different results and it is none too clear which of their results, if any, should be trusted. In all the papers the hydrodynamic interaction between pairs of particles is considered. SIMHA, VAND and, to a certain extent, DE BRUYN, in addition to hydrodynamical also take mechanical interaction (encounters between particles, formation of pairs) into account. Usually the extension to higher concentrations is given in the form of a second term proportional to φ^2 to be added to the EINSTEIN term $2.5\ \varphi$. DE BRUYN [3] expects a simpler equation for the fluidity $1/\eta$ and expressed his results accordingly [6].

Probably the most accurate equation is given by VAND in the form

$$\frac{\eta_s - \eta_o}{\eta_o} = 2.5\ \varphi + 7.349\ \varphi^2 \tag{9}$$

The derivation of this equation starts from a rather straight-forward calculation of the increase in viscosity due to a small increment in the concentration and integrating between zero and the final concentration.

The EINSTEIN term is written

$$\frac{d\eta}{\eta} = 2.5\ d\varphi \text{ or } \ln\frac{\eta_s}{\eta_o} = 2.5\ \varphi.$$

The mutual hydrodynamic interaction of the spheres is accounted for by dividing the right hand term through by $1-0.609\ \varphi$ and the effect of actual collisions by adding a term $4\ (3.125-2.5)\ \varphi^2$ representing the difference in dissipation between one pair and two single particles. The collisions are considered to be exclusively due to the hydrodynamic currents. BROWNian motion is neglected.

SIMHA who restricts his calculations to dumbbell-shaped particles (see, § 3 b, p. 353) only mentions that for spheres the φ^2 term is expected to have a coefficient larger than 4.8, which is not in contradiction to VAND's equation.

GUTH, SIMHA and GOLD, who neglected the formation of pairs, derived

$$\frac{\eta_s - \eta_o}{\eta_o} = 2.5\ \varphi + 14.1\ \varphi^2 \tag{10}$$

DE BRUYN postulated for the fluidity an equation of the form

$$\frac{\eta_o}{\eta_s} = 1 + a\varphi + b\varphi^2 \tag{11}$$

and calculated the constants a and b from the requirement that at low concentrations his equation should merge into the EINSTEIN equation ($a = -2.5$) and at the concentration of close packing ($\varphi = 0.74$) the fluidity should be zero ($b=1.55$). There exists,

[1] E. GUTH and R. SIMHA, *Kolloid-Z.*, 74 (1936) 266; O. GOLD, *Dissertation*, Vienna 1937.

[2] R. SIMHA, *J. Research Natl. Bur. Standards*, 42 (1949) 409; *J. Colloid Sci.*, 5 (1950) 386.

[3] H. DE BRUYN, *Rec. trav. chim.*, 61 (1942) 863; *Proceedings of the International Congress on Rheology, Holland 1948*, Amsterdam 1949, p. II 95.

[4] N. SAITÔ, *J. Phys. Soc. Japan*, 5 (1950) 4.

[5] V. VAND, *J. Phys. & Colloid Chem.*, 52 (1948) 277.

[6] See also J. V. ROBINSON, *J. Phys. & Colloid Chem.*, 53 (1949) 1042, and E. C. BINGHAM, *Fluidity and plasticity*, New York 1922, p. 160 ff. who also assumes the fluidity to be a nearly linear function of the concentration.

however, no theoretical justification for the assumption of the validity of eq. (11) over the whole range of concentrations. Consequently DE BRUYN's equation (11) should be considered as a semi-imperical one.

With BURGERS, DE BRUYN (l.c. 1949) has derived an equation of the form

$$\frac{\eta_o}{\eta_s} = \frac{1-\varphi}{1+1.5\,\varphi}$$

which on expansion passes into

$$\frac{\eta_s - \eta_o}{\eta_o} = 2.5\,\varphi + 2.5\,\varphi^2 + \ldots\ldots \tag{12}$$

an equation that has also been derived by SAITÔ. The coefficient 2.5 for the quadratic term is however certainly too low as it is already found by SAITÔ in a way analogous to that of VAND (see above) without considering actual interaction between pairs.

Experimental tests do not allow an unambiguous decision between the different equations proposed.

The accurate experiments by EIRICH [1] c.s. with glass spheres lead to values of 9, 12 and 13 for the coefficient of the quadratic term and do thus reasonably confirm the equation by GUTH, SIMHA and GOLD, as do more recent measurements on latex emulsions [2].

At the other extreme are monodispersed emulsions of asphalt in water, described by EILERS [3] which are in very good accord with DE BRUYN's eq. (11).

VAND [4] finally, with glass spheres in a solution of ZnI_2 in water-glycerol mixtures finds an empirical equation

$$\frac{\eta_s - \eta_o}{\eta_o} = 2.5\,\varphi + 7.17\,\varphi^2 + 16.2\,\varphi^3 \tag{13}$$

which confirms his theoretical eq. (9) perfectly.

VAND carried out his experiments using the same glass spheres that had been used by EIRICH c.s. but in a dispersion medium of very high viscosity (80 cs), which increases the reliability of his results. In contradistinction to EIRICH, VAND took account of wall effects in his measurements.

At the present time a choice cannot easily be made although there might be some preference for the work of VAND. But, even in the case with the largest second order term (eq. 10), this term for concentrations below 1%, increases the relative viscosity (η_s/η_o) by less than $1°/_{oo}$, which is about the usual experimental accuracy.

The few experiments on true hydrophobic colloids give a larger second order term. This might, however, be connected with the electroviscous effect that has not yet been calculated in the second approximation[5].

[1] F. EIRICH, cited from H. MARK, *High polymers*, Vol. 2, *The general chemistry of high polymeric substances*, Amsterdam 1940, p. 274.

[2] H. F. SMITH, *Rubber Chem. and Technol.*, 15 (1942) 301.

[3] H. EILERS, *Kolloid-Z.*, 97 (1941) 313.

[4] V. VAND, *J. Phys. & Colloid Chem.*, 52 (1948) 300.

[5] Recent mensusements by G. J. HARMSEN and J. VAN SCHOOTEN (to be published) proved the existence of a large electroviscous effect, proportional to the second and higher powers of the concentration.

BOUTARIC and VUILLAUME's [1] measurements on As_2S_3-sols can be represented by

$$\frac{\eta_s - \eta_0}{\eta_0} = 2.5 \, \varphi + 75 \, \varphi^2$$

and ODÉN's [2] experiments on sulphur sols lead to quadratic terms ranging between $30 \, \varphi^2$ and $60 \, \varphi^2$.

b. Non-spherical particles

In the light of the uncertainties on the viscosity of concentrated suspensions of spherical particles it is only to be expected that our knowledge of the higher concentrations of elongated particles is still scarcer.

SIMHA [3] indicated that already from dimensional considerations the viscosity may be represented by a series

$$\frac{\eta_s - \eta_0}{\eta_0} = a \, \varphi + k_1 \, a^2 \varphi^2 + k_2 \, a^3 \, \varphi^3 + \dots . \tag{14}$$

in which k_1, k_2 etc. are pure numbers.

Explicit equations of this type have been given by EIRICH and SIMHA [4], based upon the equation of GUTH for very long ellipsoids in the absence of BROWNIAN motion

$$\frac{\eta_s - \eta_0}{\eta_0} = \left(\frac{f}{2 \ln 2f - 3} + 2 \right) \varphi + k \frac{f^3}{(2 \ln 2f - 3)^2} \, \varphi^2 \tag{15}$$

where k is a constant probably of the order unity.

SIMHA [4] has given a complete derivation for dumbbells and obtained

$$\frac{\eta_s - \eta_0}{\eta_0} = \frac{3}{2} \, \frac{L^2}{a^2} \, \varphi + \frac{87}{50} \, \frac{L^4}{a^4} \, \varphi^2 \tag{16}$$

where $2L$ is the distance between the centres of the two spheres (radius a) of which the dumbbell is composed. The equation (16) is derived for small rates of shear and large BROWNIAN motion.

The experiments with suspensions of glass and silk rods [5] are not very conclusive. As has been mentioned in § 2b, p. 347 the viscosity extrapolated to very great dilution is not in accord with any of the theoretical equations. It cannot be expected therefore that higher concentrations will show a better agreement. Empirically EIRICH and his collaborators find for experiments in a COUETTE viscosimeter

$$\frac{\eta_s - \eta_0}{\eta_0} = 2.5 \, F \, \varphi + 8 \, F^2 \, \varphi^2 + 40 \, F^3 \, \varphi^3 \tag{17}$$

where F is a factor dependent upon the axial ratio but not upon size or concentration of the rods.

[1] A. BOUTARIC and M. VUILLAUME, *J. chim. phys.*, 21 (1924) 247.
[2] S. ODÉN, *Der kolloide Schwefel, Nova Acta Regiae Soc. Sci. Upsaliensis*, (4) 3 (1913).
[3] R. SIMHA, *J. Research Natl. Bur. Standards*, 42 (1949) 409; *J. Colloid Sci.*, 5 (1950) 386.
[4] F. EIRICH and R. SIMHA, *Monatsh.*, 71 (1937) 67. See also E. GUTH, *Kolloid-Z.*, 74(1936) 147.
[5] F. EIRICH, H. MARGARETHA, and M. BUNZL, *Kolloid-Z.*, 75 (1936) 20.

Experiments on the same suspensions in a capillary viscosimeter give essentially lower results for the viscosity and a very evident dependence of the viscosity on the rate of shear.

c. Dilatancy

In dilute stable suspensions the viscosity is purely NEWTONian, except when the rate of shear in suspensions of non-spherical particles is high. (See § 2 b, p. 345).

The behaviour of concentrated suspensions is, however, very different. For low rates of shear their viscosity is NEWTONian and more or less accurately described by the equations treated in the preceding subsections. But at somewhat higher shearing stresses the viscosity increases enormously, so that it is virtually impossible to increase the rate of shear above a certain rather low value (see chapter I, Fig. 8, p. 23).

OSBORNE REYNOLDS[1], who discovered this phenomenon in 1885 (nota bene, when looking for a model of the ether), gave it the name *dilatancy*. It can be explained in the following way. The viscosity of a concentrated suspension is mainly located in the thin layers of liquid between adjacent particles. A motion of the system is only possible when accompanied by a change in the relative positions of the particles. This leads to local increases of the concentration and as the system is already near the closest packing these concentration changes lead to a very great increase of the local viscosity. When enough of these clusters are formed to lead to a continuous network through the system, any further motion is nearly impossible until the clusters are at least partially disintegrated. The dispersion of these clusters is caused by repulsive forces between the particles, by BROWNian motion if the particles are small enough ($\sim 1\mu$) and by gravity. If the motion of the system is so slow that the clusters can be dispersed as soon as they are formed, the system will behave as one of low viscosity. At higher rates of shear, however, the dispersion of the clusters will be too slow (their time of relaxation too large) so that the build-up will outgrow the break-down, and the system will behave as one that is nearly solid.

The phenomenon of dilatancy is especially evident in suspensions (pastes) in which the particles are nearly densely packed. When such a suspension is sheared, it is inevitable that most of the particles move farther apart, although some of them come closer together. The volume occupied by the framework of particles therefore increases. If the concentrated suspension is sheared as such, without excess liquid being present, the liquid is sucked in, leaving the exterior of the paste dry. The expansion of the whole mass of particles under the influence of shear has given rise to the name *dilatancy*. It can be demonstrated [1] by bringing a concentrated mixture of sand and water with some excess of water in a rubber balloon provided with a glass tube. When the rubber balloon is pressed, the liquid level in the glass tube does not rise as would be expected, but descends.

The drying up of a sandy shore around a fresh footstep should also be explained as dilatancy.

A paste of starch in water (about 40% by volume), when gently stirred, shows only a slight resistance but turns dry and hard as soon as one tries to stir more rapidly.

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[1] OSBORNE REYNOLDS, *Phil. Mag.*, (5) 20 (1885) 469; *Nature*, 33 (1885) 429.

A mathematical theory of dilatancy has been given by REINER [1].

From general considerations on the functional relation between stress and strain or rate of strain, REINER showed that an obvious generalization of the simple NEWTONian liquid leads to a liquid in which a simple shearing stress produces in addition to a simple shearing rate of strain, a change of volume (or at constant volume, a change of pressure), a dilatation proportional to the rate of strain.

REINER's theory does not lead to specific considerations on the composition of the systems for which dilatancy is to be expected.

In our explanation of dilatancy the condition of stability is essential, because only stable suspensions can give a sediment which is dense enough (see § 5b, p. 357) to show dilatancy. In a flocculated system the concentration of particles remains too low.

The necessity of stabilization before dilatancy can occur is quite evident in an investigation by VERWEY and DE BOER [2]. They could change a suspension of iron or other powders in apolar liquids like carbon tetrachloride or benzene from a plastic (thixotropic, *vide infra*) to a dilatant state by adding traces of the stabilizing oleic acid [3].

RÖDER [4] carried out an extensive investigation on the dilatancy of suspensions of starch and quartz in water. He found that dilatancy was limited to a very small range of concentrations, *e.g.* to the range between 38% and 44% by volume of rice starch or to 41-45% by volume of quartz (diameter of the particles 1.5-5 μ). He remarks that another condition for typical dilatant behaviour is a low viscosity of the medium of dispersion. When the medium is very viscous itself, the rapid flow necessary to evoke dilatancy is impossible.

The fascinating phenomenon of *quicksand*, although judged to be caused by thixotropy by FREUNDLICH and JULIUSBURGER [5] (see § 5 d, p. 363) may in certain cases be very well explained by dilatancy, giving way as it does to continued pressure, but resisting strongly any vehement motion.

Dilatancy has found no practical applications, on the contrary, it is often troublesome. In several cases, where stable concentrated suspensions have to be used (different paints, white ink) they form, on standing, a densely packed dilatant deposit, which can only be redispersed with great difficulty.

If a system with a tendency to dilatancy is fed into a colloid mill (chapter II, § 1 b, p. 60), the mill may come to a standstill on account of the high resistance offered by rapid shearing.

In such cases it may be advisable to destroy the stability at least to a certain extent in order to avoid these difficulties.

§ 4. THE SEDIMENTATION VOLUME OF STABLE AND FLOCCULATED SYSTEMS

The sedimentation volume forms one of the characteristic differences between stable and flocculated suspensions (see chapter VIII, § 11 a, p. 336). In a stable suspension

[1] M. REINER, *Am. J. Math.*, 67 (1945) 350.

[2] E. J. W. VERWEY and J. H. DE BOER, *Rec. trav. chim.*, 57 (1938) 383.

[3] Actually as a consequence of the much denser packing of a stable system when compared to a flocculated one (see § 4, this page) the dilatancy was only evident after partial settling of the stabilized system and decanting of the supernatant liquid.

[4] H. L. RÖDER, *thesis*, Utrecht 1939; H. FREUNDLICH and H. L. RÖDER, *Trans. Faraday Soc.*, 34 (1938) 308.

[5] H. FREUNDLICH and F. JULIUSBURGER, *Trans. Faraday Soc.*, 31 (1935) 769.

sedimentation is slow, and the particles arriving at the bottom of the vessel remain apart by the same forces that prevent their aggregation (in many cases this is the double layer repulsion). This entails that the particles by rolling over one another are enabled to find the position of minimal potential energy and thus the sediment becomes very dense.

A flocculated system, on the contrary, sediments more rapidly, owing to aggregate formation, and the sediment is bulky because the particles preserve the haphazard positions in which they touched each other for the first time.

The difference is most obvious for intermediate particle dimensions. Coarse particles may be too heavy to allow any very loose packing, and with very fine (colloidal) particles, sedimentation of the stable system is often so extremely slow as to be virtually unobservable.

The influence of stability upon the sedimentation volume has already been recognized and applied to soil colloids by EHRENBERG [1].

A typical example of the difference in sedimentation volume is given by RÖDER [2].

40 grams of quartz particles (diameter 1-5 μ) stably dispersed in 25 vol. water settled in about six hours to a sediment with a height of 8.5 mm containing 54% by volume of quartz.

The same amount of quartz in 25 vol. wet [3] CCl_4 (unstable suspension) reached in 15 minutes a final sedimentation height of 53 mm corresponding to 7% by volume of quartz.

RYAN, HARKINS and GANS [4] obtained similar data on titania and other pigments, dispersed in organic liquids. See, for a discussion of these experiments, § 5 b, p. 357.

KRUYT and TROELSTRA [5] used the sedimentation volume to distinguish between several grades of loss of stability of negative silver iodide sols. In flocculations with K^+, Ba^{++}, Al^{+++} and Ag^+ they found sedimentation volumes increasing in this order, indicating that the discharge by Ag^+ leads to a completely unstable sol, whereas compression of the double layer by Al^{+++} or Ba^{++} still leaves a slight repulsion. In flocculation by K^+ a marked repulsion is left as is proved by the high density of the sediment.

§ 5. NON-NEWTONIAN FLOW AND VISCO-ELASTIC BEHAVIOUR OF FLOCCULATED SYSTEMS

a. Flow

The typical difference in rheological behaviour between stable and unstable suspensions is caused by the tendency towards formation of aggregates in the latter systems In dilute systems this difference is not striking because there aggregation is slow (see chapter VII, p. 278, on Rate of flocculation) and either has not proceeded very far, or if it has, has resulted in a large scale separation into two phases, after which rheological measurements are rather meaningless.

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[1] P. EHRENBERG, *Die Bodenkolloide*, 3rd ed., Dresden 1922.

[2] H. L. RÖDER, *thesis*, Utrecht 1939, p. 55.

[3] See H. R. KRUYT and F. G. VAN SELMS, *Rec. trav. chim.*, 62 (1943) 407, 415. See also this chapter § 5 b, p. 357.

[4] L. W. RYAN, W. D. HARKINS, and D. M. GANS, *Ind. Eng. Chem.*, 24 (1932) 1288.

[5] H. R. KRUYT and S. A. TROELSTRA, *Kolloidchem. Beihefte*, 54 (1943) 225. S. A. TROELSTRA, *thesis*, Utrecht 1941, p. 70.

In more concentrated systems, however, which for that matter are never as con-
centrated as stable ones can be (see § 3 c, p. 354; § 4, p. 355), the rate of aggregation
is so large that even in flow the aggregates do not completely disappear. Moreover,
the formation of aggregates does not necessarily result in a phase separation, but the
aggregates may form a coherent network through the whole system which then obtains
the properties of a gel or paste.

These concentrated systems (pastes, salves, creams, putty, paints, moulding clays
etc.) borrow their considerable practical importance just from these rheological pro-
perties, *in casu* from their *plasticity*. As has been pointed out in chapter I, § 4 c 1, p. 22
plasticity is characterized by a viscosity which decreases with increasing rate of shear
and usually by the presence of an actual yield stress, *i.e.* a minimum shearing stress
necessary to cause a finite rate of shear. When these systems are subjected to higher
shearing stresses, their mobility is relatively large, of the same order as that of the dis-
persion medium. They are thus easily deformed and modelled, but retain their form
when left to themselves. This is in striking contrast to tough systems like syrups, tar,
glass in the transition interval etc., which are purely NEWTONIAN liquids with a very
high viscosity but without a yield value. They flow at the command of the smallest
stresses but even for large stresses their flow remains exceedingly slow.

The rheological characterization of plastic systems cannot be given by a single con-
stant. It is necessary for this purpose to give the whole D–τ diagram (relation between
rate of shear and shearing stress) and often even the manner in which the D–τ diagram
depends upon the previous history of the system (See § 5 d, p. 363, thixotropy).

b. External influences on gel formation and plasticity

b. 1. *Flocculating agents*

Just as it is usually more difficult to prepare stable sols than flocculated systems,
there is more chance of obtaining a plastic or at least a flocculated system in preparing a
concentrated suspension than a stable, dilatant one. The agents promoting the floccu-
lated state are the same as those for dilute colloidal systems and have been treated ex-
tensively in chapter VIII. We only draw attention again to the influence of elec-
trolytes in aqueous suspensions according to the rule of SCHULZE and HARDY (*e.g.*
chapter VIII, § 10 a, p. 335).

With the concentrated systems treated here, the electrolytes present often manifest themselves
more clearly in ionic exchange than in the intermicellar liquid. Calcium clays, for instance, are usually
plastic, whereas sodium clays may be stable. In arable land a sufficiently open structure of the soil is
important for the free circulation of water and air. The soil colloids should therefore be in the flocculated
state, which normally is maintained by the presence of Ca^{++}. One of the big dangers of inundation
by sea-water is the exchange of Ca^{++} against Na^+. As long as the sodium chloride content remains
high, the flocculated state is preserved, but when after the reclaiming of the flooded region the NaCl is
washed away by the rain, the soil colloids are stabilized and a slight mechanical action may then bring
them into a dense packing which is unsuitable for plant-growth. With the knowledge of these facts
the remedy is evident. It consists in addition of Ca^{++} ions (in the form of gypsum) to the soil soon
after the reclaiming and before mechanical tillage.

In addition to the flocculating agents discussed in chapter VIII, we wish to treat
here the influence of a third phase on stability more extensively. This factor, which has

been thoroughly investigated by KRUYT and VAN SELMS [1], may be of great importance in practice, because in the preparation of suspensions in oils (*e.g.* paints) the presence of traces of water is not easily avoided and these traces may be sufficient to act as a flocculating third phase.

KRUYT and VAN SELMS measured among other things D–τ curves for suspensions of finely powdered quartz in an oil of the same density ($C_2H_2Br_4$—$C_2H_2Cl_4$) with the addition of small amounts of water. Water destabilizes the suspension, as is evident from the yield stress increasing with the water content of the system. In addition it may be
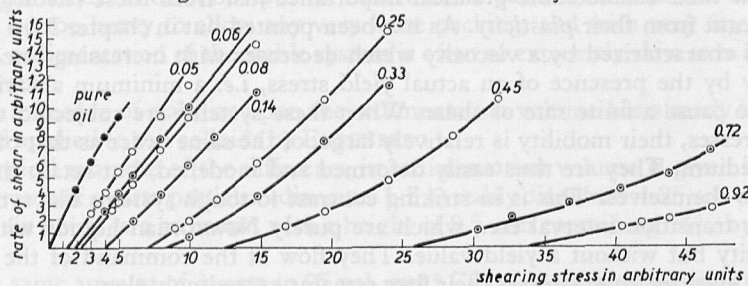
Fig. 6. Flow diagram of suspensions of quartz in mixtures of $C_2H_2Cl_4$ and $C_2H_2Br_4$ with the addition of small amounts of water, measured in a HÖPPLER type viscometer with variable inclination (F. G. VAN SELMS and H. R. KRUYT, *Rec. trav. chim.*, 62 (1943) 398). In all experiments the volume ratio quartz-oil was 1:8. The numbers along the curves give the water content in weight percent calculated on the quartz.

remarked that the increase in yield stress is accompanied by a relatively small increase in viscosity above the yield point, showing that the viscosity of the system, once it has been made to flow, is not essentially larger than that of a stable suspension of the same concentration.

The flocculating action of the water is governed by the hydrophily of the quartz. In the apolar medium the quartz particles are preferentially covered by a layer of water, but then the system contains a big interface water/oil, which can be diminished by coalescence of the water layers. As no stabilizer for the water-in-oil system is present, this coalescence will take place and any relative displacement of the particles becomes difficult because this would imply an increase in the water/oil interface.

The experiments of RYAN, HARKINS and GANS [2] on the sedimentation volume of titania in oils with different additions (see § 4, p. 355) lead to the same picture. In apolar oils the sedimentation volume is in-

Fig. 7. Illustrating the decrease of the interface water/oil by coalescence of the water layers around two particles.

creased by water in amounts of 0.06–26 % calculated on the pigment. The sediment becomes denser (stability increased) on addition of polar substances (methanol, acetone etc.) which increase the solubility of water in the oil or of substances like metal soaps, oleic acid, which are known to stabilize water-in-oil emulsions.
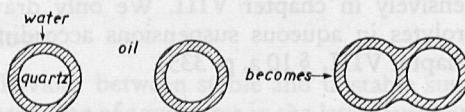
[1] H. R. KRUYT and F. G. VAN SELMS, *Rec. trav. chim.*, 62 (1943) 407, 415.
[2] L. W. RYAN, W. D. HARKINS, and D. M. GANS, *Ind. Eng. Chem.*, 24 (1932) 1288.

In order to explain certain capillary properties of wetted soil, VERSLUYS [1] had calculated how small amounts of water are distributed in the interstices between masses of spherical particles. Using this calculation, KRUYT and VAN SELMS [2] could obtain a semiquantitative explanation of the influence of the third phase on the rheological properties of suspensions.

Fig. 8a.   Starch (polar) in an apolar oil (xylene).
Left: Completely dry. Fluid.
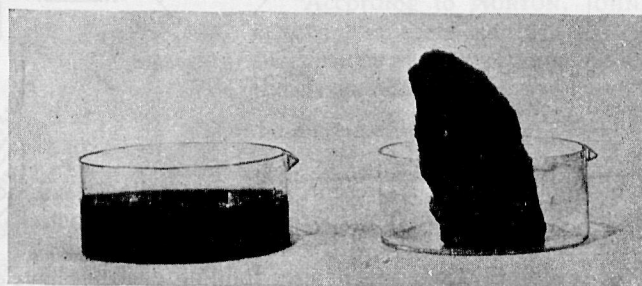Right: Starch contains 12% water. Solid.

Fig. 8b.   Coal (apolar) in water (polar).
Left: No third phase present. Fluid.
Right: After the addition of xylene (5% on coal). Solid.

A very eloquent demonstration [2] of this phenomenon is shown in Fig.8, where a suspension of starch (polar) in xylene (non-polar) appears to be fluid when completely dry but solid after the addition of water. Conversely a fluid mixture of coal (apolar) in water (polar) is solidified by the addition of some xylene.

b. 2.   Size and shape of the particles

The *size* of the particles does not have a very typical influence on plastic behaviour and gel formation. There seems to be no lower limit to the particle size for giving a ge-

[1] J. VERSLUYS, *thesis*, Delft 1916.
[2] H. R. KRUYT and F. G. VAN SELMS, *Rev. trav. chim.*, 62 (1943) 415.

latinous mass under suitable conditions. The upper limit is simply determined by the condition that sedimentation must not be too rapid. For instance wet gravel would not be considered plastic, but wet sand with a particle size of the order of 0.1 mm may be.

Shape on the contrary is a very important factor. The more elongated the particles, the more typical their plastic properties. It will be evident that, in order to form a coherent network, a much smaller amount of material is needed with rod-shaped or plate-shaped particles, than with round or cubic ones. Moreover, if long-range attractive forces were to play a part in the network formation, they also would be favoured by an elongated shape of the particles.

In low concentrations these systems will have a comparatively high yield stress and a very low viscosity above it. At higher concentrations the yield stress may rise to much higher values than can be reached with round particles, whereas the viscosity remains reasonably low.

A very typical example of the influence of particle shape is given by the behaviour of benzopurpurin 4 B and its meta analogue [1].

Benzopurpurin 4 B is an azo dye, prepared from *ortho*-tolidine and naphtionic acid and has the following formula.
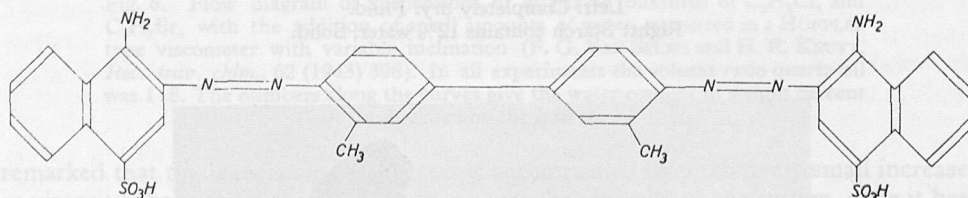
Benzopurpurin 4 B

When a slight amount of salt is present, it forms a colloidal solution, containing rod-shaped particles. The solution shows streaming double refraction. Concentrated solutions may gel and a paste of the dye with water is typically plastic.

The analogous substance derived from *meta*-tolidine does not have elongated particles in solution even when large amounts of salt have been added. It does not gelatinize and does not possess the plastic properties but gives a dilatant paste.

b. 3.   Influence of concentration

As the typical mechanical properties of flocculated systems are connected with the formation of coherent network structures, the concentration of the dispersed phase is evidently of great influence. If the concentration is low, flocculation will be the result of loss of stability. At higher concentrations, however, a gel or paste will be formed. In Table 3 data obtained by FREUNDLICH [2] are given, from which it appears that an iron hydroxide sol is flocculated at a concentration of 0.5%, whereas at a concentration of 5% it sets to a thixotropic (*vide infra*) gel.

[1] C. ROBINSON and H. A. T. MILLS, *Proc. Roy. Soc. London*, A 131 (1931) 576, 596; H. FREUNDLICH, *J. Soc. Chem. Ind. London*, 53 (1934) 222 T.
[2] H. FREUNDLICH, *Thixotropy*, Paris 1935, p. 7.

TABLE 3

GEL FORMATION AND FLOCCULATION IN IRON HYDROXIDE SOLS

Electrolyte	Flocculation value in millimols/litre sol conc. 4.92 g Fe_2O_3 per litre	Salt concentration in millimols/litre causing gelation after 400 seconds sol conc. 52.6 g Fe_2O_3 per litre
NaCl	325	45
KCl	350	45
KBr	500	62
NaOH	6.5 (reversal of charge)	18
Na_2SO_4	3.25	12
Na_2 oxalate	2.75	9.5
K_3 citrate	1.7	7

Drilling muds[1], which are used in drilling bore holes for oil wells, need a yield stress in order to prevent sedimentation of the clay and the cuttings when the drilling is temporarily stopped and a low viscosity above the yield stress, so that no energy is dissipated unnecessarily. They contain therefore an amount of clay just sufficient to give a weak gel. This amount depends strongly upon the quality of the clay and varies between 2% for highly swelling finely divided bentonites and 30% for the coarser kaolinitic types of clay.
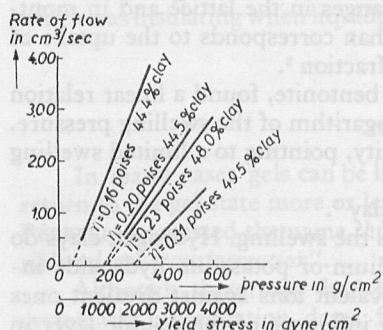

Fig. 9.   Influence of concentration of clay on yield stress and on viscosity.

According to NORTON, JOHNSON and LAWRENCE[2] the yield stresses of certain kaolinite suspensions are proportional to the third power of the clay concentrations,

$$\text{Yield stress} = k\ c^3,$$

the proportionality constant, k, increasing strongly with decreasing size of particles.

WILSON and HALL[3] give an example in which the dependence of the yield strength on the clay concentration is still stronger, the yield strength increasing about six-fold for an increase in concentration from 45 to 50%. See Fig. 9.

The sensitivity of the plastic properties upon concentration have even induced ATTERBERG[4] to introduce certain specified concentrations as a measure of the plasticity of clays. A clay is characterized by its "plastic number", which is the difference between the "upper" and "lower" plastic limits". The upper plastic limit is the moisture content at which the yield stress just becomes measurable. At the moisture content corresponding to the lower plastic limit, the yield stress is so high that the clay has lost its plastic deformability.

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[1] See D. H. LARSEN, in J. ALEXANDER, Colloid chemistry, theoretical and applied, vol. 6, New York 1946, p. 510.

[2] F. H. NORTON, A. L. JOHNSON, and W. G. LAWRENCE, J. Am. Ceram. Soc., 27 (1944) 149.

[3] R. E. WILSON and F. P. HALL, J. Am. Ceram. Soc., 5 (1922) 916.

[4] A. ATTERBERG, Die Plastizität der Tone, Intern. Mitt. Bodenk., 1(1911) 10.

One would expect the upper plastic limit to be close to the concentration of a free sediment of the clay, because the sedimentation does not proceed further than the point at which the sediment acquires a certain solidity.

c. Properties of gels and pastes

c. 1. Swelling

In most of the systems treated in this chapter, swelling is not a very pronounced phenomenon. One associates swelling in the first place with lyophilic colloids, and with good reason (see vol. II, chapter XII, § 6 b, p. 556). A partially or wholly dehydrated mass of particles may take up again a certain amount of liquid (imbibition) but a regular swelling, that is an *increase* in volume, does not easily occur, because in the formation of the network the junction points are usually of the irreversible type, preventing any extensive change of shape of the whole network.

In clays, however, swelling is not an uncommon phenomenon and it is especially pronounced in the clay minerals of the bentonite type. These minerals have, like all clays, a sheet structure, but in bentonites the possibility exists of taking up a continuously varying amount of water, up to 4 complete monolayers [1] between successive sheets of the montmorillonite lattice, thus leading to an actual swelling of the particles.

Apart from this internal swelling, swelling between particles can also exist. Kaolinitic clays *e.g.* show swelling without detectable changes in the lattice and in montmorillonite the swelling may proceed much farther than corresponds to the uptake of the four layers of water that are indicated by X-ray diffraction [2].

MATTSON [3], who measured swelling pressures of bentonite, found a linear relation between the logarithm of the water content and the logarithm of the swelling pressure. At high water content there is a deviation from linearity, pointing to a limited swelling caused by attractive forces.

Analogous data exist for kaolinite [4] and Putnam clay [5].

The type of cation present in the clays influences the swelling. Hydrogen clays do not swell, or only very slightly. Neutralizing with sodium or potassium hydroxide increases the swelling enormously. Exchange of monovalent ions against divalent ones decreases the swelling again. This points to a strong influence of the double layer in these phenomena [6].

Swelling of clays occurs not only in water but also in other polar solvents like methanol, etc. [7]. This kind of swelling has been investigated by X-ray diffraction, and the uptake of polar liquid has been proved to be restricted to 1 or a small number of monomolecular sheets in the lattice. The swelling between particles has not been investigated.

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[1] S. B. HENDRIKS and M. E. JEFFERSON, *Am. Mineral.*, 23 (1938) 863.
W. F. BRADLEY, R. E. GRIM, and G. L. CLARK, *Z. Krist.*, 97 (1936) 216.
[2] J. MERING, *Trans. Faraday Soc.*, 47 B (1946) 205.
[3] S. MATTSON, *Soil Sci.*, 33 (1932) 301.
[4] F. H. NORTON and A. L. JOHNSON, *J. Am. Ceram. Soc.*, 27 (1944) 77.
[5] C. M. WOODRUFF, *Soil Sci. Soc. Am. Proc.*, 5 (1940) 36.
[6] See C. E. MARSHALL, *The colloid chemistry of the silicate minerals*, New York 1949, p. 157.
[7] D. M. C. MAC EWAN, *Nature*, 162 (1948) 935.

c. 2.   *Electrical and optical properties of gels*

Optical properties which have a certain importance for these systems are streaming birefringence, which has been discussed in chapter III, § 3 b, p. 109, the changes in turbidity during the imbibition of a silica gel, which has been treated in volume II, chapter XII, § 6a. 3, p. 529, and the remarkable colour effects detected by COELINGH, that are due to interference in thin "gels" at different stages of imbibition, which are discussed in the same chapter (p. 531 ff.)

The experimental material on the electrical properties of the systems discussed here is rather scarce. As a rule, electrical conductivity and dielectric constant are what should be expected for a mixture of two phases of the given composition. No conspicuous change takes place during the transition from the sol to the gel state as has for instance been verified by KISTLER [1] on the dielectric constant of thixotropic (see § 5 d) Al_2O_3, Fe_2O_3 and bentonite gels.

VOET [2], however, experimenting with different suspensions of pigments in oils, found the dielectric constant of unstable systems to be higher in rest than when subjected to a shearing motion. He explains this difference as a consequence of the elongated form of the agglomerates which are disturbed in shear and are re-established in rest. The effect is not given by pure NEWTONian systems where presumably agglomeration is absent.

An analogous case has been reported of a thixotropic suspension of graphite in oil, which was insulating when liquid, but conducting after solidification (see § 5d. 4, p. 367).

d.   Thixotropy

d. 1.   *The phenomenon*

In many cases gels can be liquefied by shaking or other mechanical action but they return to the gel state more or less rapidly after the mechanical disturbance has ceased. PÉTERFI [3] suggested the name *thixotropy* (changing by touch) for this "*isothermal reversible sol-gel transformation*".

Although thixotropy had been observed several times before [4], the first more systematic investigation dates from 1923, when SZEGVARI and SCHALEK [5] published their work on the thixotropy of concentrated iron oxide and other oxide sols, where gelation is brought about by the addition of electrolytes.

Thixotropy is found both in gels derived from true hydrosols in the proper sense as in concentrated suspensions of coarser particles.

It occurs preferentially, although perhaps not exclusively, in systems with elongated (flat or long) particles. It is explained either by a certain slowness of gel formation, which may be based upon the analogue of slow flocculation (see chapter VII, § 2 and 3, p. 283 ff.) or upon the rareness of encounters between particles due to slow BROWNian motion.

[1] S. S. KISTLER, *J. Phys. Chem.*, 35 (1931) 815.

[2] A. VOET, *Proceedings of the International Rheological Congress, Holland* 1948, Amsterdam 1949, II—15; *J. Phys. & Colloid Chem.*, 53 (1949) 597.

[3] T. PÉTERFI, *Arch. Entwicklungsmech. Organ.*, 112 (1927) 689.

[4] See H. GREEN and R. N. WELTMANN, *Thixotropy*, in J. ALEXANDER, *Colloid chemistry, theoretical and applied*, vol. 6, New York 1946, p. 328.

[5] E. SCHALEK and A. SZEGVARI, *Kolloid-Z.*, 32 (1923) 318; 33 (1923) 326.

The fact that in thixotropy the contacts between the particles are difficult to form explains also their comparative rareness and thus the ease with which these few contacts are broken again by mechanical disturbance.

To simplify the statement we assumed here that in the network formation actual contact between the particles is established, but there may also exist cases where a simple juxtaposition of particles is sufficient to keep them together by long range forces (see chapter VIII, § 7b. 5, p. 330). Rather typical for this possibility is an observation by HAUSER [1], that in a thixotropic suspension of bentonite two particles that are close to each other gradually loose their visible BROWNian motion, although there is no material contact between them.

The same observation has also been made by SCHALEK and SZEGVARI (l.c.) on the thixotropic sol of V_2O_5.

It is uncertain whether thixotropy is of perfectly general occurrence in any gelling system. It looks indeed as if this might be the case, with the restriction that there are systems (especially the coarser ones) with negligible setting time, which is distinguished from the usual thixotropy with finite setting time by the name "false body" [2].

d. 2. Measurement of thixotropy

A quantitative estimate of thixotropy should at least contain two different kinds of information, one about the strength of the gel formed, and the other about the rate of solidification. In the determination of the time of solidification, introduced by SCHALEK and SZEGVARI and much used by FREUNDLICH, the rate of gelation is measured, but all different samples are compared at one and the same gel strength.

In this method the time is determined in which in a test tube of standardized dimensions a sol sets to a gel that is just sufficiently solid not to flow out when the tube is held upside down. The method gives a good idea of the rate of solidification and is extremely simple.

In a method of investigation introduced by PRYCE JONES [3] the inner cylinder of a COUETTE viscometer is turned through a certain angle out of its equilibrium position. After a certain time of waiting the cylinder is released, and the rate of its return to the equilibrium position is reco. led. When the gel strength is zero, the cylinder returns to its equilibrium position. After a waiting time, the rate of return is slower and the cylinder stops before the normal zero is reached. This is illustrated in Fig. 10.

VAN SELMS and KRUYT [4] applied the principle of the rolling sphere viscometer (HÖPPLER viscometer) to thixotropic or rathe to false body systems. The method allows one to obtain D-τ curves though not on an absolute scale. Consequently it gives a measure for the gel strength and if the measurements are repeated after different waiting times, also for the rate of solidification.

GOODEVE and WHITFIELD [5], reasoning that even during the measurement of viscosity the gel is building up, tried to find a measure of viscosity from a single D-τ curve, where each set of values corresponded to the stationary state reached after a

[1] E. A. HAUSER, Kolloid-Z., 48 (1929) 57.

[2] J. PRYCE JONES, J. Oil & Colour Chemists' Assoc., 17 (1934) 305; 19 (1936) 295.

[3] J. PRYCE JONES, J. Oil & Colour Chemists' Assoc., 17 (1934) 305; Proc. Univ. Durham Phil. Soc., 10 (1946) 427—467.

[4] F. G. VAN SELMS and H. R. KRUYT, Rec. trav. chim., 62 (1943) 398.

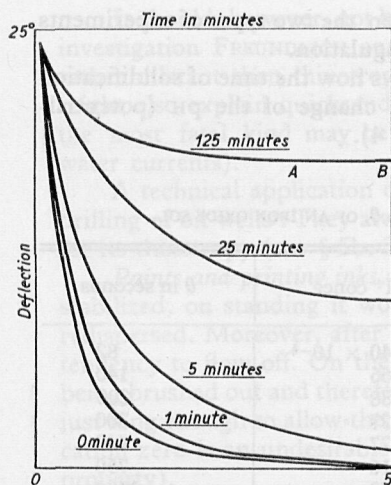[5] C. F. GOODEVE and G. W. WHITFIELD, Trans. Faraday Soc., 34 (1938) 511.

Fig. 10. Deflection-time curves for a thixotropic system. The curve marked 0 is a truly exponential return to equilibrium. After waiting for periods of 1, 5, 25 and 125 minutes, the return is slower, not exponential and does end in a finite deflection, as for instance in the 125 min curve, where the part A B is already parallel to the abscissa.

sufficiently long time of shear. The building up of the gel should then just be equal to the breakdown by shear. The method, although having the advantage of avoiding long waiting periods, has been severely criticized by GREEN and WELTMAN (l.c., p. 363), who remarked that the *coefficient of thixotropy* used by GOODEVE and WHITFIELD is not different from a BINGHAM yield value and that consequently their method gives no information on the rate of solidification. Any plastic system is therefore classified as thixotropic by GOODEVE and WHITFIELD and it seems more useful to reserve this name for systems with a typical slow build-up.

GREEN and WELTMAN themselves also apply the COUETTE viscometer to characterize thixotropy but they let their systems gel during different periods, then break down the structure partially by shear of different strength and durations and determine the residual rheological properties at a lower rate of shear.

In conclusion we might say that we do not yet possess a universal method for measuring thixotropy but that a very typical feature of the phenomenon is conveniently measured by the "time of solidi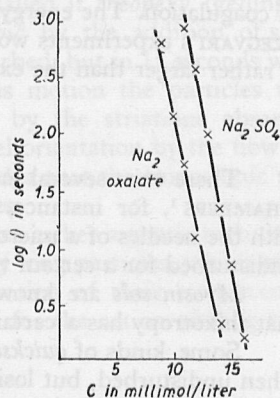fication". When more information is wanted, determination of a series of consistency curves (PRYCE JONES, VAN SELMS and KRUYT, GREEN and WELTMAN) seems to be more to the point than the application of the single consistency curve method of GOODEVE and WHITFIELD.

d. 3. *Influence of certain additions and of the temperature upon thixotropy.*

As thixotropic gelation may be considered as a form of flocculation, it will cause no surprise that it is very sensitive to all kinds of additions. In the first place the time of solidification, θ, is strongly dependent upon the concentration of electrolyte, c, according to the empirical equation [1]

$$\log \theta = A - B c.$$

This equation, which describes the experiments [2] very well (see Fig. 11) resembles the equation derived by REERINK for slow flocculation (see chapter VIII, § 5, p. 319) except that REERINK finds log c instead of c. For the very small range of concentrations covered in Fig. 11

Fig. 11. Time of solidification of an iron oxide sol as a function of the concentration of electrolytes.

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[1] E. SCHALEK and A. SZEGVARI, *Kolloid-Z.*, 33 (1923) 326.

[2] H. FREUNDLICH, *Thixotropy*, Paris 1935, pp. 7, 29.

the difference would be small. The agreement between the two types of experiments supports the idea that thixotropic gelation is a slow coagulation.

Another example mentioned by FREUNDLICH [1] shows how the time of solidification of an iron oxide sol changes a hundred-fold upon a change of the pH (potential-determining electrolyte) by less than a unit. (See Table 4).

TABLE 4

INFLUENCE OF THE pH ON THE TIME OF SOLIDIFICATION, θ, OF AN IRON OXIDE SOL.

Amount of NaOH or HCl added (millimols/litre)		pH	H^+ conc.	θ in seconds
6.3	NaOH	3.86	1.40×10^{-4}	82
5.4	,,	3.78	1.66	140
4.5	,,	3.73	1.88	200
3.6	,,	3.65	2.27	300
2.7	,,	3.56	2.77	440
1.8	,,	3.50	3.16	750
0.9	,,	3.43	3.70	1300
0.45	,,	3.39	4.08	about 1600
0		3.37	4.31	,, 2000
0.45	HCl	3.32	4.76	,, 3300
0.9	,,	3.26	5.52	,, 4800
1.8	,,	3.18	6.61	,, 6600
2.7	,,	3.11	7.71	,, 9000

Alcohol, which usually decreases the stability of hydrophobic colloids, also promotes thixotropic gelation (SCHALEK and SZEGVARI). After evaporation of the alcohol the gel returns to the sol state.

On raising the temperature the time of solidification is shortened as is the time of coagulation. The energy of activation of 22,000 cal. calculated form SCHALEK and SZEGVARI's experiments would correspond to an energy barrier of about 35 kT, which is rather larger than the expected value.

d. 4. Applications

There exist several indications that as a rule *protoplasm* has thixotropic properties. CHAMBERS [1], for instance, mentions that it behaves rather like a liquid when stirred with the needles of a micromanipulator, but obtains more elastic properties when left undisturbed for a certain time.

Myosin sols are known to form strongly thixotropic gels [2], which might indicate that thixotropy has a certain significance for muscular action.

Some kinds of *quicksand* may be thixotropic in nature, having a solid appearance when undisturbed, but losing its resistance when once motion has started. FREUNDLICH and JULIUSBURGER [3] give an example of quicksand from Knott End, Fleetwood, which was distinctly thixotropic due to the admixture of a few percent of very fine clay.

[1] R. CHAMBERS, *Proc. Soc. Expt. Biol. Med.*, 19 (1921) 87; See also T. PÉTERFI, *Arch. Entwicklungsmech. Organ.*, 112 (1927) 689.
[2] A. L. VON MURALT and J. T. EDSALL, *J. Biol. Chem.*, 89 (1930) 341.
[3] H. FREUNDLICH and F. JULIUSBURGER, *Trans. Faraday Soc.*, 31 (1935) 769.

It should, however, not be concluded that all quicksand is thixotropic. In the same investigation FREUNDLICH and JULIUSBURGER find two kinds of quicksand which are rather dilatant than thixotropic. In § 3 c, p. 354, we have expounded how dilatancy might also explain quicksand. Finally it is fairly certain that quicksand and perhaps the most fatal kind may be caused by purely hydrographic circumstances [1] (rising water currents).

A technical application on a large scale is found in the *drilling muds* used in the drilling of oil wells[2]. They always contain a certain amount of plastic clays responsible for its thixotropy (see § 5b. 3, p. 360).

Paints and printing inks are usually thixotropic. If the pigment were completely stabilized, on standing it would form a very compact sediment, which is not easily redispersed. Moreover, after brushing the paint on a vertical surface, it would have a tendency to flow off. On the other hand of course, the system should be capable of being brushed out and therefore behave like a liquid. Its time of solidification should be just long enough to allow the strokes of the brush to be levelled out. A time of solidification zero is an undesirable property in a paint (hence the name *false body* for this property).

A good example of thixotropic gelation is given by a suspension of graphite in a mineral oil, [3] which is non-conducting when fluid, but conducting after gelation, proving that, in this case at least, gelation is accompanied by the formation of a continuous network of graphite particles in contact with each other.

e. Rheopexy

The time of solidification of thixotropic sols with strongly anisodimensional particles (V_2O_5) may be greatly decreased by gentle systematic motion. FREUNDLICH and JULIUSBURGER [4] who discovered the phenomenon, called it *rheopexy* (gelling by motion). A V_2O_5-sol, which had been made thixotropic by the addition of some H_2SO_4, set to a gel in about 60 minutes when left undisturbed, but in 15 seconds when slowly rolled between the palms of the hands. By this motion the particles were oriented in nearly horizontal planes as was indicated by the striations observed. FREUNDLICH and JULIUSBURGER concluded that the parallel orientation by the flow was a favourable factor in gelling, thus corroborating their idea that the thixotropic state was caused by long range forces between parallel particles.

LAWRENCE [5], however, assumes that the motion causes rather a gentle turbulence, which favours the coming into mutual contact of the very long particles, which otherwise will have only a very slow rotatory BROWNian motion of their own account. Consequently, rheopexy cannot be used as an argument for the action of long range forces in these systems.

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[1] See J. VERSLUYS, *Ingenieur Utrecht*, 41 (1926) 589; A. J. HAGEDOORN, *De Natuur*, 10 (1890) 38, 69.

[2] See D. H. LARSEN, in J. ALEXANDER, *Colloid chemistry, theoretical and applied*, volume 6, New York 1946, p. 510.

[3] A. E. ALEXANDER and P. JOHNSON, *Colloid science*, vol. 2, Oxford 1949, p. 611.

[4] H. FREUNDLICH and F. JULIUSBURGER, *Trans. Faraday Soc.*, 31 (1935) 920.

[5] A. S. C. LAWRENCE, *Ann. Repts. on Progress Chem. Chem, Soc. London*, 37 (1940) 119.

f. Syneresis

Many gels, especially thixotropic ones with a low content of dispersed matter, contract in the long run with liberation of a part of the intermicellar liquid. This phenomenon is called *syneresis* and is easily explained by the fundamental instability of gels, at least of the lyophobic type. The system, in gelling, has only formed a relatively small number of contact places, and by forming a greater number of contacts, which inevitably entails a contraction of the dispersed phase (see Fig. 12), the free energy can be lowered.
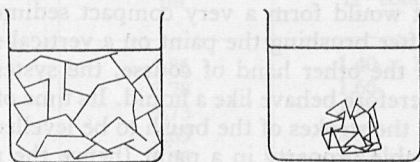

Fig. 12. Schematic picture of syneresis. The number of rods has remained the same, but the number of contacts has been greatly increased.

Syneresis is promoted by all influences which promote coagulation[1], such as increasing concentration of particles, of electrolyte, addition of alcohol, increase of temperature.

A striking example of syneresis is given by the CeO_2-sol, which can be made to gel even in the low concentration of 0.3%, but which then shows syneresis and contracts to a fraction of its original volume within a few days or hours [2].

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[1] S. Liepatoff, *Kolloid-Z.*, 41 (1927) 200; 43 (1927) 396; 47 (1929) 21; 48 (1929) 62; 49 (1929) 321, 441.

[2] H. R. Kruyt and Miss J. E. M. van der Made, *Rec. trav. chim.*, 42 (1923) 277.